We shall see momentarily that in addition to avoiding highly overlapping applications, it is critical to avoid preference for a large intermolecular overlap is maintained in these charged dimers. Importantly, the preference for electron (3e/mc) multicenter bonding in contrast to the 2e/mc bonding that occurs for the neutral radical dimers. The strong...
Scheme 1. Monomers, Dimer Complexes, and Their Key Parameters Studied in This Work

1. R=H, Phenalenyl (PLY)
2. R=F, Perfluoro-phenalenyl (PF-PLY)
3. R=H, Olympicenyl (OPY)
4. R=F, Perfluoro-olympicenyl (PF-OPY)

“Notice the atom-over-atom stacking in the dimers, which is indicative of some covalent character in the intermolecular bonding interaction. The PLY dimer displays two-electron 12-center (2e/12c) bonding at the $D_{12}$ symmetry, and the (OPY)$_2$ dimer displays two-electron 20-center (2e/20c) bonding at the $C_{2h}$ symmetry. See also Scheme S2.

Scheme 2 illustrates a molecular orbital interaction diagram for PLY and its neutral and charged dimers for the three types of dimer bonding.

(a) Singly occupied molecular orbital of the PLY radical localized on $\alpha$-carbons (Scheme S1 illustrates the SOMO for OPY), (b) bonding and antibonding combination of the two SOMOs in a pancake bonding configuration with a $D_{12}$ stacking geometry, and (c) orbital occupancies and formal pancake bond orders (PBOs) of a neutral radical dimer, a dimer cation, and a dimer anion.

Scheme 2

2. COMPUTATIONAL METHODS

The geometries of the neutral phenalenyl (PLY, 1) and olympicenyl (OPY, 3), the perfluoro-phenalenyl (PF–PLY, 2) and perfluoro-olympicenyl (PF-OPY, 4) dimers, and their singly charged cationic and anionic analogues were optimized using the (U)M05-2X/6-311G(d) level of theory, in which the broken-symmetry spin-unrestricted (U) formalism was used for the neutral species. All isomers were confirmed as local minima using frequency computations. The geometries of all neutral and singly charged dimers considered here were also fully optimized by MR-AQCC/3-21G for the neutral, +1, and −1 charged dimers of both PLY and PF–PLY. Additionally, the geometries of the neutral, +1, and −1 charged dimers of PLY were also optimized with MR-AQCC using the larger 6-31G(d) basis. Good agreement was found between the results obtained with the two basis sets, which was used as the justification for continuing the MR-AQCC calculations with the computationally much more efficient smaller basis set. Molecular orbitals (MOs) created by the CASSCF method were used in the MR-AQCC calculations with the same CAS(2,2) as used in the CASSCF calculations for the neutral systems, whereas the state-averaged (SA) CAS(1,2) and CAS(3,2) calculations were used for the optimizations of the cationic and anionic species, respectively. MR-AQCC/3-21G was used to compute the rigid rotation and dissociation potential energy scans for all the neutral and charged dimers with further extensive computations using the larger 6-31G(d) basis. The MR-AQCC calculations were performed using the COLUMBUS program suite. The unpaired electron population analysis was completed using the TheoDOR program.

For interpretative purposes, the separation of the different energy terms is highly desirable, especially the separation of the covalent-like bonding interaction due to the SOMO–SOMO overlap that produces the electron delocalization over the dimer versus the vdW interaction, $E_{vdW}$. $E_{vdW}$ includes dispersion, Pauli (steric) repulsion, and electrostatic interactions. We found it useful to separate the vdW component ($E_{vdW}$), from the attractive SOMO–SOMO interaction, $E_{SOMO–SOMO}$, a term that reflects a covalent-like component of the interaction energy. This decomposition, albeit approximate, is useful for two reasons. First, there are no directly applicable energy decomposition schemes available for the MR-AQCC method, while the presented energy decomposition shown below is applicable for it as well as for any other approach, including DFT. This scheme is based on total energies computed with the respective method and does not rely on any

\[ PBO = 1/2(N_{\text{bind}} - N_{\text{ant}}) \]

where $N_{\text{bind}}$ is the number of electrons in the bonding orbitals and $N_{\text{ant}}$ is the number of electrons in antibonding orbitals. As a practical matter, only the intermolecular bonding and antibonding orbitals need to be counted.

The main components of the interactions between the two phenalenyls in each dimer are analyzed using dissociation and rotational potential energy surface (PES) scans. Rotational scans are particularly insightful for PLY dimers because the SOMO-SOMO overlap can be turned on ($D_{3h}$ $\theta = 60^\circ$) or turned off ($\theta = 30^\circ$). Such a simple tool is not available for OPY due to its lower symmetry. Partly for this reason, we also use an energy decomposition analysis (EDA) that is applicable regardless of the symmetry. We rely to a large extent on the high-level multireference-averaged coupled cluster (MR-AQCC/6-31G(d)) method, which has been shown to have good performance due to the balance of the description of the multireference effects (static electron correlation) induced by the two near-lying orbitals $\phi_{\text{a}}$ and $\phi_{\text{b}}$, as illustrated in Scheme 2, and the dynamic electron correlation responsible for the dispersion-type intermolecular electron correlation energy. Additionally, appropriate DFT computations have been performed.

pancake bonding under discussion here: two-electron multicenter bonding (2e/mc) with PBO = 1; one-electron multicenter bonding (1e/mc) with PBO = 1/2; and three-electron multicenter bonding (3e/mc), also with PBO = 1/2. Here PBO stands for a formal through space pancake bond order defined as
asymptotic expansion scheme of the interaction energy. Second, this decomposition provides essential insights by allowing us to focus on the SOMO–SOMO interaction component, which drives the pancake bonding interaction.39,46

The following procedure was applied for the neutral pancake-bonded dimers:39,46

\[ E_{\text{int}}(R) = E_{\text{Total}}(R) - E_{\text{Total}}(10.0 \text{ Å}) = -E_{\text{binding}} \]  \hspace{1cm} (2)

where \( R \) stands for the contact distance between the monomers. The key assumption is that the two components of the interaction are approximately additive

\[ E_{\text{int}} \approx E_{\text{SOMO–SOMO}} + E_{\text{vdW}} \]  \hspace{1cm} (3)

The \( E_{\text{SOMO–SOMO}} \) term is approximated by the interaction energy of the high-spin state (triplet in this case) \( E_{\text{SOMO}} \) and taken at the same unrelaxed ground state geometry of the singlet.39

\[ E_{\text{SOMO–SOMO}}(\text{at the geometry of the singlet}) \approx E_{\text{SOMO}}(\text{at the geometry of the singlet}) \]  \hspace{1cm} (4)

The interaction energy and its components at the equilibrium geometry of the singlet are particularly relevant and will be listed and discussed. These assumptions were justified and validated for PLY.39

The following approximation will be used for both the neutral and the charged PLY and PF–PLY dimers:

\[ E_{\text{SOMO–SOMO}}(60) \approx E_{\text{int}}(60) - E_{\text{int}}(30^\circ) \]  \hspace{1cm} (5)

An important aspect of this approximation is that it is applicable for the singly charged PLY and PF–PLY dimers, while the approximation based on eqs 3 and 4 is not applicable because they are doublet ground-state dimers. As a validation, we refer to ref 39, where the rotation-based method and the multiplicity-based method gave very close estimates for the value of \( E_{\text{SOMO–SOMO}} \).

The intermolecular Coulomb interaction energy \( (E_{\text{Coul}}) \) is defined by equ 6

\[ E_{\text{Coul}} = \sum q_i q_j \frac{1}{d_{ij}} \]  \hspace{1cm} (6)

where \( q_i \) and \( q_j \) are the atomic charges and \( d_{ij} \) is the distance between the atoms \( i \) and \( j \). The summation is limited to atom pairs that belong to different monomers in the dimer.

As an alternative, we also used the energy decomposition analysis (EDA) developed by Ziegler and Rauk,38 using (U)PBE0-MBD\(^{17}\)/TZP level of theory with the ADF\(^{19}\) program package. The many-body dispersion (MBD) refers to the method of Tkatchenko et al. \(^{17}\) that provides an accurate description of vdW interactions, which include both screening effects and a high-order treatment of the many-body van der Waals energy. The interaction energy and its components are denoted here differently from those in eqs 3–5, with a \( \Delta \) symbol to refer specifically to the EDA analysis. \( \Delta E_{\text{int}} \) is the difference between the energy of the dimer and the energies of the constituent monomers. In the current case, it is divided into four main components as follows:

\[ \Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}} \]  \hspace{1cm} (7)

The term \( \Delta E_{\text{elstat}} \) corresponds to the quasi-classical electrostatic interaction between the unperturbed charge distributions calculated from the orbital densities. The Pauli repulsion, \( \Delta E_{\text{Pauli}} \) contains the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction \( \Delta E_{\text{orb}} \) accounts for charge transfer, delocalization, and polarization effects. The vdW interaction energy in this scheme, \( \Delta E_{\text{disp}} \), is then approximately the sum of the dispersion interaction, electrostatic interaction, and the Pauli repulsion as follows:

\[ E_{\text{vdW}} = E_{\text{disp}} + \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} \]  \hspace{1cm} (8)

Further computational details are summarized in Section 2 of the Supporting Information (SI).

3. RESULTS AND DISCUSSION

We present results in four subsections. First, we show strong evidence that while \( \sigma \)-bonded configurations are often energetically competitive with \( \pi \)-stacking configurations for pancake bonding with \( \text{PBO} = 1/2 \), this is not the case with \( \text{PBO} = 1/2 \) dimers.39 Then, evidence is provided to show that \( \pi \)-stacking geometries are maintained for \( \text{PBO} = 1/2 \) dimers, displaying subtle but systematic differences between positively and negatively charged dimers in correlation with the presence or absence of fluorination, respectively. This is then put into the context of the total energy computations to show that, surprisingly, while the fluorinated anion dimers have stronger pancake bonding with \( \text{PBO} = 1/2 \), for the parent unfluorinated ones it is the cations that have the stronger pancake bonding. The interpretation, including an energy component analysis, indicates that changes in the intermolecular electrostatics play a key role in this effect.15

3.1. The Stability of the \( \pi \)-Dimer Versus the \( \sigma \)-Dimer

\( \sigma \)-Bonded configurations are often energetically competitive with \( \pi \)-stacking configurations, as shown, for example, by the presence of fluxional bonding in some phenalenyls\(^{49,50}\) and their derivatives.52 Therefore, we first investigate the effect of fluorine substitution and the total charge on the relative energies of the dimers of PLY and OPY, with key data summarized in Table 1; the structures are illustrated in Figure S2.49 50 The lower-symmetry \( \pi \)-stacked structures are illustrated in Figure S3.49 50 Converges to \( \pi(3) \); for details, see Tables S5 and S6.

Table 1. Relative Energies (kcal/mol) of \( \pi \) and \( \sigma \)-Dimers of Neutral and Charged PLY\(_2\) (1) and PF–PLY\(_2\) (2) at the UM05-2X/6-311G(d) Level

| \( \sigma^a \) | \( \sigma^b \) (RR1) | \( \sigma^b \) (RR2) | \( \sigma^b \) (RR3) | \( \sigma^b \) (RS1) | \( \sigma^b \) (RS2) |
|---|---|---|---|---|---|
| \( \text{PLY}^+ \) | 0.0 | -2.6 | -2.9 | -4.1 | -1.2 | -4.0 |
| \( \text{PF} \) | 0.0 | -7.8 | -7.1 | -7.9 | -6.4 | -7.1 |

\( \Delta E_{\text{disp}} \) corresponds to the \( \pi \)-stacking dimer, \( \text{D}_{\pi} \). Notation for \( \sigma \)-dimer configurations is from ref S0 and is illustrated in Figure S2. The lower-symmetry \( \pi \)-stacked structures are illustrated in Figure S3. Converges to \( \pi(3) \); for details, see Tables S5 and S6.
The preparation of these charged dimer species viable. The cationic neutral and charged dimers of singly charged PLY2 can be understood as follows. First, the bonding shows strong preference for the maximum of the con sections.

Note that all these additionally identified π-dimers (listed in Table 1 and illustrated in Figure S3) are less stable and in most cases significantly less stable than the staggered $D_{3d}$ π-dimer configuration. This indicates that the multicenter pancake bonding shows strong preference for the maximum of the SOMO–SOMO overlapping geometry even with one or three electrons (1e/mc or 3e/mc). We will gain further insights into this effect based on the geometry and energy analysis in the next sections.

The relative weakness of the σ-bonded configuration for the singly charged PLY$_2^+$ can be understood as follows. First, the σ-bond is much weaker for a single or three electron bond versus a two-electron bond. Second, the local pyramidalization needed for two-electron bond. Third, shorter intermolecular distances in the π-dimer configuration more favorable compared to the σ-dimer, so much so that σ-dimers do not even exist as local minima for the charged PLY$_2^+$ and PF–PLY$_2^+$. This effect makes that the π-dimer configuration more favorable compared to the σ-dimer and larger aggregates avoid σ-bonding due to these effects.

### 3.2. The Effect of Charge on the Structures of the π-Dimers

The most remarkable charge effect can be seen when comparing the direct C–C intermolecular distances in the geometries of the 12 optimized π-dimers, four neutral ones with full PBO = 1 and eight charged ones with PBO = 1/2, which are given in Table 2 and Table S7. Note that the geometry optimization at the MR-AQCC/6-31G(d) level for the PLY systems shown in Table S7 displays the same trends as the DFT geometry data shown in Table 2. The surprising overall observation is that all these contact distances are without exception significantly shorter than 3.40 Å, the vdW distance for C⋯C contacts. Due to the SOMO orbital, both PLY$^-$ and PLY$^-$ are stable, making the preparation of these charged dimer species viable. The cationic PLY$^+$ has clearly shorter average intermolecular distances as compared to those of the anionic species, PLY$^-$, while both correspond to PBO = 1/2. The situation is reversed for the perfluorinated species, where PF–PLY$_2^+$ has significantly longer intermolecular distances as compared to those of the anionic species, PF–PLY$_2^-$. Similar trends are seen in the charged dimers of OPY and PF–OPY. This is quite significant because it implies a control over contact distances and thereby allows a control of bandwidths in pancake-bonded systems not seen before.

### 3.3. Energetics of the π-Dimers

The interaction energy values are collected in Table 3 for all 12 dimeric species discussed in this work. Table S9 provides validation results at a higher optimization level for the six smaller systems.
for the negatively charged dimers of the perfluorinated species PF−PLY and PF-OYP. The differences are dramatic considering the scale of the typical intermolecular interactions, adding approximately 9−13 kcal/mol to the binding energies for $1^+_2$, $2^+_2$, $3^+_2$, and $4^+_2$ compared to those of their neutral counterparts according to Table 2. In what follows, we trace the enhancement of the interaction to electrostatic effects.

The total energy scans provide further insights. Figure 1 shows energy scans with respect to the intermolecular distance, $D_{co}$, for the all six PLY dimers plus the triplets of the two neutral ones. Note that the 3-21G basis set presents a good performance with reference to 6-31G(d) (Figure 1a, dashed line) using the MR-AQCC method. The significant electrostatic interaction accounts for the lowest $E_{int}$ value in the cationic PLY$_2^+$ and anionic PF−PLY$_2^-$ dimers, which will be discussed in the next subsection.

Most striking is the fact that even at long range, where overlap is nearly negligible, a clearly enhanced interaction appears for PLY$_2^+$ compared to both PLY$_2$ and PLY$_2^-$. While for the perfluoro case the opposite charge is preferred, as PF−PLY$_2^-$ is more stable near dissociation compared to PF−PLY$_2$ and PLY$_2^+$. This behavior provides further evidence that the preference is directed by the electrostatic interaction in the distance range relevant for pancake bonding. At distances shorter than the equilibrium distances for the dimers, the orders of some of these states interchange, as shown in Figure 1.

Next, we analyze the interaction energy by reporting rotational scans based on the M05-2X/6-311G(d) geometries and using the energy at the MR-AQCC/6-31G(d) level. The respective $E_{d_{vdw}}$ and $E_{SOMO−SOMO}$ terms for all six PLY-based dimers are listed in Table 3. While the approximations presented in eqs 3 and 4 do not separate out the electrostatic component from the dispersion attraction and Pauli repulsion components, we can discuss the rest of the trends as follows. For PLY$_2$, the total vdW term is positive and contains some Pauli repulsion due to the shorter-than-vdW contacts. The negative charge distributed in the intermolecular space in the neutral dimer provides another repulsive term. The latter is reduced in the positively charged PLY$_2^+$ compared to the negatively charged PLY$_2^-$. The elongated C···C contacts in the charged dimers mentioned in connection with Table 2 reduce the Pauli repulsion. Assumming that changes in the dispersion energy are less sensitive to the single charge added to the dimer, this explains that the total vdW interaction becomes a negative (attractive) value for PLY$_2^+$ and becomes less repulsive for PLY$_2^+$ as compared to the neutral PLY$_2$ dimer. For the PF−PLY$_2$ series, the effects of the signs of the charges are reversed, as discussed above.

For the PLY$_2$ dimer, the $E_{SOMO−SOMO}$ term is significantly lower in the charged species as compared to that for the neutral one, but the vdW repulsion that includes the reduced electrostatic repulsion even becomes attractive in the cationic dimer. Thus, the largest binding energy occurs for the cationic dimer despite the reduced $E_{SOMO−SOMO}$ value. The $E_{SOMO−SOMO}$ terms all are smaller in the PF−PLY$_2$ series as compared to those in the PLY$_2$ series, but the vdW interaction becomes attractive for PF−PLY$_2^+$. The anionic PF−PLY$_2^-$ dimer has a large attractive vdW interaction, leading to the largest binding energy in the PF−PLY$_2$ series. The reduction of the SOMO−SOMO interaction in the PLY$_2$ series upon charging affects the overall properties of pancake-bonded systems because this reduction amounts to a reduction of the strong preference for specific orientations for pancake-bonded systems. Nevertheless, as demonstrated by the data in Figure S1(c) and Table 3, the SOMO−SOMO energy term leads to a barrier of 12 to 22 kcal/mol between the low- and high-energy conformers, a sufficiently large driving force to strongly favor one of the two atom-over-atom configurations, which in the case of all PLY dimers discussed is the $D_{3d}$ staggered configuration.

3.4. Consequences of the Electrostatic Environment

In this subsection, we trace the following trends based on the computed total interaction energies shown in Table 3 to differences in intermolecular electrostatic interactions in the dimers under study.

These trends are as follows:

1. For the unfluorinated dimers, the absolute values of the interaction energies are larger by 8−9 kcal/mol for the positively charged dimers: $1^+ vs 1^-$ and $3^+ vs 3^-$. For the perfluorinated dimers, the absolute values of the interaction energies are larger by 8−9 kcal/mol for the negatively charged dimers: $2^- vs 2^-$ and $4^- vs 4^-$. The same trends are reflected in the average optimized contact distances (in Table 1) that are slightly shorter for the

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**Figure 1.** (a) Rigid dissociation energy scans of singlet and triplet states of the phenalenyl dimer ($1_2$, PLY$_2$) and the doublet states of the charged phenalenyl dimers (PLY$_2^+$ and PLY$_2^-$) in the $D_{3d}$ staggered configuration as a function of the intermolecular distance ($D_{co}$) using MR-AQCC(n, 2)/3-21G, where the values of $n = 1−3$ correspond to the cationic, neutral, and anionic dimers, respectively. (b) The scans of the neutral and the charged PF−PLY dimers ($2_2$). In panel a, the dashed line corresponds to the MR-AQCC(n, 2)/6-31G(d) level.
positively charged unfluorinated dimers and the negatively charged perfluorinated dimers.

We employ qualitative arguments, followed by two approaches toward energy decomposition: Coulomb interaction energies based on the atomic point charge model and a Morokuma–Ziegler–Rauk-type EDA. It is worth mentioning that energy decomposition is only able to provide trends, since the interaction energy component terms are not physical observables.

These trends in the C···C contact distances can be qualitatively understood on the basis of the charge distributions around the monomers as illustrated in Scheme 3, which highlights that the charge distributions and electrostatic potentials have opposite signs between unfluorinated and perfluorinated monomers. The strongly polarized distribution of the atomic charges in PLY and PF–PLY is at the source of their relatively longer contacts compared to those of the oppositely charged PLY and PF–PLY. Based on the charge distribution in Schemes 3 and S2 (charged species), the efficient way to reduce the intermolecular electrostatic repulsion would require an extra positive charge for PLY and OPY and an extra negative charge on PF–PLY and PF–OPY.

We follow these arguments with Coulomb interaction energies based on point charges, as summarized in Tables 4 and S8a and b. Atomic charges, as is well-known, can differ strongly. However, the atomic point charge-based intermolecular Coulomb interaction is well-defined by eq 6.

These data support the qualitative conclusions based on the charge distributions of the monomers discussed above in connection with Scheme 3. The singlet and triplet Coulomb interaction energy terms of the neutral dimers are virtually the same for all four systems, which is in line with eq 4. More importantly, comparing the positively charged nonfluorinated $P_L^+$ and $P_F^+$ to the negatively charged $P_F^−$ and $P_L^−$, the latter are strongly destabilized by approximately 23–25 kcal/mol. This substantial effect is the source of the relative preference for the positively charged dimers versus the negatively charged dimers. For the perfluorinated dimers, the charge preference has the opposite sign; in this case the negatively charged dimers display an approximately 33 kcal/mol preference over the positively charged ones when considering these point charge-based models for estimating the Coulomb repulsion. Due to their intrinsically arbitrary elements, these models are not conclusive but do support the switch of preference between the positively and negatively charged dimers as a function of the perfluorination.

The alternative to a point charge model for estimating intermolecular electrostatic interactions is the use of quantum mechanical energy decomposition schemes. While such schemes are plagued by various limitations,57,58 for the current purposes they still provide useful insights into the origin of the charge effects under discussion. The respective data are presented in Table 5 and Figure S4.

### Table 4. Intermolecular Coulomb Interaction Energy ($E_{\text{Coul}}$ kcal/mol) of Dimers Based on Atomic Point Charges from Natural Population Analysis (NPA) by UM05-2X/6-311G(d)^

|        | $P_L^+$ | $P_F^+$ | $P_F^−$ | $P_L^−$ |
|-------|---------|---------|---------|---------|
| $E_{\text{Coul}}$ | 15.9 | 19.2 | 42.4 | 15.6 |
| $E_{\text{elstat}}$ | 31.8 | 63.8 | 31.0 | 31.8 |
| $E_{\text{orb}}$ | 3.8 | 3.8 | 3.8 | 3.8 |
| $E_{\text{disp}}$ | 19.1 | 19.7 | 45.0 | 17.9 |
| $E_{\text{int}}$ | 35.9 | 67.3 | 34.0 | 35.9 |

*All geometries correspond to the optimized structures, except for the triplet that corresponds to the geometry of the optimized singlet.

Table 5. Energy Decomposition Analysis (EDA; kcal/mol) of the Intermolecular Interaction Energy in the Neutral and Charged Dimers of PLY (1), PF–PLY (2), OPY (3), and PF–OPY (4) using UPBE0-MBD//TZP//UM05-2X/6-311G(d) at the Most Stable $D_{3d}$ and $C_{2h}$ Configurations

|        | $P_L^+$ | $P_F^+$ | $P_F^−$ | $P_L^−$ |
|-------|---------|---------|---------|---------|
| $\Delta E_{\text{elstat}}$ | −12.9 | −24.5 | −15.6 | −12.7 |
| $\Delta E_{\text{orb}}$ | 47.6 | 26.4 | 27.3 | 38.6 |
| $\Delta E_{\text{disp}}$ | −22.2 | −16.2 | −8.3 | −15.2 |
| $\Delta E_{\text{int}}$ | −14.9 | −12.6 | −13.1 | −18.3 |
| $\Delta E_{\text{elstat}}$ | −23.4 | −22.2 | −21.4 | −17.8 |
| $\Delta E_{\text{orb}}$ | −15.4 | −28.3 | −18.6 | −18.0 |
| $\Delta E_{\text{disp}}$ | 40.8 | 35.0 | 34.0 | 44.7 |
| $\Delta E_{\text{int}}$ | −19.2 | −21.2 | −11.9 | −17.8 |
| $\Delta E_{\text{elstat}}$ | −20.7 | −19.5 | −20.0 | −26.3 |
| $\Delta E_{\text{orb}}$ | −16.3 | −22.6 | −20.7 | −18.7 |

The key result of this analysis is as follows. The electrostatic energy, $\Delta E_{\text{elstat}}$, provides a relative preference of −8 to −10 kcal/mol for $P_L^+$ and $P_F^+$ compared to $P_F^−$ and $P_L^−$, respectively. For the perfluorinated pairs, this additional electrostatic stabilization was computed at −17 to −18 kcal/mol. While the specific decomposition depends on the details of the level of theory and the overlap between the interacting molecules, there should be no doubt about the importance of the electrostatic component of the intermolecular interaction to explain the relative stabilities of these pancake-bonded dimers as a function of charge and perfluorination.
A brief overview of the other terms of this EDA shows consistency with respect to the analysis based on eqs 3 and 4. The orbital interaction term, $\Delta E_{\text{orb}}$, accounts for the charge transfer, delocalization, and polarization effects, which can also be considered to include the main contributions to the SOMO–SOMO interaction, while the other three terms ($\Delta E_{\text{elstat}}, \Delta E_{\text{Pauli}}, \text{and } \Delta E_{\text{disp}}$) added together can be considered to represent the vdW interaction, $\Delta E_{\text{vdW}}$, as used in eq 3 above. Figure S4a and b show the total energy curves of the four main components of the EDA as a function of $\theta$ for PLY$_2$ and PF–PLY$_2$, respectively. Figure S4c displays the difference between singlet and triplet scans, which approximately represents the SOMO–SOMO interaction as per eqs 3 and 4. Compared to that for the PLY$_2$ dimer, the magnitude of the SOMO–SOMO interaction is significantly smaller in the PF–PLY$_2$ dimer, which is fully consistent with our MR-AQCC analysis. Moreover, it reflects that the SOMO–SOMO interaction is the main component for the difference of the total interaction between the singlet and the triplet. On the other hand, $\Delta E_{\text{elstat}}$ and $\Delta E_{\text{disp}}$ are nearly constant, and the value of $\Delta E_{\text{Pauli}}$ has only small variations, indicating that $\Delta E_{\text{vdW}}$ does not change significantly from 60° to 30°, which is again consistent with our MR-AQCC analysis.

For the neutral dimers in their singlet states, the orbital term is smaller in PF–PLY$_2$ as compared to that in PLY$_2$; however, the former has a larger dispersion term, which is consistent with the rotational scans. Comparing the different-charged PLY$_2$, or PF–PLY$_2$ dimers, the electrostatic term is a crucial factor in strengthening the interaction, as reflected in $\Delta E_{\text{elstat}}$. This provides further evidence that the PLY$_2^-$ and PF–PLY$_2^-$ have stronger overall pancake bonds compared to the oppositely charged dimers, PLY$_2^+$ and PF–PLY$_2^+$, respectively.

Additional supporting evidence for this interpretation is provided in Table S10, which displays the total number of effectively unpaired electrons for all 12 dimers under discussion. This parameter signals a degree of electron unpairing on a comparable scale across each of the two series. These data confirm the trends, showing that electron pairing decreases ($N_U$ increases) upon the charged dimers moving from PBO = 1 to 1/2 as expected, further underlining the point that the strength of pancake bonding for this charge effect is not due to increased electron pairing but instead to a reduced electrostatic repulsion between the PAHs.

4. CONCLUSION

As a practical matter, properly charged pancake-bonded systems can increase their stability and avoid o-bonding more easily than neutral pancake-bonded systems. The second observation is that the charged dimers can display stronger pancake bonding compared to the neutral radical-based dimers even though charging reduces the formal pancake bond order from 1 to 1/2. The associated intermolecular distances with PBO = 1/2 are typically longer than those of pancake bonds with PBO = 1.

The interaction energy in charged pancake-bonded systems is less dominated by the SOMO–SOMO interactions, and electrostatic effects become more important. The reduced SOMO–SOMO interaction in the PLY$_2$ and OPY$_2$ series upon charging is still sufficiently robust to maintain their strong preferences for the specific orientations typical for pancake-bonded systems by maintaining a maximum overlap with atom-over-atom configurations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00272.

Atomic notation, SOMO coefficients, computational details, energy scans, structures and coordinates of dimers, energy decomposition, Coulomb energies, charge distribution, and physical properties (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (nos 11874178, 11922405, and 91961204). This work was supported by Beijing National Laboratory for Molecular Sciences (BNLMS201910). M.K. is member of the Georgetown University Institute of Soft Matter. Computer time was partially provided by the School of Pharmaceutical Science and Technology, Tianjin University on the computer cluster Arran, which is gratefully acknowledged.

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