Supporting Information for

Importance of Side-chains on Molecular Characteristics of Interacting Organic Molecules

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In this Supporting Information, we will show correlations among optimized stabilization energy, barycentric distance, angle between the two molecular planes, dipole moment, and electronic coupling for PCBM, PDI, and PDI **1** bi-molecular systems. In the text, only the correlations between the stabilization energy and the other physical quantity were shown in Figs. 4, 5, and 6.

The features of the figure shown below reflect the following general tendencies:

(1) PCBM bi-molecular system shows the pattern more complicated than PDI and PDI **1** systems do. This reflects the fact that PCBM has a spherical molecular core so that the intermolecular interaction takes on a variety of barycentric distances and relative intermolecular orientations.

(2) PDI **1** shows the pattern more complicated than PDI does. This is due to the fact that the intermolecular interactions via the side-chains of the former make it possible to take on a variety of intermolecular configurations. PDI has no side-chains and therefore has only a strong intermolecular π-π stacking interaction between the two rigid aromatic cores [S1, S2]. As a result, the bi-molecular PDI system can only take on a limited number of intermolecular configurations.

(3) If the diagram includes either of the dipole moment or the relative orientation of the molecules, the physical quantity of interest takes on a complicated form. Moreover, if both of them are included, the pattern becomes much more complicated. This is because the dipole moment is a vectorial physical quantity so that the complicated pattern exhibited below reflects the orientational dependence of the relative position.

1. *Correlations among optimized stabilization energy, barycentric distance, angle between the two molecular planes, dipole moment, and electronic coupling for PCBM bi-molecular system*.

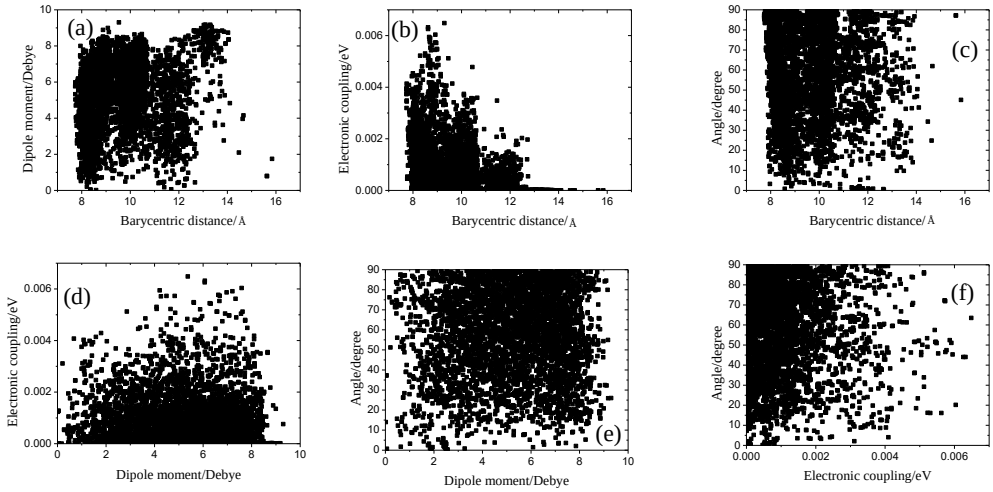
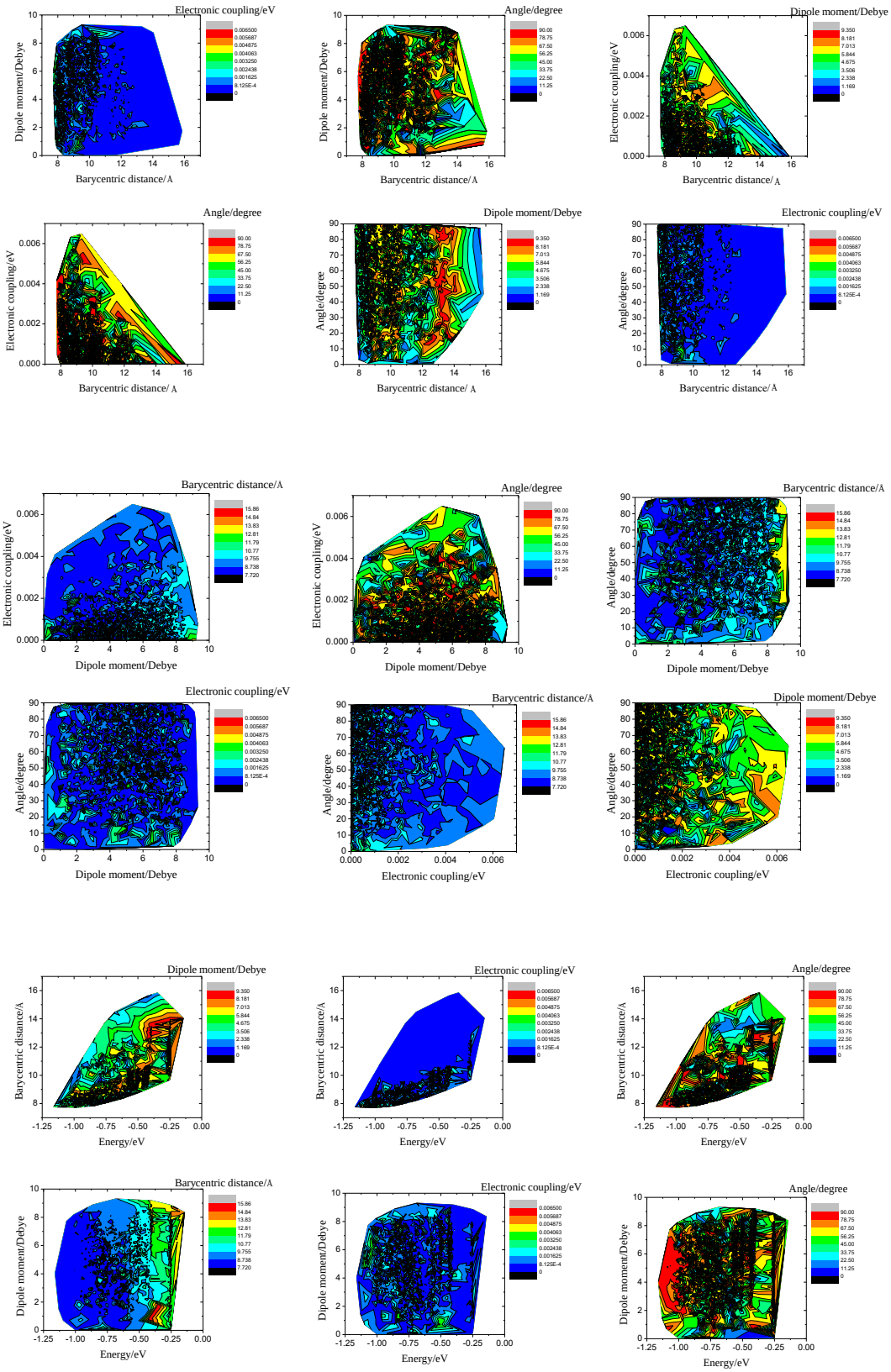


Figure.S1 Correlations between two of the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PCBM bi-molecular system. (a) dipole moment versus barycentric distance, (b) electronic coupling versus barycentric distance, (c) angle between the two molecular planes versus barycentric distance, (d) electronic coupling versus dipole moment, (e) angle between the two molecular planes versus dipole moment, and (f) angle between the two molecular planes versus electronic coupling.


Electronic coupling/eV
Dipole moment/Debye
Barycentric distance/A
Angle/degree
Dipole moment/Debye
Barycentric distance/A
Dipole moment/Debye
Electronic coupling/eV
Barycentric distance/A
Angle/degree
Electronic coupling/eV
Barycentric distance/A
Dipole moment/Debye
Electronic coupling/eV
Angle/degree
Barycentric distance/A
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Energy/eV
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Energy/eV

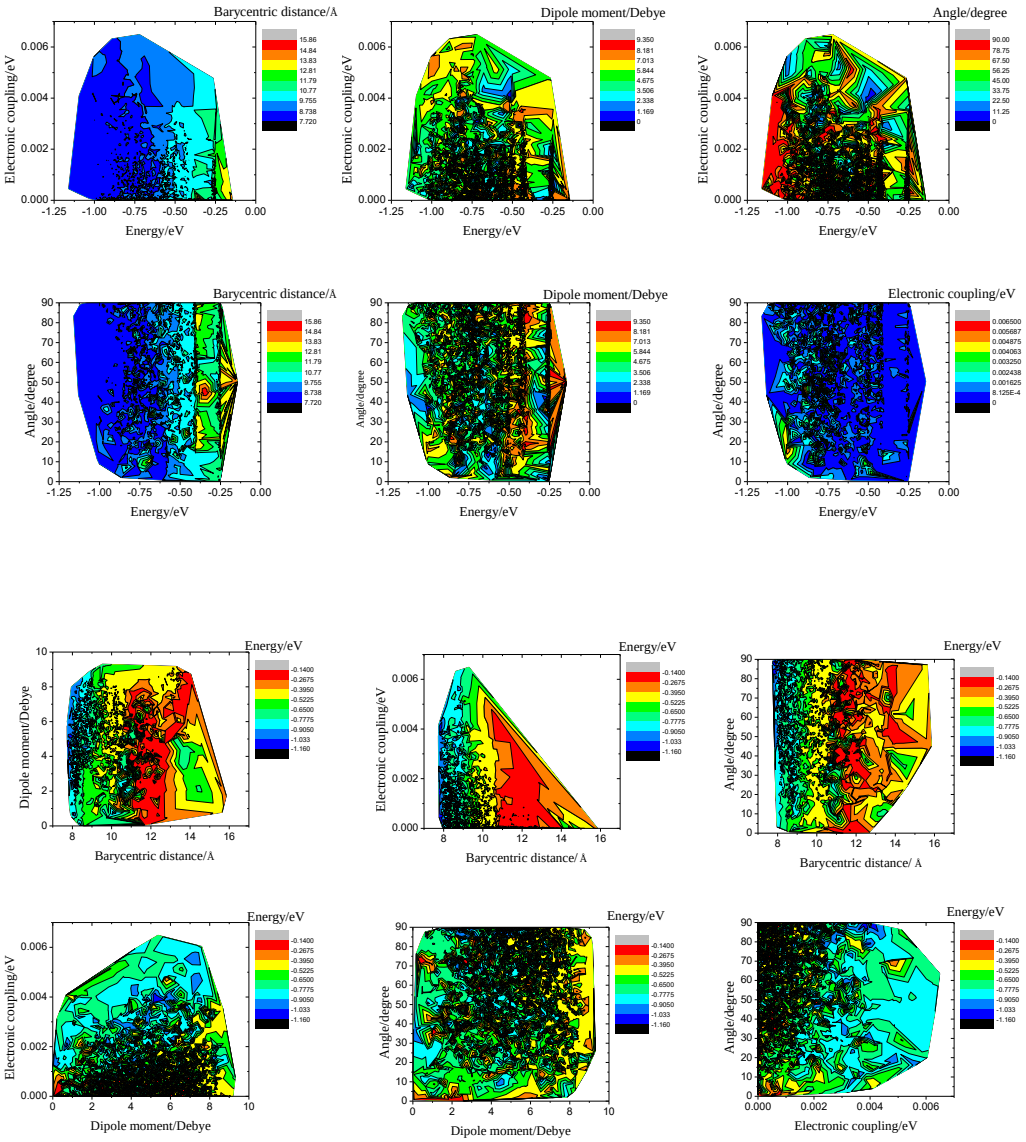


Figure.S2 Correlations among three of the stabilization energy, the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PCBM bi-molecular system.

2. *Correlations among optimized stabilization energy, barycentric distance, angle between the two molecular planes, dipole moment, and electronic coupling for PDI bi-molecular system.*

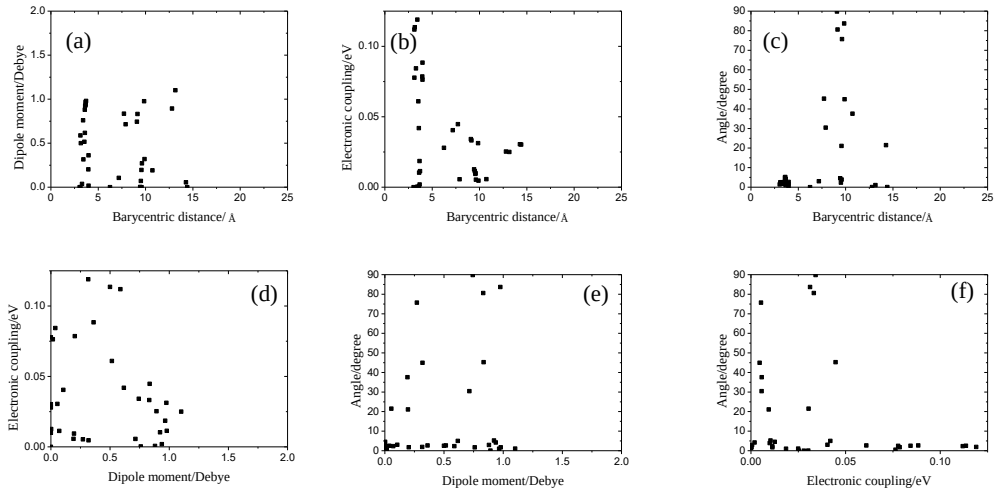
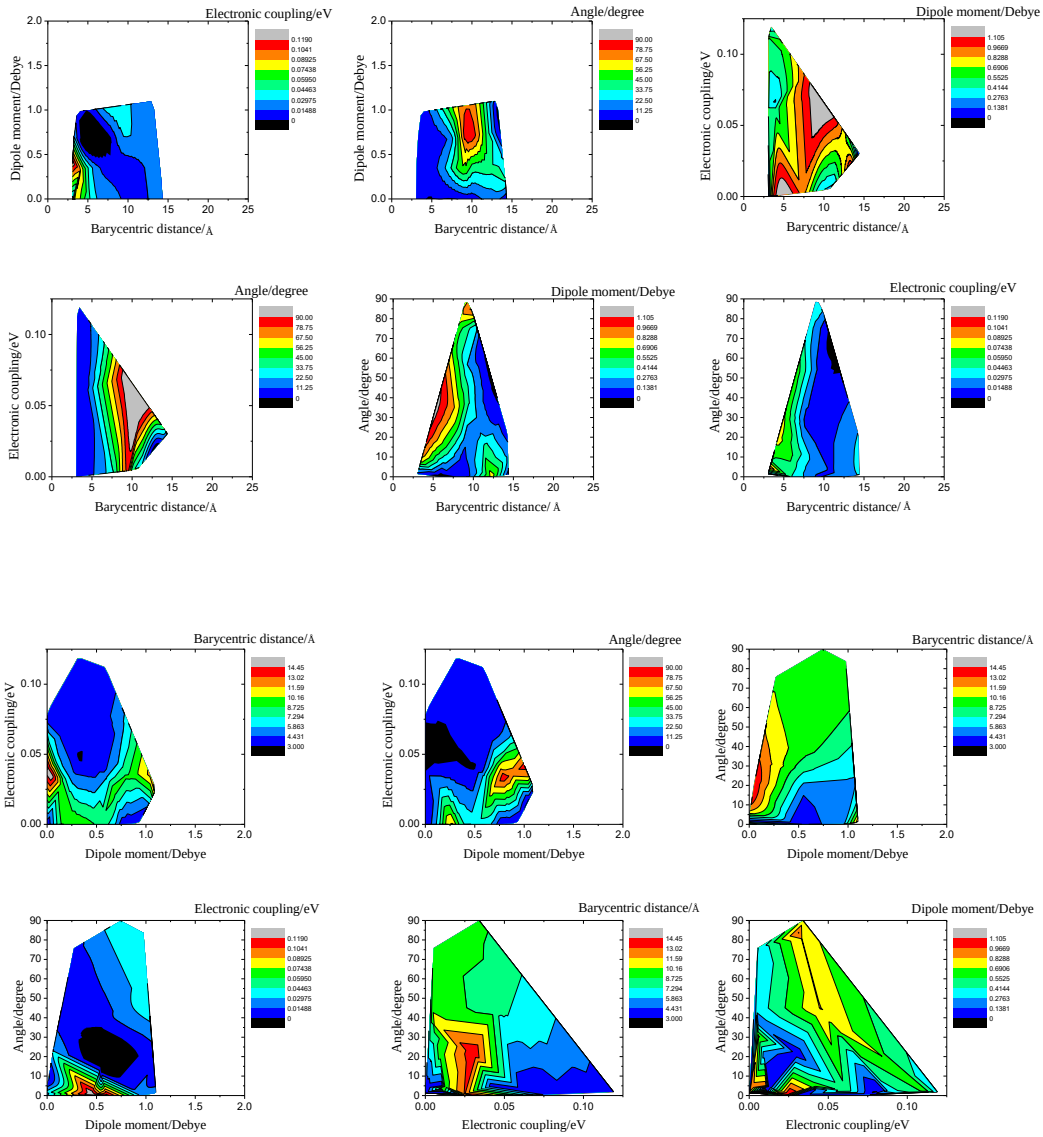


Figure.S3 Correlations between two of the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PDI bi-molecular system. (a) dipole moment versus barycentric distance, (b) electronic coupling versus barycentric distance, (c) angle between the two molecular planes versus barycentric distance, (d) electronic coupling versus dipole moment, (e) angle between the two molecular planes versus dipole moment, and (f) angle between the two molecular planes versus electronic coupling.


Electronic coupling/eV
Dipole moment/Debye
Barycentric distance/Å
Angle/degree
Dipole moment/Debye
Barycentric distance/Å
Dipole moment/Debye
Electronic coupling/eV
Barycentric distance/Å
Angle/degree
Electronic coupling/eV
Barycentric distance/Å
Dipole moment/Debye
Angle/degree
Barycentric distance/Å
Electronic coupling/eV
Electronic coupling/eV
Barycentric distance/Å
Dipole moment/Debye
Angle/degree
Barycentric distance/Å
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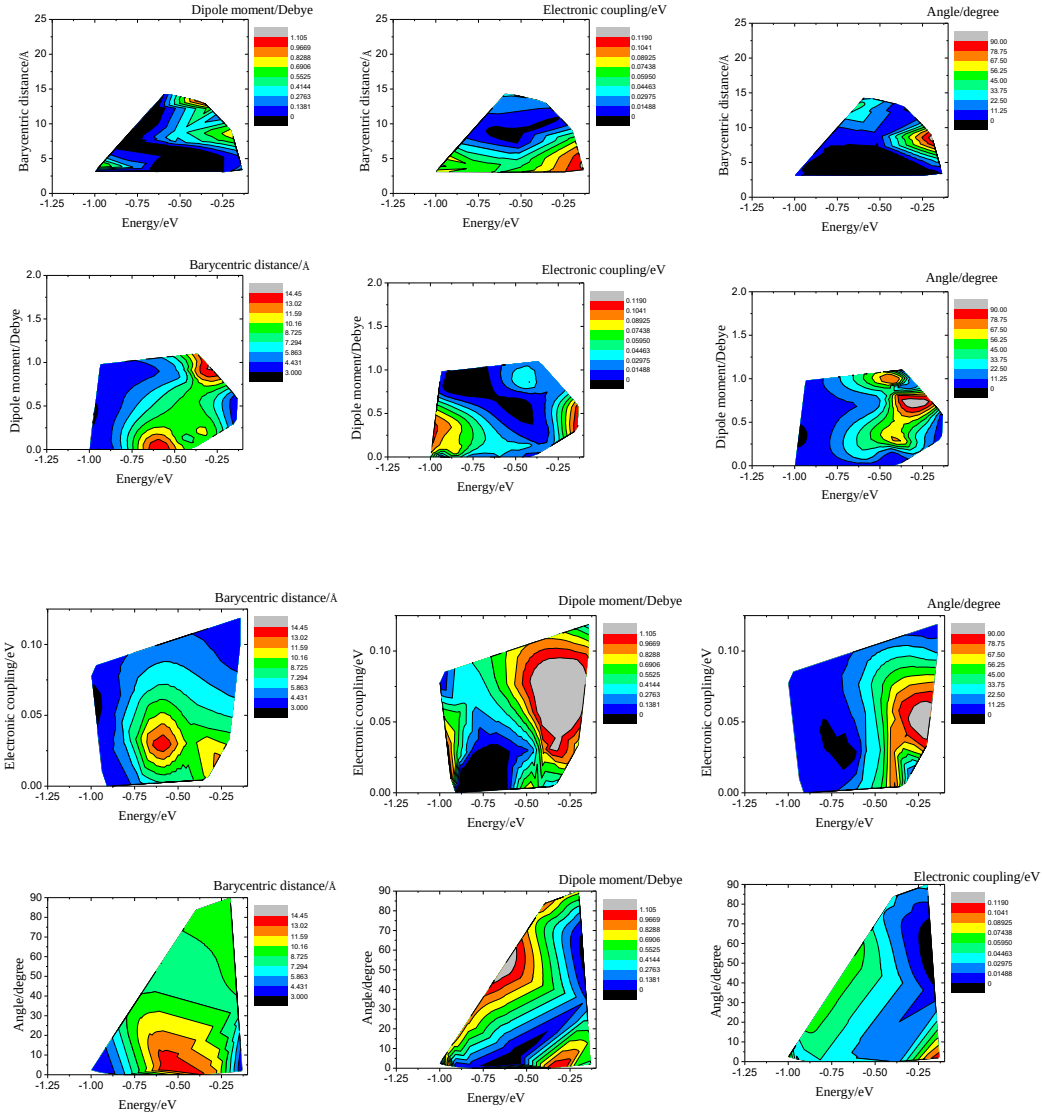
Angle/degree
Electronic coupling/eV


Dipole moment/Debye
Electronic coupling/eV
Angle/degree
Barycentric distance/Å
Dipole moment/Debye
Electronic coupling/eV
Angle/degree
Barycentric distance/Å
Electronic coupling/eV
Dipole moment/Debye
Angle/degree
Barycentric distance/Å
Dipole moment/Debye
Electronic coupling/eV
Energy/eV

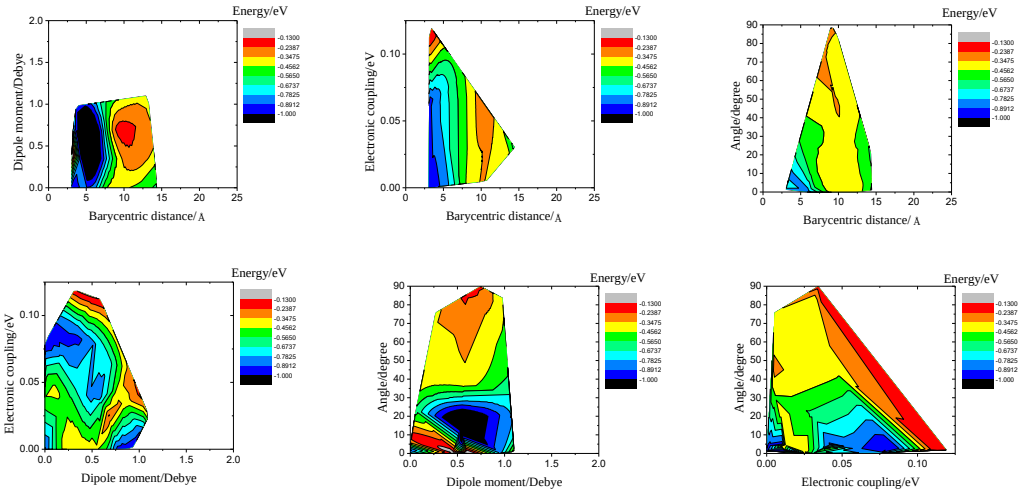


Figure.S4 Correlations among three of the stabilization energy, the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PDI bi-molecular system.

3. *Correlations among optimized stabilization energy, barycentric distance, angle between the two molecular planes, dipole moment, and electronic coupling for PDI* ***1*** *bi-molecular system*.

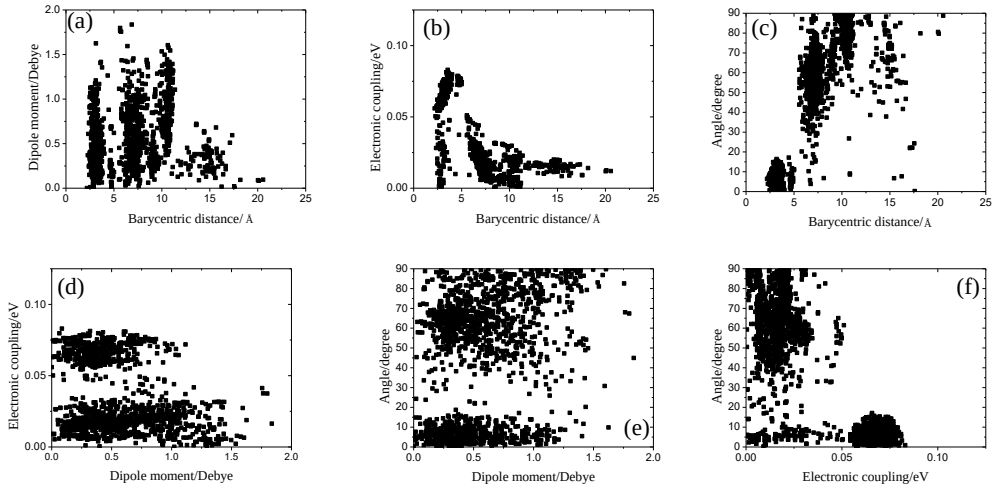
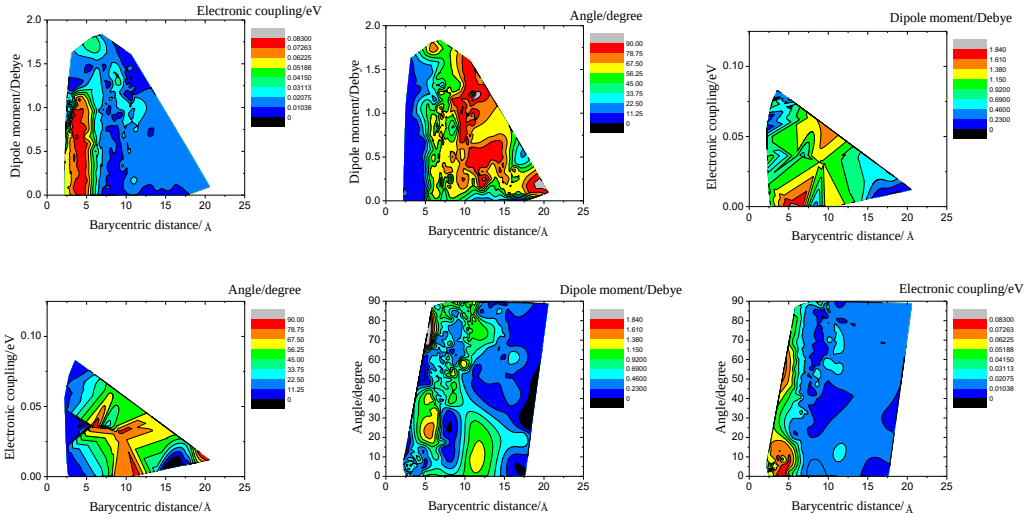
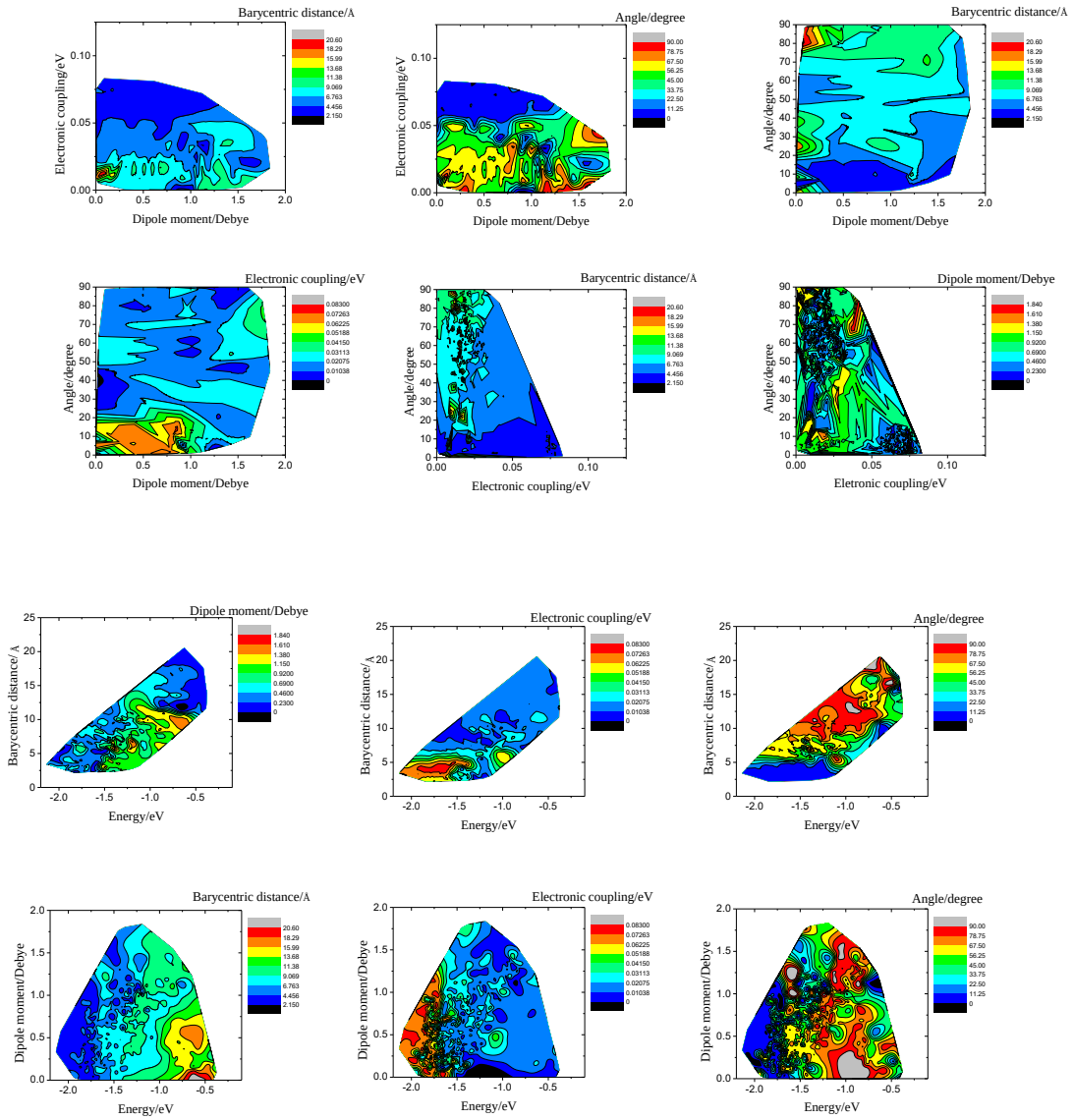


Figure.S5 Correlations between two of the stabilization energy, the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PDI **1** bi-molecular system. (a) dipole moment versus barycentric distance, (b) electronic coupling versus barycentric distance, (c) angle between the two molecular planes versus barycentric distance, (d) electronic coupling versus dipole moment, (e) angle between the two molecular planes versus dipole moment, and (f) angle between the two molecular planes versus electronic coupling.


Electronic coupling/eV
Dipole moment/Debye
Barycentric distance/ Å
0.08300
0.07263
0.06225
0.05188
0.04150
0.03113
0.02075
0.01038
0
Angle/degree
Dipole moment/Debye
Barycentric distance/Å
90.00
78.75
67.50
56.25
45.00
33.75
22.50
11.25
0
Dipole moment/Debye
Electronic coupling/eV
Barycentric distance/ Å
1.840
1.610
1.380
1.150
0.9200
0.6900
0.4600
0.2300
0
Angle/degree
Electronic coupling/eV
Barycentric distance/ Å
Dipole moment/Debye
Angle/degree
Barycentric distance/Å
Electronic coupling/eV
Angle/degree
Barycentric distance/ Å


Barycentric distance/Å
Electronic coupling/eV
Dipole moment/Debye
Angle/degree
Electronic coupling/eV
Dipole moment/Debye
Barycentric distance/Å
Angle/degree
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Electronic coupling/eV
Angle/degree
Dipole moment/Debye
Barycentric distance/Å
Angle/degree
Electronic coupling/eV
Dipole moment/Debye
Angle/degree
Eletronic coupling/eV
Dipole moment/Debye
Barycentric distance/ Å
Energy/eV
Electronic coupling/eV
Barycentric distance/Å
Energy/eV
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Barycentric distance/Å
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Barycentric distance/Å
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Energy/eV

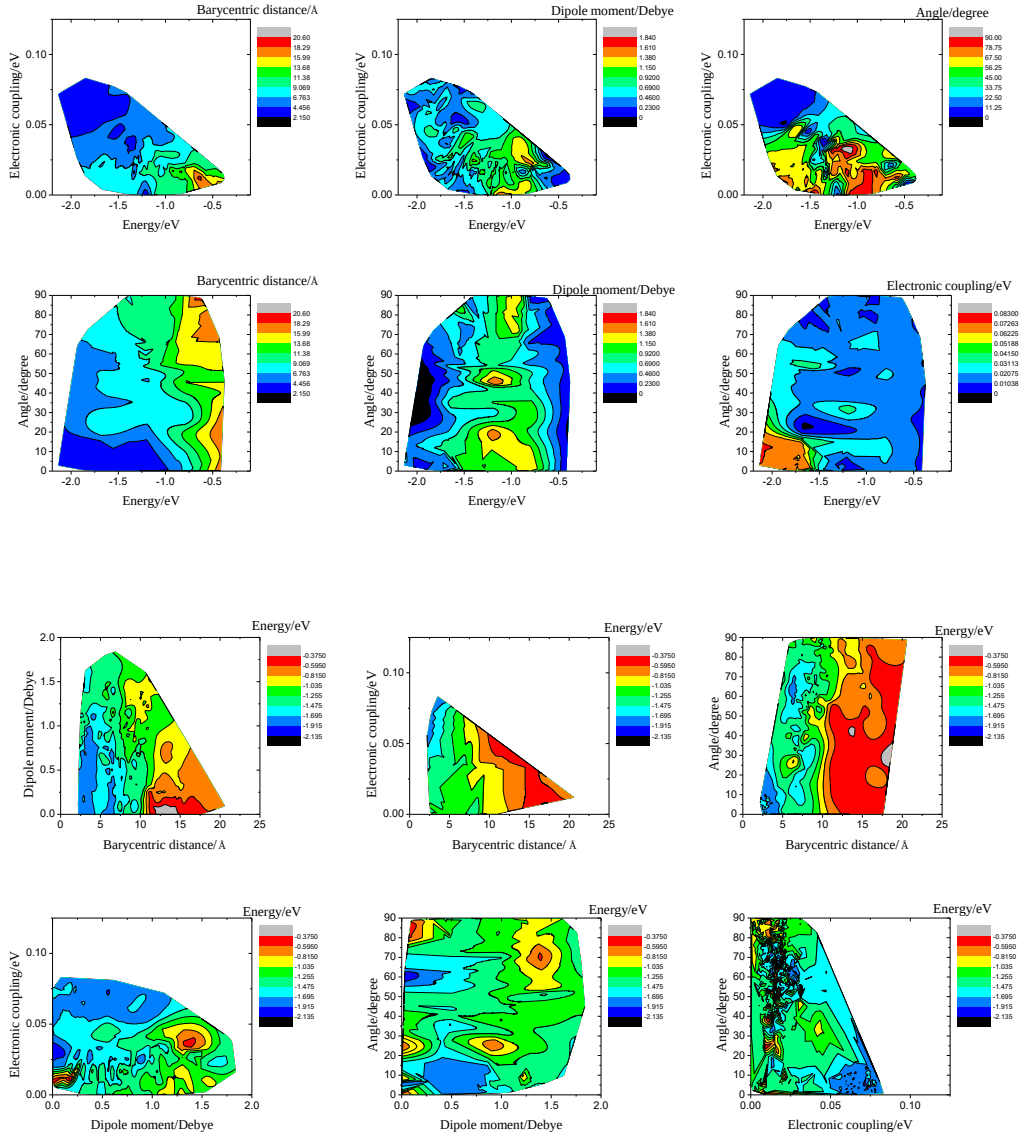

Figure.S6 Correlations among three of the stabilization energy, the barycentric distance, the angle between the two molecular planes, the dipole moment, and the electronic coupling for PDI **1** bi-molecular system.

[S1] Geng, Y., Li, H.-B., Wu, S.-X., Su, Z.-M., The interplay of intermolecular interactions, packing motifs and electron transport properties in perylene diimide related materials,: a theoretical perspectives. J. Mater. Chem. **2012**, *22*, 20840-20851.

[S2] Giaimo, J. M., Lockard, J. V., Sinks, L. E., Scott, A. M., Wilson, T. M., Wasielewski, M. R. Excited singlet states of covalently bound, cofacial dimers and trimers of perylene-3,4:9,10-bis(dicarboximide)s. J. Phys. Chem. C **2008**, *112*, 2322-2330.