Electronic supplementary information (ESI)

Accuracy of intermolecular interaction energies, particularly those of hetero-atom containing molecules obtained by DFT calculations with Grimme's D2, D3 and D3BJ dispersion corrections

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Estimation procedure of CCSD(T) level interaction energy at the basis set limit, Effects of basis set and electron correlation correction, Interaction energies for each complex, Geometries of complexes, Comparison of HF, MP2 and CCSD(T) level intermolecular interaction potentials, Basis set effects on B3LYP-D3 (B3LYP functional with Grimme's D3 dispersion correction), HF, MP2 and CCSD(T) level intermolecular interaction potentials calculated for slipped-parallel benzene dimer, Comparison of intermolecular interaction potentials obtained by DFT calculations using several functionals and Grimme's dispersion correction methods with CCSD(T) level intermolecular interaction potential.

Estimation procedure of CCSD(T) level interaction energy at the basis set limit

The CCSD(T) level interaction energy at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] for the complex was obtained according to equation (1)

$$E_{\mathrm{CCSD(T)(limit)}} = E_{\mathrm{MP2(limit)}} + \Delta\mathrm{CCSD(T)(limit)}, \quad (1)$$

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term [ΔCCSD(T)] at the basis set limit. The ΔCCSD(T) [= $E_{\mathrm{CCSD(T)}}$ - E_{MP2}] is the difference between the CCSD(T) level interaction energy [$E_{\mathrm{CCSD(T)}}$] and the MP2 level interaction energy (E_{MP2}). The ΔCCSD(T)(limit) was obtained by equation (2)

$$\Delta\mathrm{CCSD(T)(limit)} = \Delta\mathrm{CCSD(T)(M)} + \Delta\mathrm{(M)}\Delta\mathrm{CCSD(T)}, \quad (2)$$

where ΔCCSD(T)(M) denotes ΔCCSD(T) obtained using a Medium size basis set. The aug-cc-pVDZ basis set was used for the Medium size basis set in this work. The ΔCCSD(T) has a weak basis set dependence. Δ(M)ΔCCSD(T) is a correction term for slight underestimation of the ΔCCSD(T) by the Medium size basis set. The Δ(M)ΔCCSD(T) corresponds to a difference between the ΔCCSD(T)(limit) and ΔCCSD(T)(M).

We can calculate the Δ(M)ΔCCSD(T), if we know the value of $F_{\mathrm{corr(M)}}$, which is defined by equation (3)

$$F_{\mathrm{corr(M)}} = \Delta\mathrm{CCSD(T)(M)}/\Delta\mathrm{CCSD(T)(limit)} \quad (3).$$

From equations (2) and (3) we can obtained equation (4)

$$\Delta\mathrm{(M)}\Delta\mathrm{CCSD(T)} = \Delta\mathrm{CCSD(T)(M)} \times (1 - F_{\mathrm{corr(M)}})/F_{\mathrm{corr(M)}} \quad (4).$$

We calculated the $F_{\mathrm{corr(M)}}$ value by equation (5) in this work

$$F_{\mathrm{corr(M)}} = E_{\mathrm{corr(MP2)(M)}}/E_{\mathrm{corr(MP2)(limit)}} \quad (5),$$

where the $E_{\mathrm{corr(MP2)(M)}}$ denotes the MP2 level electron correlation effect on the calculated interaction energy ($E_{\mathrm{corr(MP2)}} = E_{\mathrm{MP2}} - E_{\mathrm{HF}}$) using the medium size basis set. The $E_{\mathrm{corr(MP2)(limit)}}$ denotes the MP2 level electron correlation effect at the basis set limit (= $E_{\mathrm{MP2(limit)}} - E_{\mathrm{HF(limit)}}$). We can obtain sufficiently accurate $F_{\mathrm{corr(M)}}$ value by equation (5), if the basis set dependence of the CCSD(T) level electron correlation effect is close to that of $E_{\mathrm{corr(MP2)}}$. The E_{HF} calculated using the aug-cc-pVTZ basis set was used as the $E_{\mathrm{HF(limit)}}$, since the basis set dependence of the E_{HF} beyond the aug-cc-pVTZ basis set is small.

Effects of electron correlation

The MP2 and CCSD(T) level intermolecular interaction potentials at the basis set limit [$E_{\mathrm{MP2(limit)}}$ and $E_{\mathrm{CCSD(T)(limit)}}$, respectively] estimated for the slipped-parallel benzene dimer are shown in Figure 1S(a). The Hartree-Fock (HF) level interaction potential calculated using the aug-cc-pVQZ basis set is also shown. The comparison of the HF and CCSD(T) level potentials shows that the attraction increases greatly by the electron correlation correction, which shows that the strong dispersion interactions exist in the benzene dimer, since the dispersion interactions have their origin in electron correlation. The comparison of HF, MP2 and CCSD(T) potentials of other complexes summarized in Figures S1(b)-(k) also show that the attraction by the dispersion interactions in these complexes are significant. The large dispersion interactions in these complexes show that these complexes are appropriate for evaluating the accuracy of the calculations of the dispersion interactions by the dispersion corrected DFT methods. The comparison of MP2 and CCSD(T) level interaction potentials of benzene dimer (Figure 1S(a)) shows that the MP2 calculations greatly overestimate the attraction in the benzene dimer compared with the more reliable CCSD(T) calculations. Similar overestimation of the attraction by the MP2 calculations is observed in the calculations of the interaction potentials of other aromatic molecules as shown in Figure 1S(c), (e)-(k), although the MP2 level potentials for the propane and perfluoromethane dimers are not largely different from the CCSD(T) level potentials (Figure 1S(b) and (d)).

Basis set effects on DFT calculations of intermolecular interaction energy

The basis set effects on intermolecular interaction energies obtained by dispersion corrected DFT calculations are small as in the case of HF calculations, although significant basis set effects are observed in the MP2 and CCSD(T) calculations in general. The basis set effects on the B3LYP-D3 (B3LYP functional with Grimme's D3 dispersion correction), HF, MP2 and CCSD(T) level intermolecular interaction potentials calculated for the slipped-parallel benzene dime are shown in Figure 2S. Small basis sets such as the 6-31G* and cc-pVDZ basis sets underestimate the attraction in the MP2 and CCSD(T) level calculations compared with large basis sets, since these small basis sets underestimate molecular polarizability owing to their insufficient flexibility, and therefore underestimate the dispersion interactions. The DFT calculations using the B3LYP functional can evaluate the contributions of exchange-repulsion and electrostatic interactions as in the case of the HF calculations, although the B3LYP functional cannot evaluate the attraction by the dispersion interactions. It is well known that the basis set effects on the intermolecular interaction energies obtained by DFT calculations are weak in general, if basis sets including polarization functions are used. The energy for the dispersion interactions are obtained using empirical potentials in the dispersion corrected DFT calculations, which is not affected by the choice of basis set. Therefore, the basis set effects on the interaction potentials obtained by B3LY-D3 calculations are weak.

Interaction energies for each complex

Interaction energies for benzene dimer

The intermolecular interaction potentials for the slipped-parallel benzene dimer obtained by DFT calculations using several functionals and the three dispersion correction methods are compared with the CCSD(T) [$E_{\mathrm{CCSD(T)(limit)}}$] level potential as shown in Figure 3S. The agreement with the CCSD(T) level potential depends strongly on the choice of functional and dispersion correction method. The performance of each combination of functional and correction method is shown in Table 1. Several combinations of functionals and dispersion correction methods show very good performance. The interaction potentials calculated using the B97D functional, which includes the D2 correction, the TPSS functional with the D2 correction, the BLYP, BPBE, PBE, TPSS, B3LYP, B3PW91, PBE1PBE, LC-ωPBE, M052X, M062X, M06L, B97D functionals with the D3 correction, and the PBE, TPSS, B3LYP, PBE1PBE, CAM-B3LYP functionals with the D3BJ correction are very close to the CCSD(T) level interaction potential. Some other combinations also show good performance. The potentials calculated using the ωB97XD functional, which includes the D2 correction, the BP86, PBE, B3LYP functionals with the D2 correction, the BP86, M05, M06HF functionals with the D3 correction, and the BLYP, LC-ωPBE functionals with the D3BJ correction are close to the CCSD(T) level interaction potential. The potentials obtained using the BMK and APF functionals do not agree with the CCSD(T) level interaction potential, even after the dispersion corrections. The interaction potentials calculated using the B2PLYPD and mPW2PLYPD functionals, which include the D2 correction, underestimate the attraction significantly compared with the CCSD(T) level potential.

The interaction potentials obtained using the selected functionals with the three dispersion correction methods (D2, D3 and D3BJ) are compared with the CCSD(T) level potential as shown in Figure 2. The potentials obtained with the D3 correction agree with CCSD(T) level potential better than the potentials obtained with the D2 correction in general. The potentials obtained with the D2 correction often underestimate the attraction. Although the D3BJ correction is an improved version of the D3 correction, the potentials obtained with the D3 correction agree with CCSD(T) level potential better than the potentials obtained with the D3BJ correction. The potentials obtained with the D3BJ correction often overestimate the attraction.

Interaction energies for propane dimer

The intermolecular interaction potentials for the propane dimer obtained by DFT calculations are compared with the CCSD(T) level potentials as shown in Figure 4S. The functional and dispersion correction method dependence of the calculated interaction potential for the propane dimer is somewhat different from the dependence observed in the calculations of the benzene dimer as shown in Table 1. The calculations using the M06, M06L, ωB97, ωB97X functionals, the BPBE, B3PW91, LC-ωPBE, M062X, M06HF functionals with the D3 correction, and the BLYP, TPSS, B3LYP, PBE1PBE, CAM-B3LYP, LC-ωPBE functionals with the D3BJ correction show very good performance. The calculations using the M062X functional, the APFD functional, which includes dispersion correction, the B97D3 functional, which includes the D3BJ correction, the BLYP, BP86, TPSS, B3LYP, PBE1PBE, CAM-B3LYP, M052X, M06L, B97D functionals with the D3 correction, and the BP86, PBE, B3PW91 functionals with the D3BJ correction show good performance.

The interaction potentials obtained using the selected functionals with the three dispersion correction methods (D2, D3 and D3BJ) are compared with the CCSD(T) level potential as shown in Figure 14S. The potentials obtained with the D2 correction overestimate the attraction compared with CCSD(T) level potential. The agreement is improved using the D3 or D3BJ correction, although the potentials obtained using some functionals with the D3 or D3BJ correction slightly overestimate the attraction.

Interaction energies for benzene-methane complex

The intermolecular interaction potentials for the benzene-methane complex obtained by DFT calculations are compared with the CCSD(T) level potential as shown in Figure 5S. The calculated interaction potentials for the benzene-methane complex show similar dependence on the functional and dispersion correction method as in the case of the propane dimer as shown in Table 1. The calculations using the ωB97, ωB97X, B97D functionals, the BLYP, BP86, BPBE, TPSS, B3LYP, B3PW91, CAM-B3LYP, M06, M062X, M06HF, B97D functionals with the D3 correction, and the BLYP, BMK, BP86, BPBE, PBE, TPSS, B3LYP, B3PW91, PBE1PBE, CAM-B3LYP, LC-ωPBE functionals with the D3BJ correction show very good performance. The calculations using the M062X, APFD, ωB97XD, B97D3 functionals, the BLYP, BP86, PBE, TPSS, B3LYP functionals with the D2 correction, and the PBE, BE1PBE, LC-ωPBE, M05, M052X functionals with the D3 correction show good performance.

The interaction potentials obtained using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potential as shown in Figure 15S. Most of the potentials obtained with the D2 correction overestimate the attraction compared with CCSD(T) level potential. The agreement is improved using the D3 or D3BJ correction. The potentials obtained using various functionals with the D3 or D3BJ correction show good performance.

Interaction energies for perfluoromethane dimer

The intermolecular interaction potentials for the perfluoromethane dimer obtained by DFT calculations are compared with the CCSD(T) level potentials as shown in Figure 6S. The calculated interaction potentials for the perfluoromethane dimer show completely different dependence on functional and dispersion correction method compared with the calculated interaction potentials for the three complexes of hydrocarbon molecules as shown in Table 1. Most of the potentials calculated for the perfluoromethane dimer using various functionals and dispersion correction methods do not reproduce the CCSD(T) level potential. Only the calculations using the PBE, M062X, M06HF functionals with the D3 correction show very good performance. The calculations using the M052X, M062X, ωB97XD functionals, mPW2PLYPD functional, which includes the D2 correction, and the TPSS, PBE1PBE, CAM-B3LYP, M05 functionals with the D3 correction show good performance.

The calculated interaction potentials using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potential as shown in Figure 3. The potentials obtained with the D2 correction overestimate the attraction compared with CCSD(T) level potential except for the ωB97XD functional. On the other hand, most of the potentials obtained with the D3 or D3BJ correction underestimate the attraction.

Interaction energy for benzene-chlorobenzene and benzene-bromobenzene complexes

The intermolecular interaction potentials for the benzene-chlorobenzene and benzene-bromobenzene complexes obtained by DFT calculations are compared with the CCSD(T) level potentials as shown in Figures 7S and 8S. The dependence of functional and dispersion correction method on the calculated interaction potentials for the benzene-chlorobenzene and benzene-bromobenzene complexes is similar to the dependence observed in the calculations of the interaction potential for the benzene dimer as shown in table 1.

The calculations for the benzene-chlorobenzene complex using the APFD functional, the BLYP, BP86, BPBE, B3LYP, B3PW91, LC-ωPBE, B97D functionals with the D3 correction, and the BLYP, BP86, BPBE, B3LYP, B3PW91, PPBE1PBE, LC-ωPBE functionals with the D3BJ correction show very good performance. The calculations using the B97D3 functional, the PBE functional with the D2 correction, the PBE, TPSS, PPBE1PBE, CAM-B3LYP, M05, M052X, M062X functionals with the D3 correction, and the PBE, TPSS, CAM-B3LYP functionals with the D3BJ correction show good performance.

The calculations for the benzene-bromobenzene complex using the B97D functional, the PBE, TPSS functionals with the D2 correction, the PBE, TPSS, B3LYP, PBE1PBE, CAM-B3LYP, LC-ωPBE, M05, B97D functionals with the D3 correction, and the PBE, TPSS, B3LYP, PBE1PBE, CAM-B3LYP, LC-ωPBE functionals with the D3BJ correction show very good performance. The calculations using the ωB97, ωB97X, AFPD, ωB97XD, B97D3 functionals, the B3LYP functional with the D2 correction, the BLYP, BP86, B3PW91, M052X, M062X functionals with the D3 correction, and the BLYP, B3PW91 functionals with the D3BJ correction show good performance.

The calculated interaction potentials using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potentials as shown in Figures 16S and 17S. Most of the potentials obtained with the D2 correction underestimate the attraction compared with CCSD(T) level potential. The agreement is improved using the D3 or D3BJ correction. The potentials obtained using various functionals with the D3 or D3BJ correction show good performance.

Interaction energies for furan, thiophene and selenophene dimers

The intermolecular interaction potentials for the furan, thiophene and selenophene dimers obtained by DFT calculations are compared with the CCSD(T) level potentials as shown in Figures 9S-11S. The calculated interaction potentials for the furan, thiophene and selenophene dimers depend strongly on functional and dispersion correction method. Only the interaction potentials calculated for the furan dimer using limited combinations of functionals and dispersion correction methods are close to the CCSD(T) level interaction potential as shown in Table 1. The interaction potentials calculated for thiophene and selenophene dimers using some functionals with the D3 or D3BJ corrections are close to the CCSD(T) level potentials.

The calculations for the furan dimer using the PBE, M052X functionals with the D3 correction show very good performance. The calculations using the PBE functional with the D2 correction, the BLYP, TPSS, B3LYP, PBE1PBE, M05, M06, M06L functionals with the D3 correction, and the PBE, CAM-B3LYP functionals with the D3BJ correction show good performance.

The calculations for the thiophene dimer using the BLYP, BP86, BPBE, PBE, B3LYP, B3PW91, PBE1PBE, LC-ωPBE, B97D functionals with the D3 correction, and the PBE, TPSS, PBE1PBE, CAM-B3LYP, LC-ωPBE functionals with the D3BJ correction show very good performance. The calculations using ωB97X, B97D3 functionals, the TPSS, CAM-B3LYP, M05, M052X, M06, M062X functionals with the D3 correction, and the B3LYP functional with the D3BJ correction show good performance.

The calculations for the selenophene dimer using the ωB97 functional, the PBE, TPSS functionals with the D2 correction, the BLYP, PBE, TPSS, B3LYP, PBE1PBE, CAM-B3LYP, LC-ωPBE, B97D functionals with the D3 correction, and the PBE, CAM-B3LYP functionals with the D3BJ correction show very good performance. The calculations using the ωB97X, ωB97XD, B97D, functionals, the BP86 functional with the D2 correction, the B3PW91, M05, M06, M062X functionals with the D3 correction, and the TPSS, PBE1PBE, LC-ωPBE functionals with the D3BJ correction show good performance.

The calculated interaction potentials using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potentials as shown in Figures 4, 5 and 18S. Most of the potentials obtained for the furan dimer with the D2 correction overestimate the attraction compared with CCSD(T) level potential. On the other hand, most of the potentials obtained for the furan dimer with the D3 or D3BJ correction underestimate the attraction. The dependence of functional and dispersion correction method on the calculated interaction potentials for the thiophene and selenophene dimers is similar to the dependence observed in the calculations of the interaction potentials for the benzene dimer. The potentials obtained with the D2 correction underestimate the attraction. The potentials obtained with the D3 correction agree with CCSD(T) level potential better than the potentials obtained with the D3BJ correction. The potentials obtained with the D3BJ correction often overestimate the attraction.

Interaction energies for pyridine and phosphorine dimers

The intermolecular interaction potentials for the pyridine and phosphorine dimers obtained by DFT calculations are compared with the CCSD(T) level potentials as shown in Figures 12S and 13S. The calculated interaction potentials for the pyridine and phosphorine dimers depend strongly on functional and dispersion correction method. Only the interaction potentials calculated with limited combinations of functionals and dispersion correction methods are close to the CCSD(T) level interaction potentials as shown in Table 1.

The calculations for the pyridine dimer using the APFD, B97D3 functionals, the BLYP, BP86, M06L functionals with the D3 correction, and the BLYP, BMK, BP86, BPBE, B3LYP functionals with the D3BJ correction show very good performance. The calculations using the BPBE, PBE, TPSS, M05 functionals with the D3 correction and the PBE, TPSS, B3PW91 functionals with the D3BJ correction show good performance.

The calculations for the phosphorine dimer using the BP86, BPBE, B3PW91, M06 functionals with the D3 correction and the PBE, PBE1PBE, CAM-B3LYP functionals with the D3BJ correction show very good performance. The calculations using the ωB97 functional, the PBE1PBE, LC-ωPBE, M062X, B97D functionals with the D3 correction, and the TPSS, B3LYP functionals with the D3BJ correction show good performance.

The calculated interaction potentials using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potentials as shown in Figures 19S and 20S. The potentials obtained for the pyridine dimer with the D2 correction underestimate the attraction compared with CCSD(T) level potential. Most of the potentials obtained with the D3 correction also underestimate the attraction. The agreement was improved using the D3BJ correction. The potentials obtained using some functionals with the D3BJ correction show good performance.

The potentials obtained for the phosphorine dimer with the D2 correction underestimate the attraction compared with CCSD(T) level potential. The agreement is improved using the D3 correction, although the potentials obtained with the D3 correction still slightly underestimate the attraction. On the other hand, most of the potentials obtained with the D3BJ correction overestimate the attraction.

Geometries of complexes

Benzene dimer (R = 4.0 Å)

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---------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.782013    0.485662    0.000000
      2          6           0        1.782013   -0.211159    1.206930
      3          6           0        1.782013   -1.604802    1.206930
      4          6           0        1.782013   -2.301624    0.000000
      5          6           0        1.782013   -1.604802   -1.206930
      6          6           0        1.782013   -0.211159   -1.206930
      7          1           0        1.782013    1.567114    0.000000
      8          1           0        1.782013    0.329567    2.143495
      9          1           0        1.782013   -2.145528    2.143495
     10          1           0        1.782013   -3.383076    0.000000
     11          1           0        1.782013   -2.145528   -2.143495
     12          1           0        1.782013    0.329567   -2.143495
     13          6           0       -1.782013   -0.485662    0.000000
     14          6           0       -1.782013    0.211159    1.206930
     15          6           0       -1.782013    1.604802    1.206930
     16          6           0       -1.782013    2.301624    0.000000
     17          6           0       -1.782013    1.604802   -1.206930
     18          6           0       -1.782013    0.211159   -1.206930
     19          1           0       -1.782013   -1.567114    0.000000
     20          1           0       -1.782013   -0.329567    2.143495
     21          1           0       -1.782013    2.145528    2.143495
     22          1           0       -1.782013    3.383076    0.000000
     23          1           0       -1.782013    2.145528   -2.143495
     24          1           0       -1.782013   -0.329567   -2.143495
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Propane dimer (R = 3.8 Å)

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---------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.900000    0.000000    1.000000
      2          6           0        1.900000    0.851692   -0.262476
      3          6           0        1.900000    0.851692    2.262476
      4          1           0        1.026492   -0.653489    1.000000
      5          1           0        2.773508   -0.653489    1.000000
      6          1           0        1.900000    0.239314   -1.162742
      7          1           0        1.020524    1.494636   -0.294502
      8          1           0        2.779476    1.494636   -0.294502
      9          1           0        1.900000    0.239314    3.162742
     10          1           0        2.779476    1.494636    2.294502
     11          1           0        1.020524    1.494636    2.294502
     12          6           0       -1.900000    0.000000    1.000000
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```
    13         6         0       -1.900000   -0.851692   -0.262476
    14         6         0       -1.900000   -0.851692    2.262476
    15         1         0       -1.026492    0.653489    1.000000
    16         1         0       -2.773508    0.653489    1.000000
    17         1         0       -1.900000   -0.239314   -1.162742
    18         1         0       -1.020524   -1.494636   -0.294502
    19         1         0       -2.779476   -1.494636   -0.294502
    20         1         0       -1.900000   -0.239314    3.162742
    21         1         0       -2.779476   -1.494636    2.294502
    22         1         0       -1.020524   -1.494636    2.294502
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Benzene-methane complex (*R* = 3.8 Å)

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---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
     1          6           0        1.393643    0.000000    1.000000
     2          6           0        0.696821    1.206930    1.000000
     3          6           0       -0.696821    1.206930    1.000000
     4          6           0       -1.393643    0.000000    1.000000
     5          6           0       -0.696822   -1.206930    1.000000
     6          6           0        0.696821   -1.206930    1.000000
     7          1           0        2.475095    0.000000    1.000000
     8          1           0        1.237548    2.143495    1.000000
     9          1           0       -1.237547    2.143495    1.000000
    10          1           0       -2.475095    0.000000    1.000000
    11          1           0       -1.237548   -2.143495    1.000000
    12          1           0        1.237548   -2.143495    1.000000
    13          6           0        0.000000    0.000000   -2.800000
    14          1           0        0.000000    0.000000   -1.714626
    15          1           0        1.023300    0.000000   -3.161791
    16          1           0       -0.511650   -0.886204   -3.161791
    17          1           0       -0.511650    0.886204   -3.161791
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Perfluoromethane dimer (*R* = 4.0 Å)

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---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
     1          6           0        0.000000    0.000000    2.000000
     2          9           0        0.000000    0.000000    3.319353
     3          9           0        0.000000    1.243898    1.560216
     4          9           0        1.077247   -0.621949    1.560216
     5          9           0       -1.077247   -0.621949    1.560216
     6          6           0        0.000000    0.000000   -2.000000
     7          9           0        0.000000    0.000000   -3.319353
     8          9           0        0.000000   -1.243898   -1.560216
     9          9           0        1.077247    0.621949   -1.560216
    10          9           0       -1.077247    0.621949   -1.560216
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Benzene-chlorobenzene complex (R = 3.4 Å)

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 -------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 -------------------------------------------------------------------
      1          6           0        0.000000    0.000000    1.861074
      2          6           0        0.000000    1.212914    2.543714
      3          6           0        0.000000   -1.212914    2.543714
      4          6           0        0.000000    1.205033    3.936463
      5          6           0        0.000000   -1.205033    3.936463
      6          6           0        0.000000    0.000000    4.635874
      7         17           0        0.000000    0.000000    0.125674
      8          1           0        0.000000    2.140676    1.990382
      9          1           0        0.000000   -2.140676    1.990382
     10          1           0        0.000000    2.144381    4.472034
     11          1           0        0.000000   -2.144381    4.472034
     12          1           0        0.000000    0.000000    5.716574
     13          6           0       -1.393643    0.000000   -3.274326
     14          6           0       -0.696822    1.206930   -3.274326
     15          6           0        0.696822    1.206930   -3.274326
     16          6           0        1.393643    0.000000   -3.274326
     17          6           0        0.696822   -1.206930   -3.274326
     18          6           0       -0.696822   -1.206930   -3.274326
     19          1           0       -2.475095    0.000000   -3.274326
     20          1           0       -1.237548    2.143495   -3.274326
     21          1           0        1.237548    2.143495   -3.274326
     22          1           0        2.475095    0.000000   -3.274326
     23          1           0        1.237548   -2.143495   -3.274326
     24          1           0       -1.237548   -2.143495   -3.274326
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Benzene-bromobenzene complex (R = 3.6 Å)

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 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 -------------------------------------------------------------------
      1          6           0        0.000000    0.000000    2.010183
      2          6           0        0.000000    1.213329    2.692840
      3          6           0        0.000000   -1.213329    2.692840
      4          6           0        0.000000    1.204969    4.085986
      5          6           0        0.000000   -1.204969    4.085986
      6          6           0        0.000000    0.000000    4.785183
      7         35           0        0.000000    0.000000    0.125783
      8          1           0        0.000000    2.143407    2.143655
      9          1           0        0.000000   -2.143407    2.143655
     10          1           0        0.000000    2.144334    4.621727
     11          1           0        0.000000   -2.144334    4.621727
     12          1           0        0.000000    0.000000    5.865883
     13          6           0       -1.393600    0.000000   -3.474217
     14          6           0       -0.696800    1.206893   -3.474217
     15          6           0        0.696800    1.206893   -3.474217
     16          6           0        1.393600    0.000000   -3.474217
     17          6           0        0.696800   -1.206893   -3.474217
     18          6           0       -0.696800   -1.206893   -3.474217
     19          1           0       -2.475100    0.000000   -3.474217
```

20	1	0	-1.237550	2.143499	-3.474217
21	1	0	1.237550	2.143499	-3.474217
22	1	0	2.475100	0.000000	-3.474217
23	1	0	1.237550	-2.143499	-3.474217
24	1	0	-1.237550	-2.143499	-3.474217

Furan dimer (*R* = 4.0 Å)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.985571	-2.174671	0.000000
2	6	0	0.174671	-2.174671	1.090200
3	6	0	0.174671	-2.174671	-1.090200
4	6	0	-1.136465	-2.174671	0.712695
5	6	0	-1.136465	-2.174671	-0.712695
6	1	0	0.670479	-2.174671	2.043132
7	1	0	0.670479	-2.174671	-2.043132
8	1	0	-1.986078	-2.174671	1.371806
9	1	0	-1.986078	-2.174671	-1.371806
10	8	0	0.174671	1.014429	0.000000
11	6	0	0.174671	1.825329	1.090200
12	6	0	0.174671	1.825329	-1.090200
13	6	0	0.174671	3.136465	0.712695
14	6	0	0.174671	3.136465	-0.712695
15	1	0	0.174671	1.329521	2.043132
16	1	0	0.174671	1.329521	-2.043132
17	1	0	0.174671	3.986078	1.371806
18	1	0	0.174671	3.986078	-1.371806

Thiophene dimer (*R* = 4.8 Å)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.185769	-2.400469	0.000000
2	6	0	-0.000469	-2.400469	1.233300
3	6	0	-0.000469	-2.400469	-1.233300
4	6	0	1.271980	-2.400469	0.706990
5	6	0	1.271980	-2.400469	-0.706990
6	1	0	-0.294994	-2.400469	2.269038
7	1	0	-0.294994	-2.400469	-2.269038
8	1	0	2.162405	-2.400469	1.316934
9	1	0	2.162405	-2.400469	-1.316934
10	16	0	-0.000469	1.214231	0.000000
11	6	0	-0.000469	2.399531	1.233300
12	6	0	-0.000469	2.399531	-1.233300
13	6	0	-0.000469	3.671980	0.706990
14	6	0	-0.000469	3.671980	-0.706990
15	1	0	-0.000469	2.105006	2.269038
16	1	0	-0.000469	2.105006	-2.269038
17	1	0	-0.000469	4.562405	1.316934

18	1	0	-0.000469	4.562405	-1.316934

Selenophene dimer (R = 5.0 Å)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	34	0	1.112559	-2.288859	0.000000
2	6	0	-0.211141	-2.288859	1.279700
3	6	0	-0.211141	-2.288859	-1.279700
4	6	0	-1.460801	-2.288859	0.708298
5	6	0	-1.460801	-2.288859	-0.708298
6	1	0	0.027556	-2.288859	2.330223
7	1	0	0.027556	-2.288859	-2.330223
8	1	0	-2.364038	-2.288859	1.301111
9	1	0	-2.364038	-2.288859	-1.301111
10	34	0	-0.211141	1.387441	0.000000
11	6	0	-0.211141	2.711141	1.279700
12	6	0	-0.211141	2.711141	-1.279700
13	6	0	-0.211141	3.960801	0.708298
14	6	0	-0.211141	3.960801	-0.708298
15	1	0	-0.211141	2.472444	2.330223
16	1	0	-0.211141	2.472444	-2.330223
17	1	0	-0.211141	4.864038	1.301111
18	1	0	-0.211141	4.864038	-1.301111

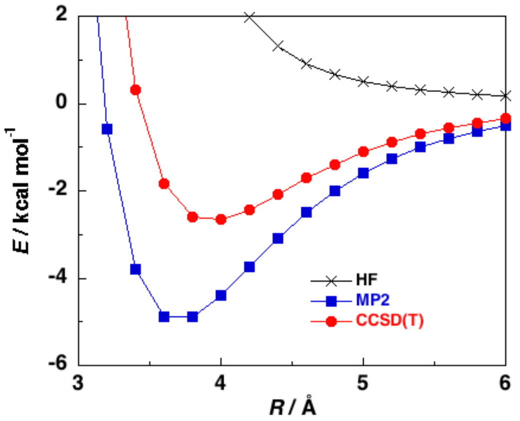
Pyridine dimer (R = 4.6 Å)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	7	0	1.412937	-2.309237	0.000000
2	6	0	0.710502	-2.309237	1.141031
3	6	0	0.710502	-2.309237	-1.141031
4	6	0	-0.680999	-2.309237	1.193939
5	6	0	-0.680999	-2.309237	-1.193939
6	6	0	-1.394463	-2.309237	0.000000
7	1	0	1.291757	-2.309237	2.054798
8	1	0	1.291757	-2.309237	-2.054798
9	1	0	-1.186811	-2.309237	2.148980
10	1	0	-1.186811	-2.309237	-2.148980
11	1	0	-2.475663	-2.309237	0.000000
12	7	0	0.009237	0.887063	0.000000
13	6	0	0.009237	1.589498	1.141031
14	6	0	0.009237	1.589498	-1.141031
15	6	0	0.009237	2.980999	1.193939
16	6	0	0.009237	2.980999	-1.193939
17	6	0	0.009237	3.694463	0.000000
18	1	0	0.009237	1.008243	2.054798
19	1	0	0.009237	1.008243	-2.054798
20	1	0	0.009237	3.486811	2.148980
21	1	0	0.009237	3.486811	-2.148980

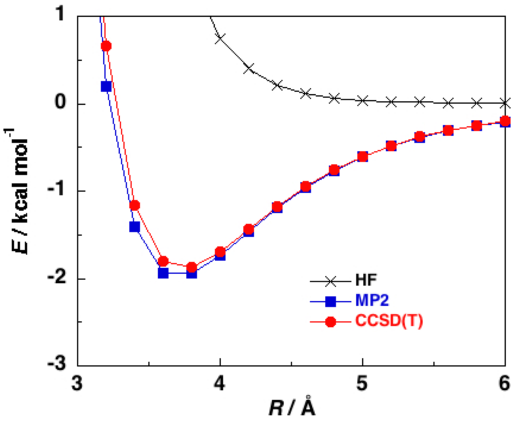
```
    22          1          0        0.009237    4.775663    0.000000
 ---------------------------------------------------------------------
```

Phosphorine dimer (R = 5.2 Å)

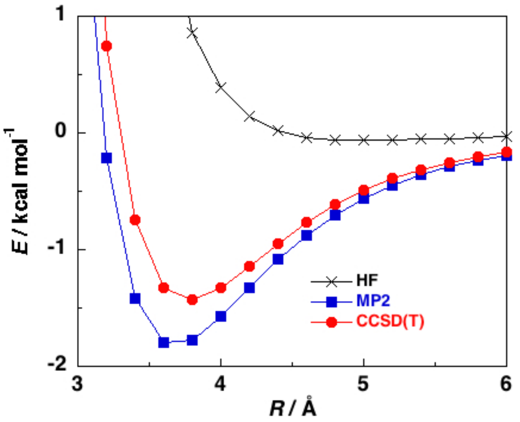
```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
    1         15          0       -2.549859   -1.536859    0.000000
    2          6          0       -2.549859   -0.419249    1.331909
    3          6          0       -2.549859   -0.419249   -1.331909
    4          6          0       -2.549859    0.967908    1.222800
    5          6          0       -2.549859    0.967908   -1.222800
    6          6          0       -2.549859    1.637141    0.000000
    7          1          0       -2.549859   -0.850591    2.326523
    8          1          0       -2.549859   -0.850591   -2.326523
    9          1          0       -2.549859    1.560573    2.130137
   10          1          0       -2.549859    1.560573   -2.130137
   11          1          0       -2.549859    2.719141    0.000000
   12         15          0        1.063141    0.050141    0.000000
   13          6          0        2.180751    0.050141    1.331909
   14          6          0        2.180751    0.050141   -1.331909
   15          6          0        3.567908    0.050141    1.222800
   16          6          0        3.567908    0.050141   -1.222800
   17          6          0        4.237141    0.050141    0.000000
   18          1          0        1.749409    0.050141    2.326523
   19          1          0        1.749409    0.050141   -2.326523
   20          1          0        4.160573    0.050141    2.130137
   21          1          0        4.160573    0.050141   -2.130137
   22          1          0        5.319141    0.050141    0.000000
 ---------------------------------------------------------------------
 Rotational constants (GHZ):           1.4790002           0.3347618           0.323
```



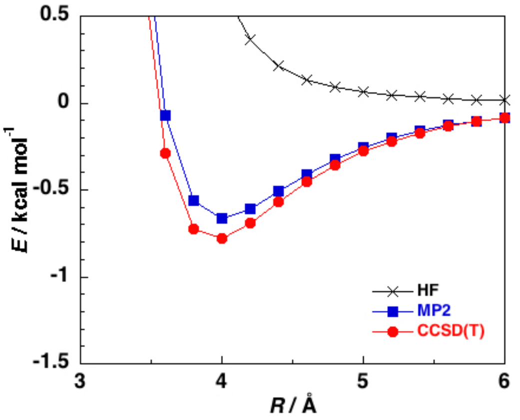
(a) C_6H_6-C_6H_6



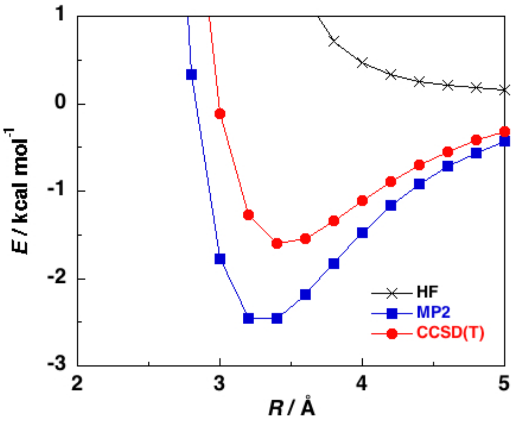
(b) C_3H_8-C_3H_8



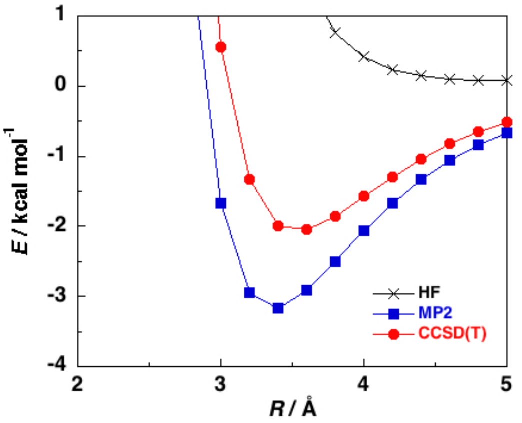
(c) C_6H_6-CH_4



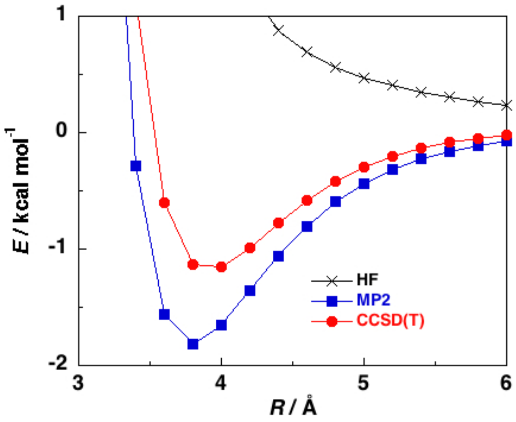
(d) CF_4-CF_4



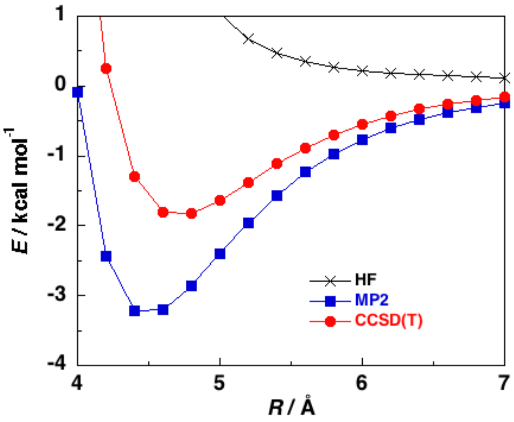
(e) C_6H_6-C_6H_5Cl



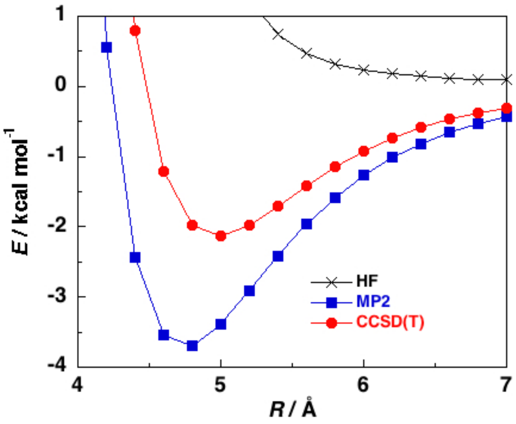
(f) C_6H_6-C_6H_5Br



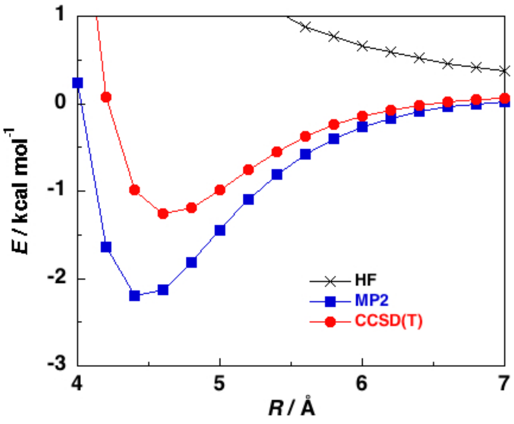
(g) C_4H_4O-C_4H_4O



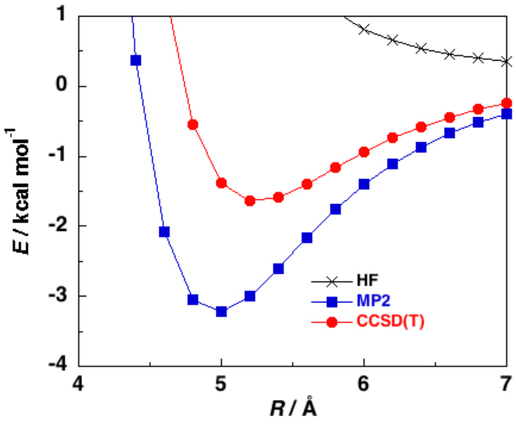
(h) C_4H_4S-C_4H_4S



(i) C_4H_4Se-C_4H_4Se

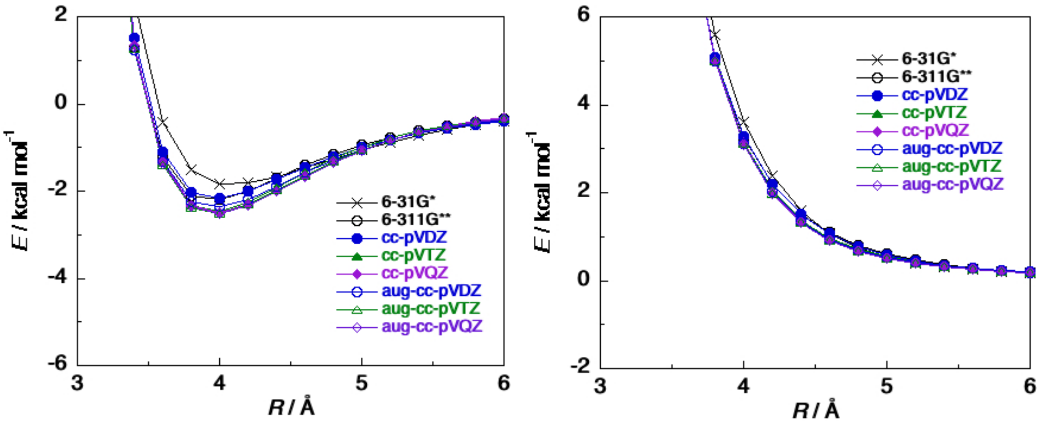


(j) C_5H_5N-C_5H_5N

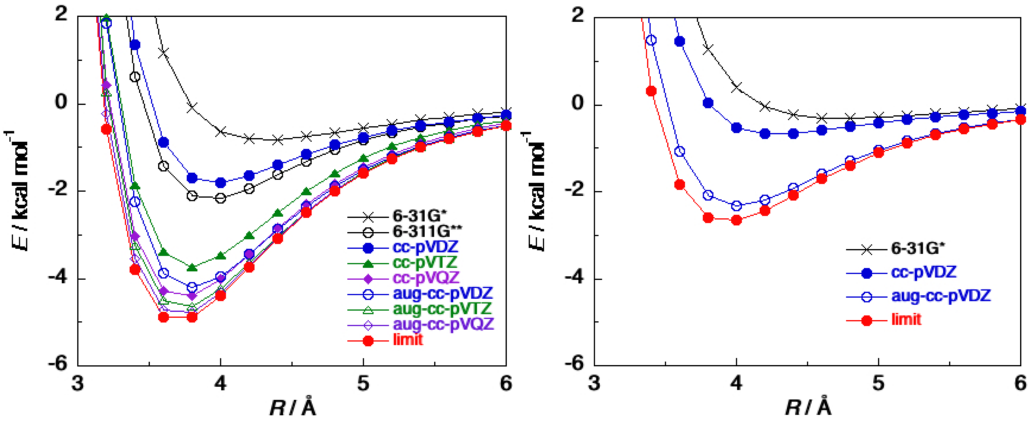


(k) C_5H_5P-C_5H_5P

Figure 1S. HF, MP2 and CCSD(T) level intermolecular interaction potentials calculated for (a) benzene dimer; (b) propane dimer; (c) benzene-methane complex; (d) perfluoromethane dimer; (e) benzene-chlorobenzene complex; (f) benzene-bromobenzene complex; (g) furan dimer; (h) thiophene dimer; (i) selenophene dimer; (j) pyridine dimer; (k) phosphorine dimer. The geometries of complexes are shown in Figure 1. The MP2 and CCSD(T) level interaction potentials were obtained from estimated interaction energies at the basis set limit. The HF level potentials were obtained by HF/aug-cc-pVQZ calculations.

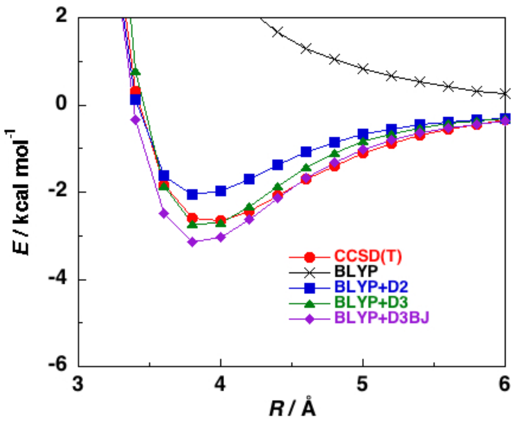


(a) B3LYP-D3 (b) HF

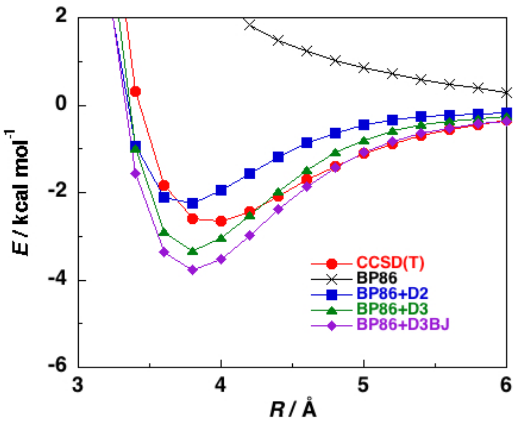


(c) MP2 (d) CCSD(T)

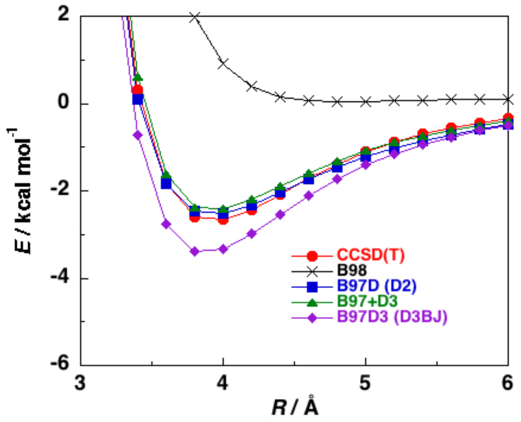
Figure 2S. Basis set effects on B3LYP-D3 (B3LYP functional with Grimme's D3 dispersion correction), HF, MP2 and CCSD(T) level intermolecular interaction potentials calculated for C_{2h} slipped-parallel benzene dimer. The geometry of dimer is shown in Figure 1. The estimated MP2 and CCSD(T) level interaction potentials at the basis limit (limit) are also shown.


2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

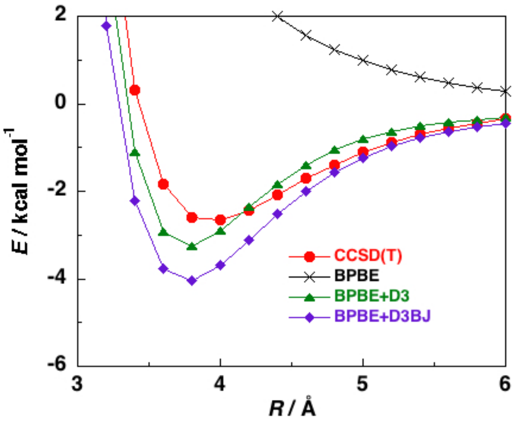
(a)


2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

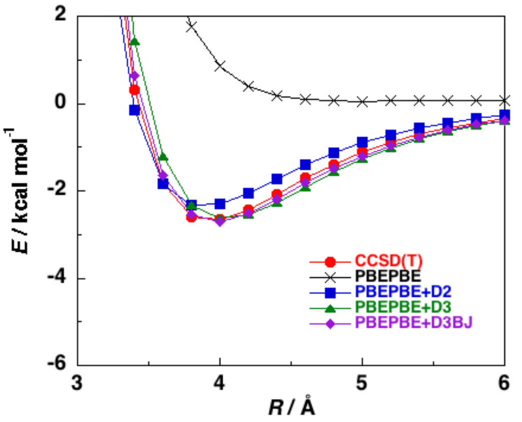
(b)


2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

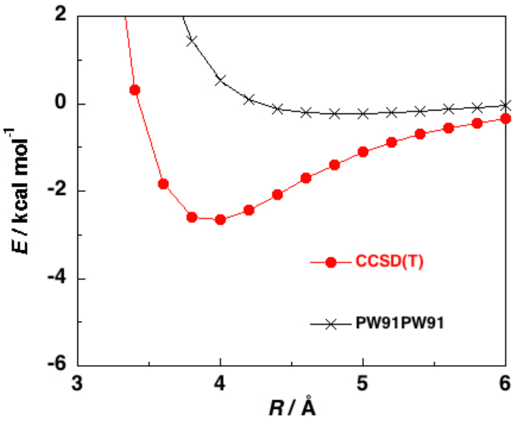
(c)


2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

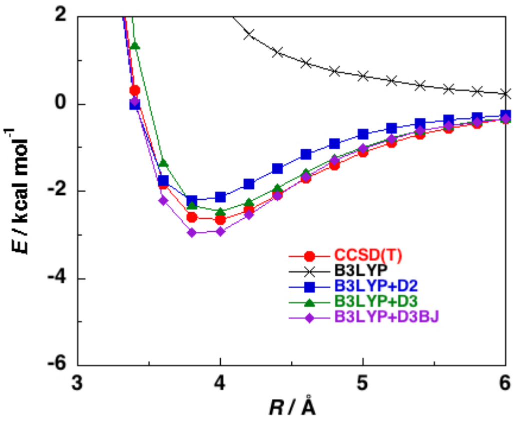
(d)


2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

(e)

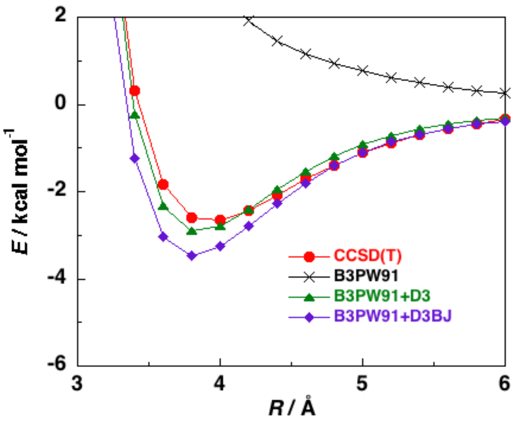

2
0
-2
-4
-6
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
PW91PW91

(f)



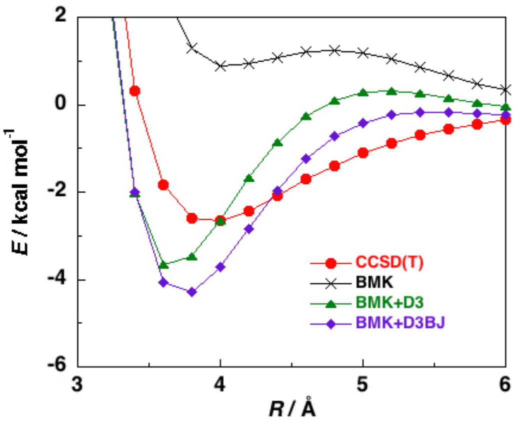
2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

(g)



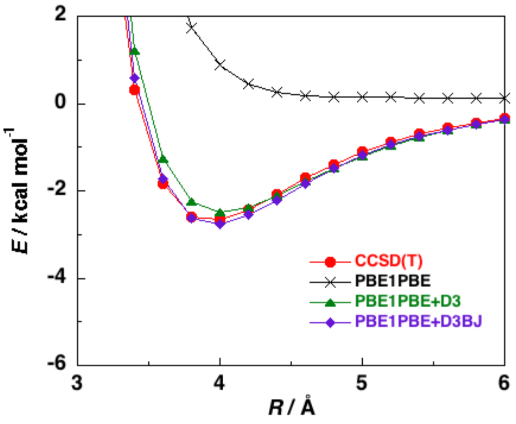
2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

(h)



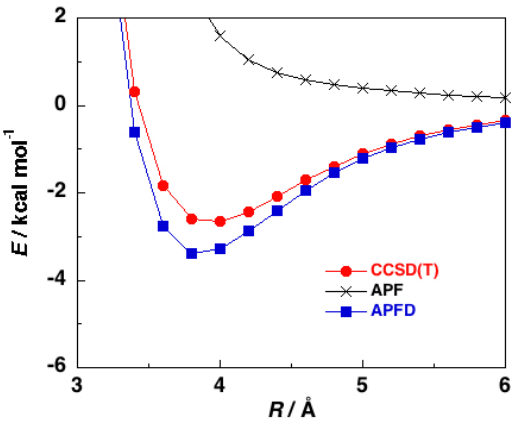
2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

(i)



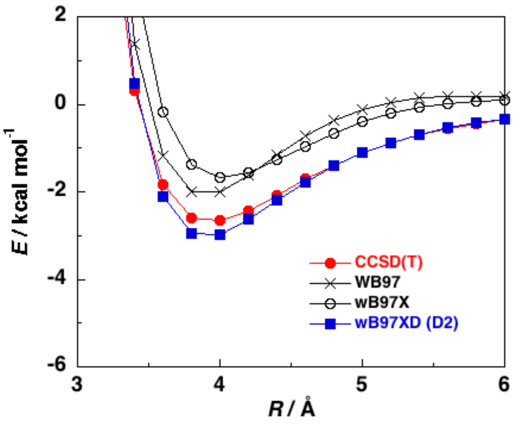
2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

(j)



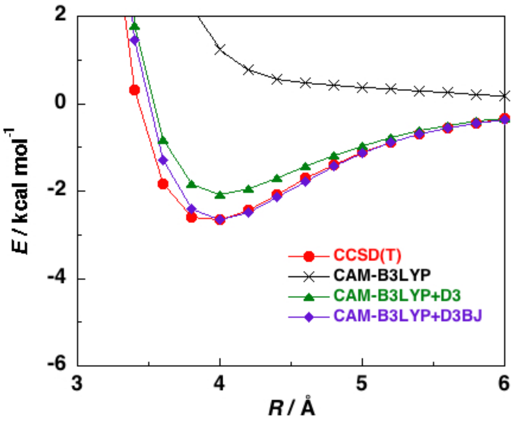
2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
APF
APFD

(k)

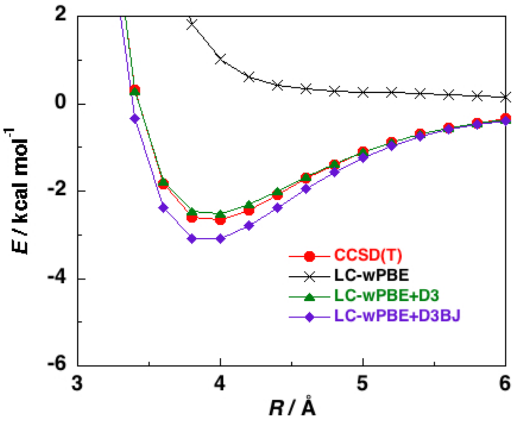


2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

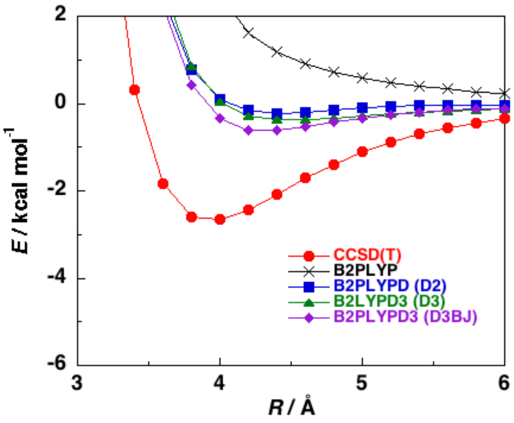
(l)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

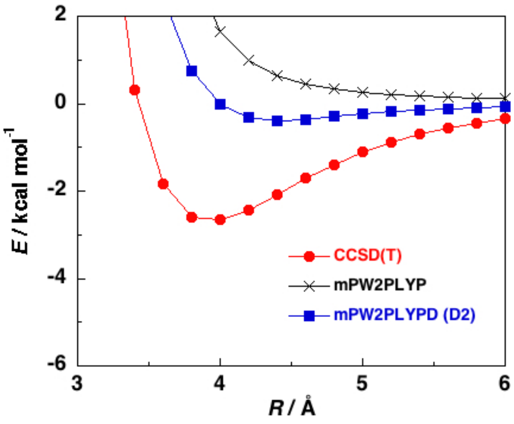
(m)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

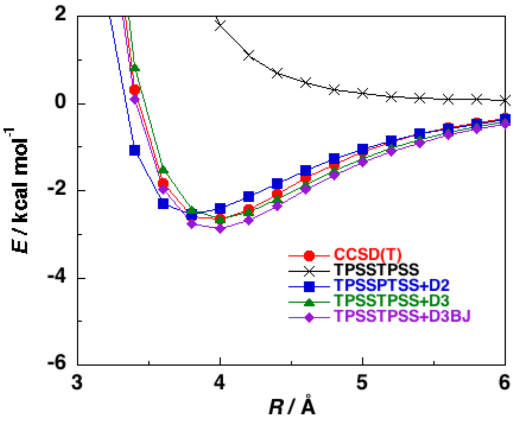
(n)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

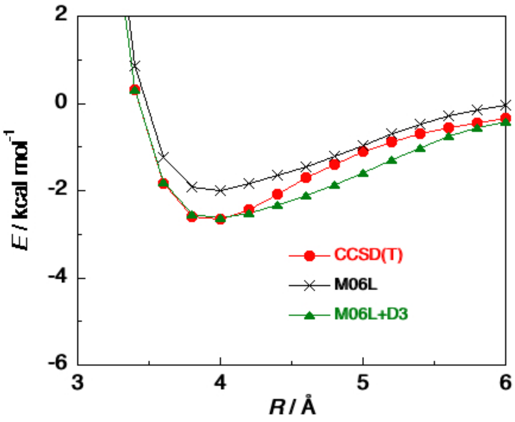
(o)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

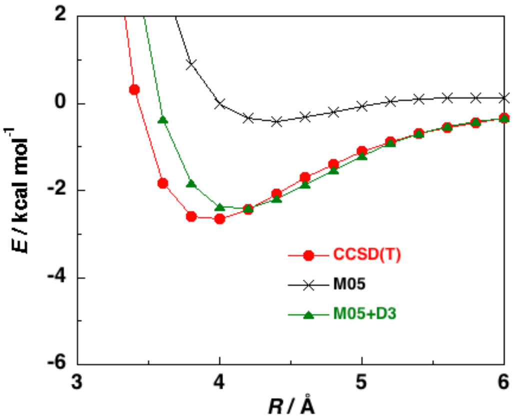
(p)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

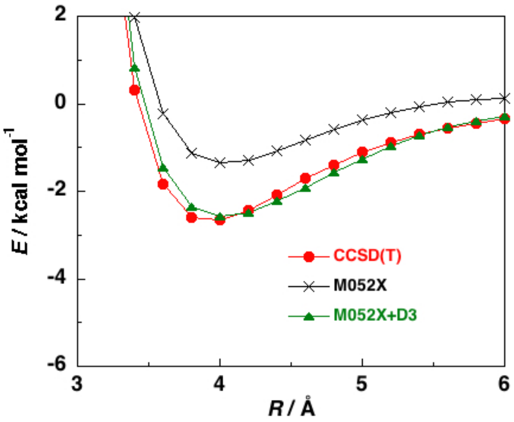
(q)


E / kcal mol^{-1}
R / Å
2
0
-2
-4
-6
3
4
5
6
CCSD(T)
M06L
M06L+D3

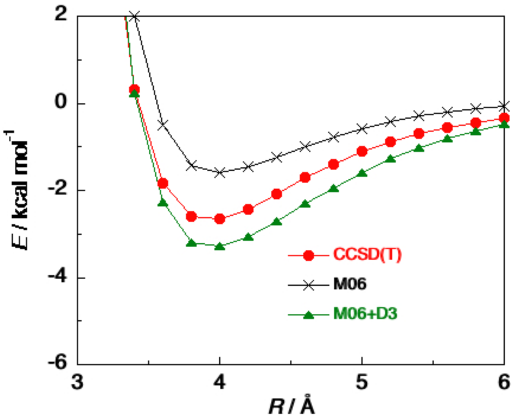
(r)


2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M05
M05+D3

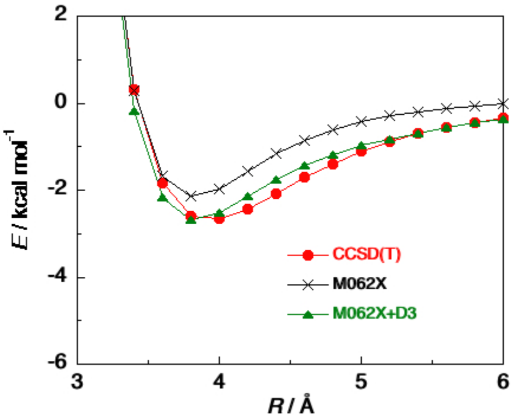
(s)


2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M052X
M052X+D3

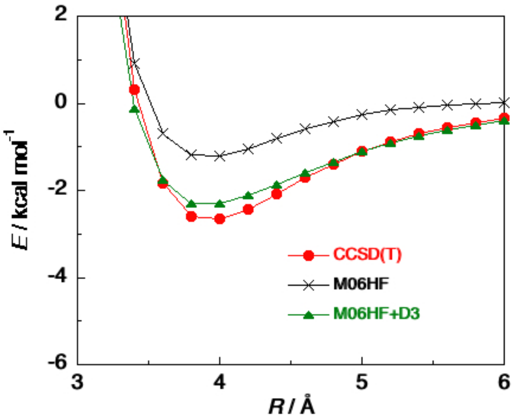
(t)


2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06
M06+D3

(u)

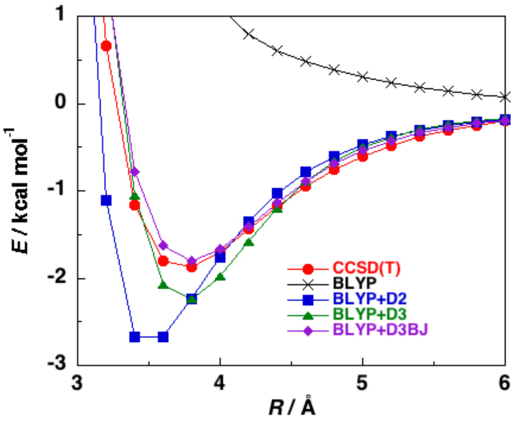

2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M062X
M062X+D3

(v)

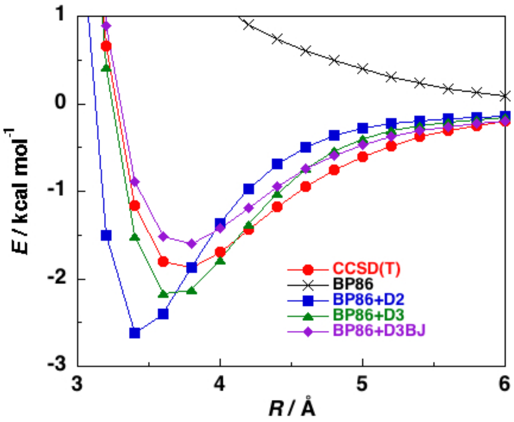

2
0
-2
-4
-6
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

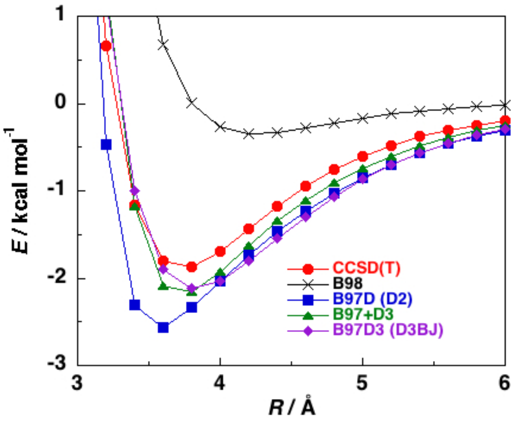
Figure 3S. Intermolecular interaction potentials obtained for C_{2h} slipped-parallel benzene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry centers of two benzenes.


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

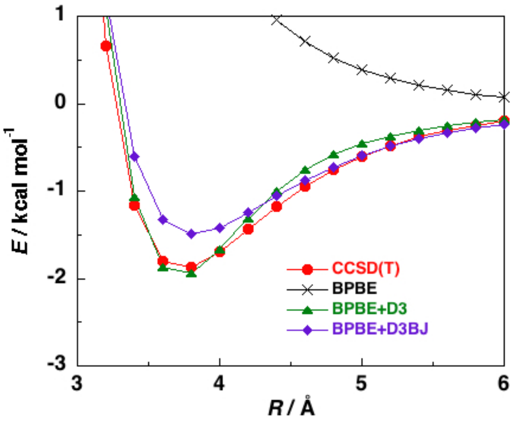
(a)


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

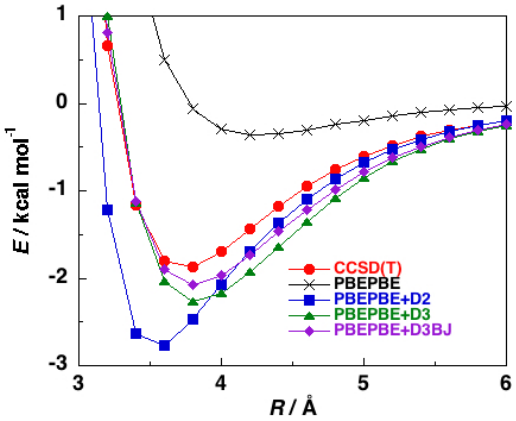
(b)


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

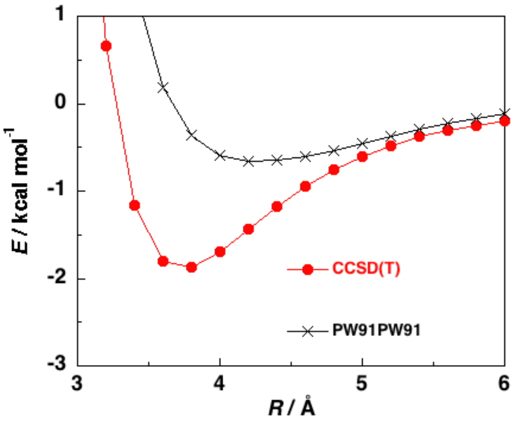
(c)


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

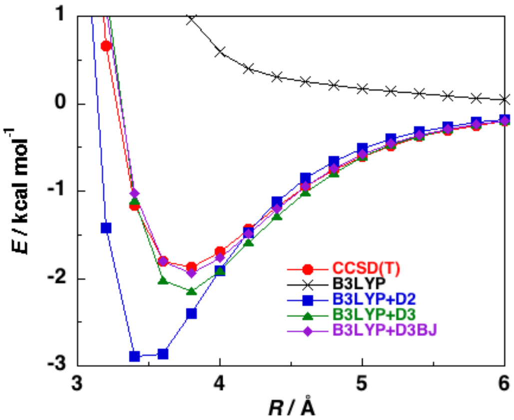
(d)


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

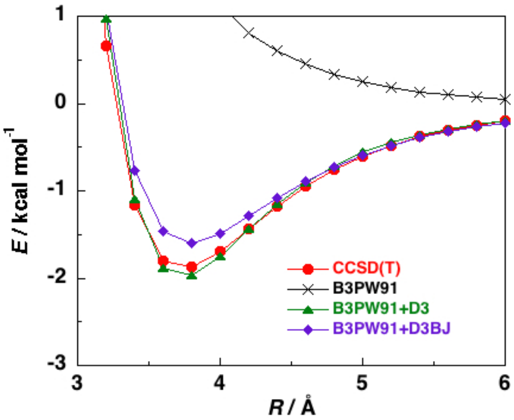
(e)


1
0
-1
-2
-3
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
PW91PW91

(f)



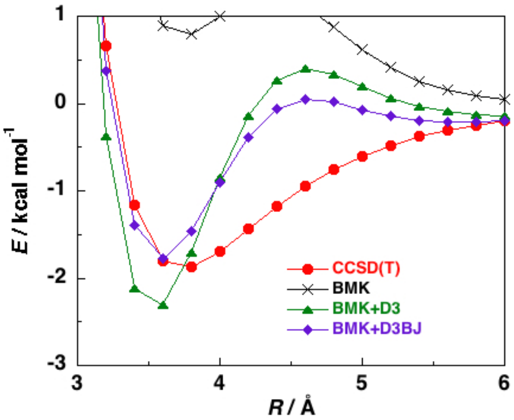
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6



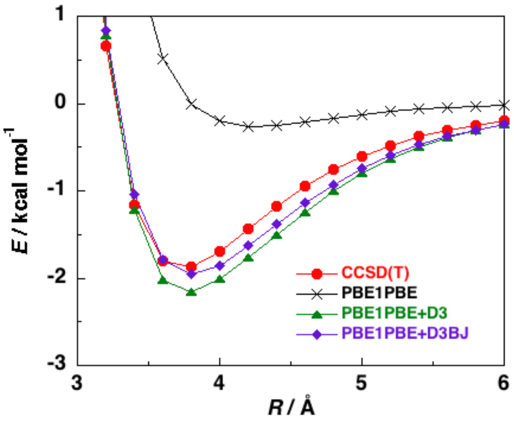
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6

(g)

(h)



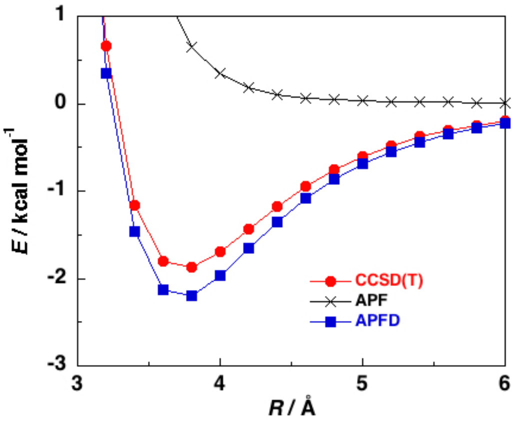
CCSD(T)
BMK
BMK+D3
BMK+D3BJ
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6



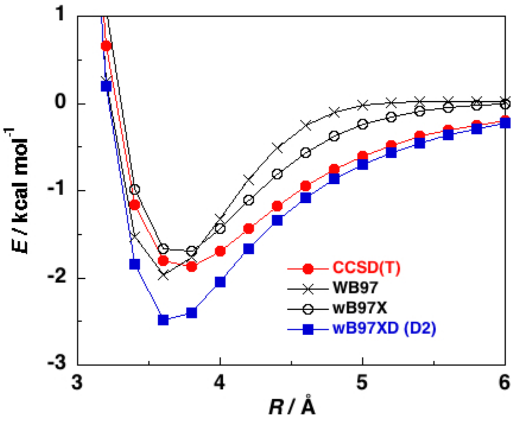
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6

(i)

(j)



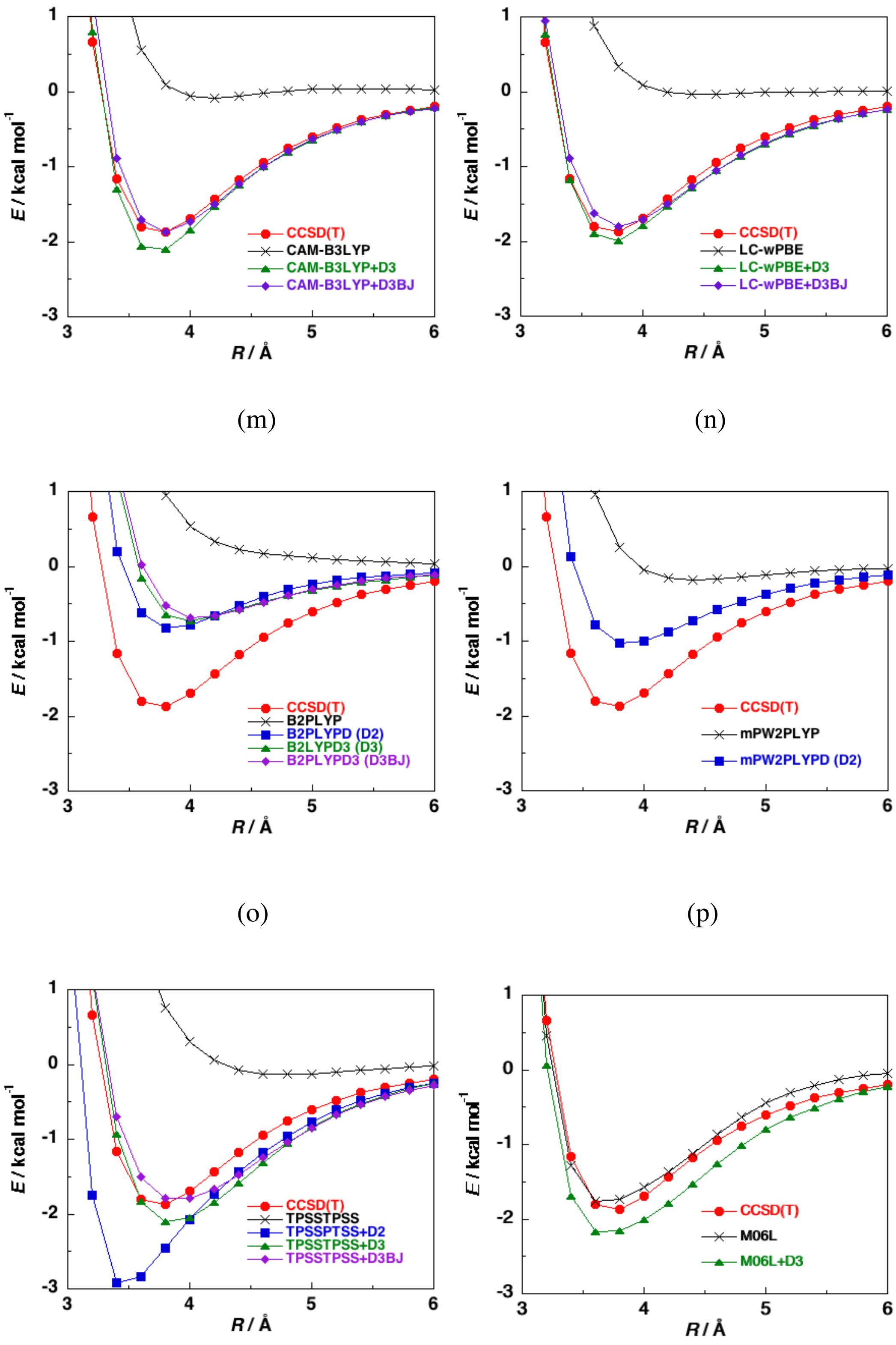
CCSD(T)
APF
APFD
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6



CCSD(T)
WB97
wB97X
wB97XD (D2)
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6

(k)

(l)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
3
4
5
6
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)
mPW2PLYP
mPW2PLYPD (D2)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ
M06L
M06L+D3

(m)

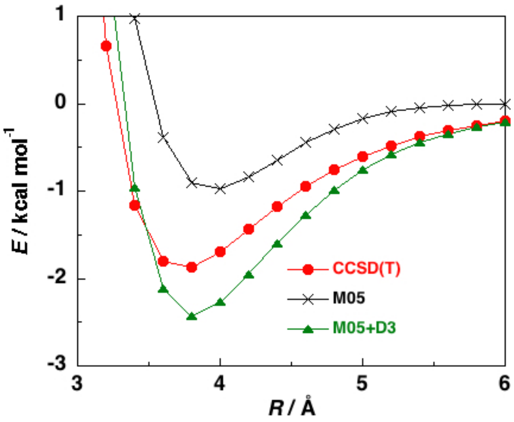
(n)

(o)

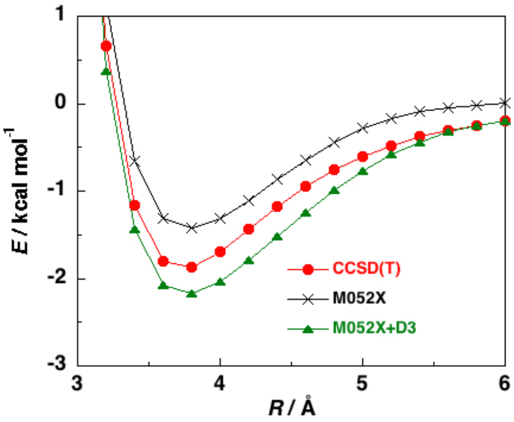
(p)

(q)

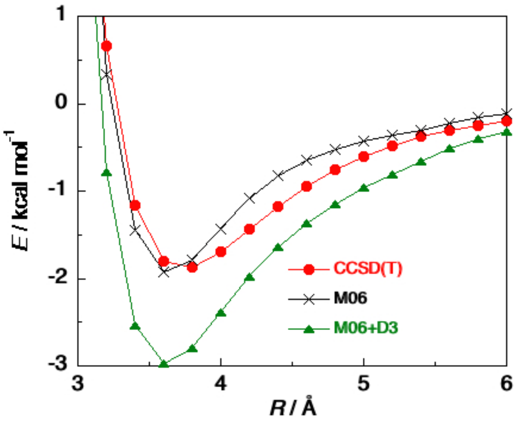
(r)


1
0
-1
-2
-3
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
M05
M05+D3

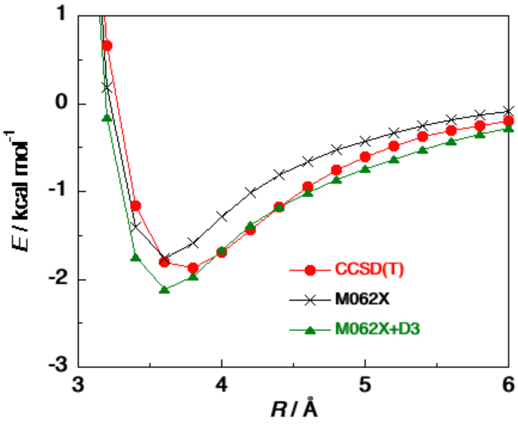
(s)


1
0
-1
-2
-3
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
M052X
M052X+D3

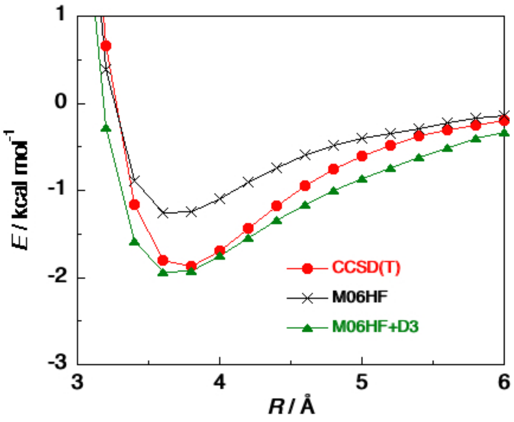
(t)


1
0
-1
-2
-3
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
M06
M06+D3

(u)

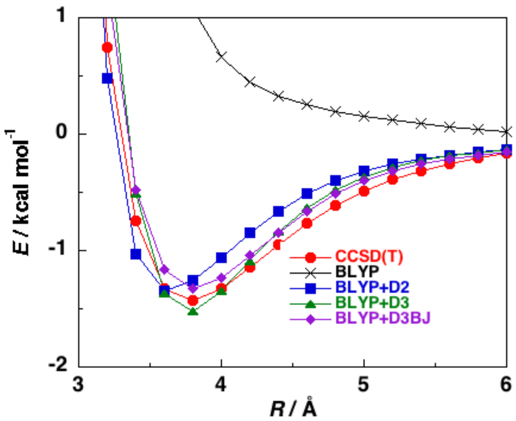

1
0
-1
-2
-3
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
M062X
M062X+D3

(v)

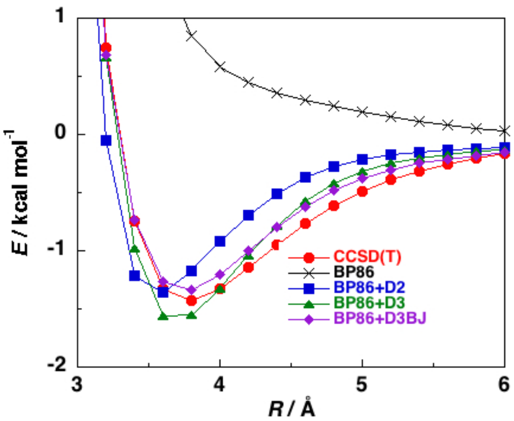

1
0
-1
-2
-3
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

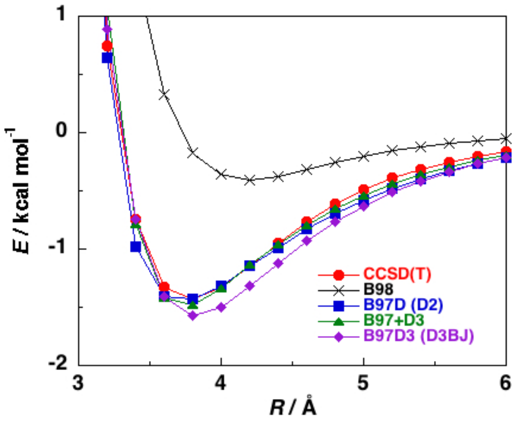
Figure 4S. Intermolecular interaction potentials obtained for C_{2h} propane dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. R is the distance between the central carbon atoms of two propanes.


E / kcal mol^{-1}
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

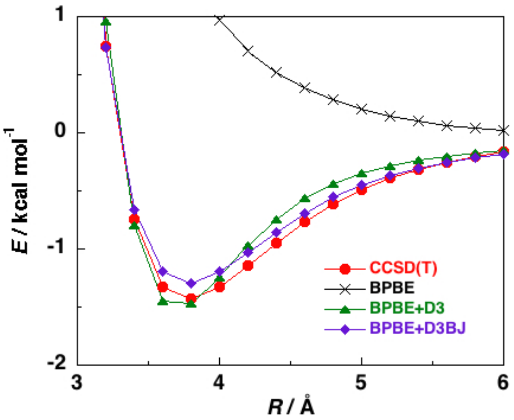
(a)


E / kcal mol^{-1}
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

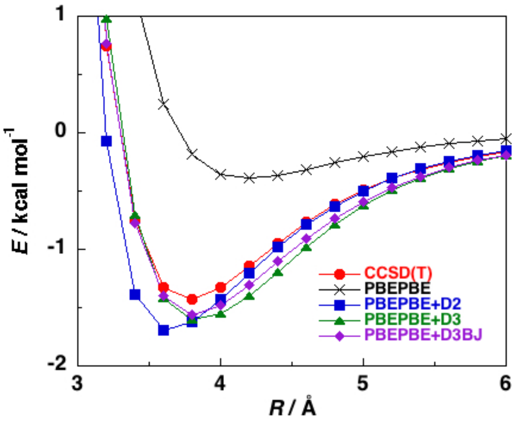
(b)


E / kcal mol^{-1}
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

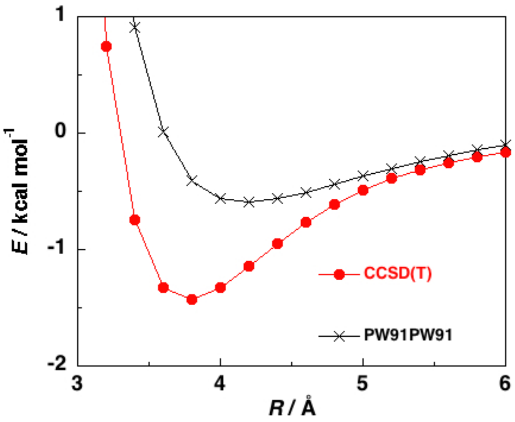
(c)


E / kcal mol^{-1}
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

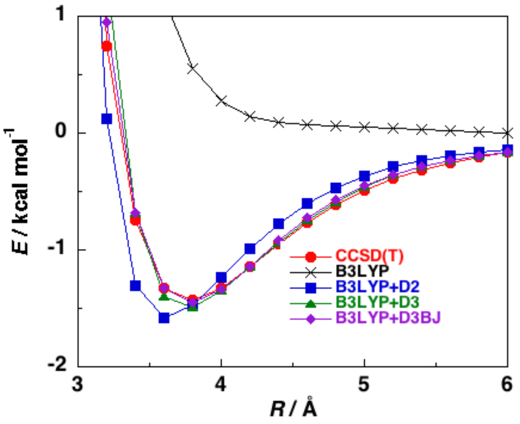
(d)


E / kcal mol^{-1}
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

(e)

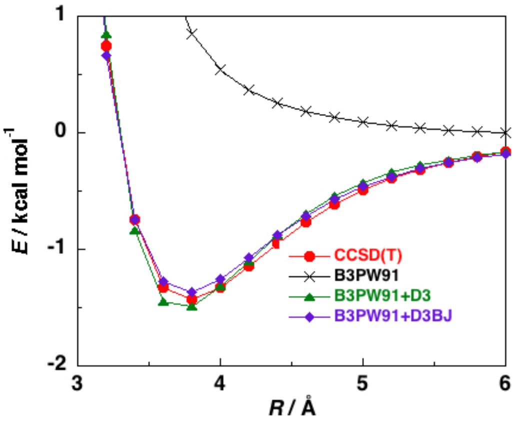

E / kcal mol^{-1}
R / Å
CCSD(T)
PW91PW91

(f)



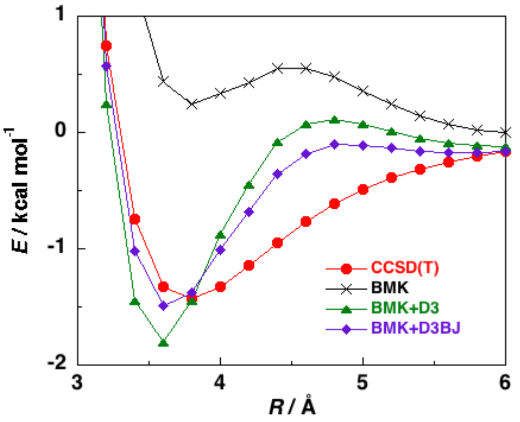
1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

(g)



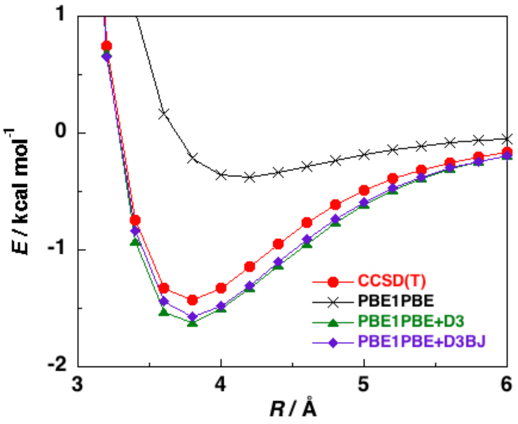
1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

(h)



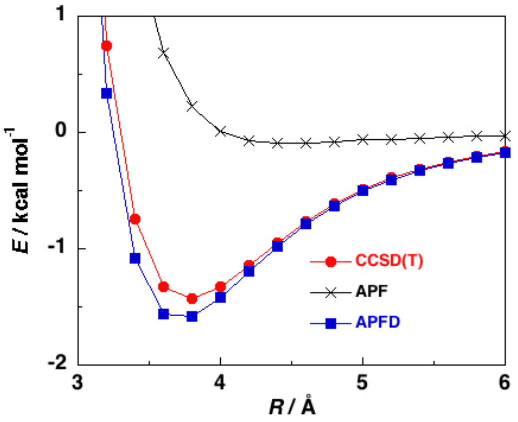
1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

(i)



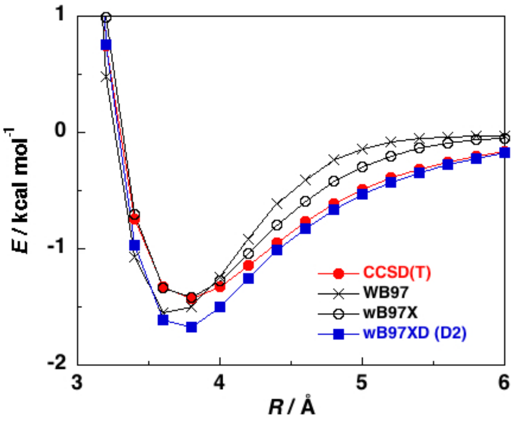
1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

(j)



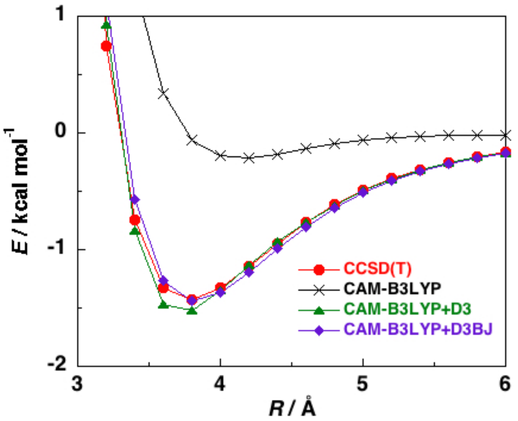
1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
APF
APFD

(k)

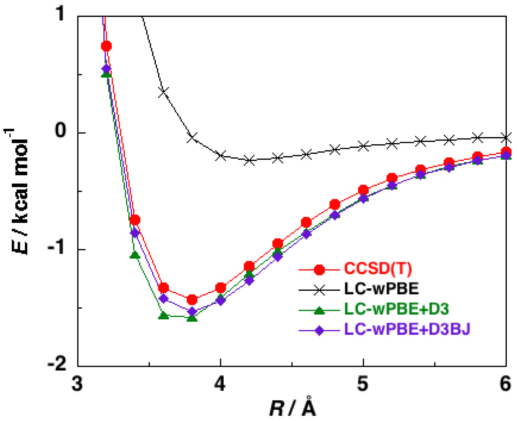


1
0
-1
-2
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

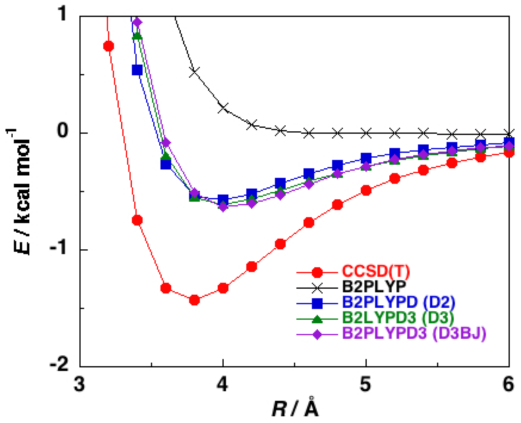
(l)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

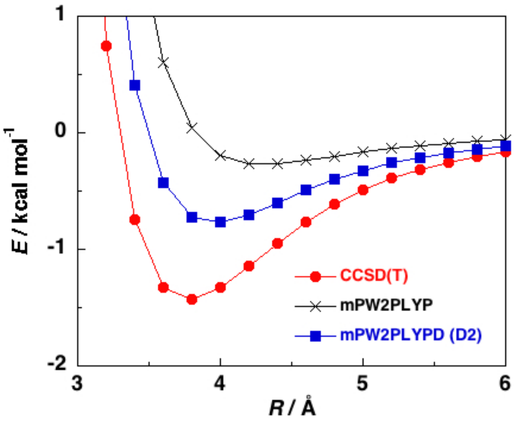
(m)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

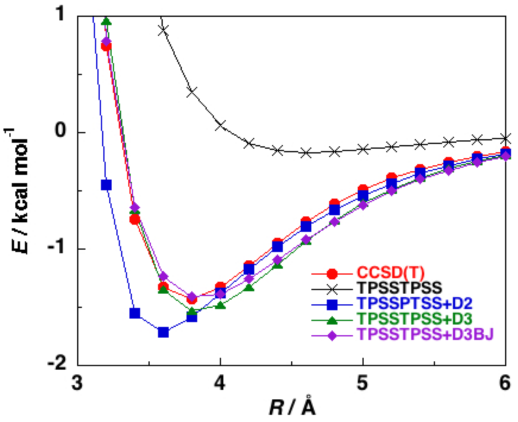
(n)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

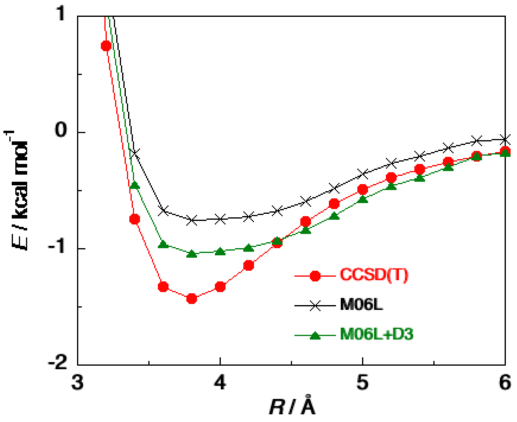
(o)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

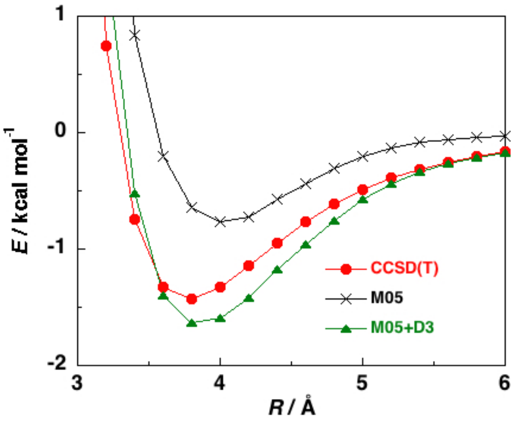
(p)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

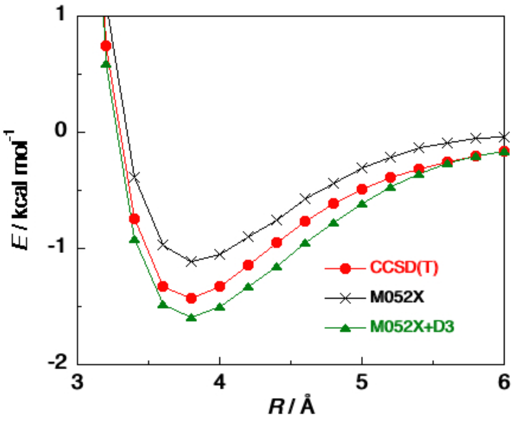
(q)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06L
M06L+D3

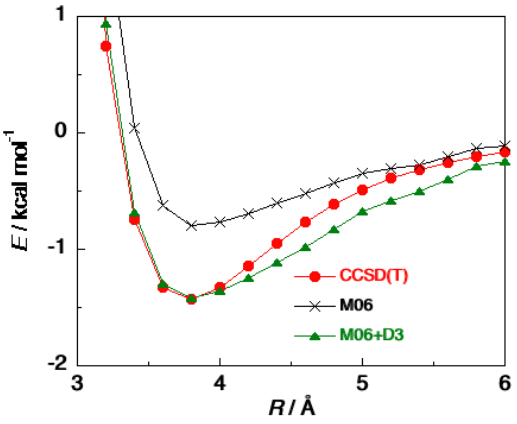
(r)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M05
M05+D3

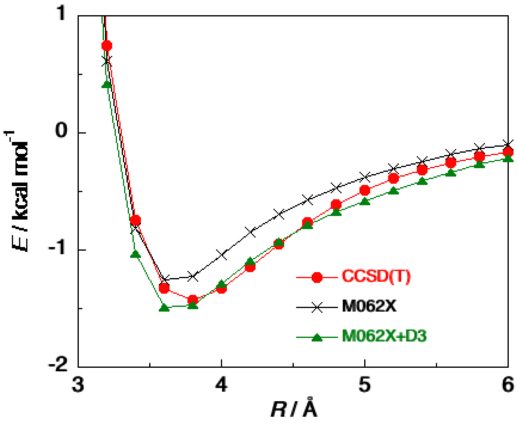
(s)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M052X
M052X+D3

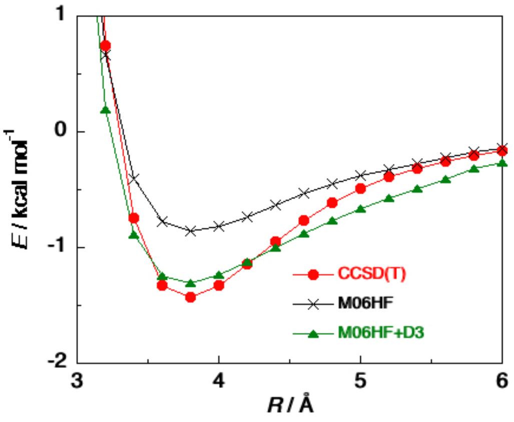
(t)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06
M06+D3

(u)

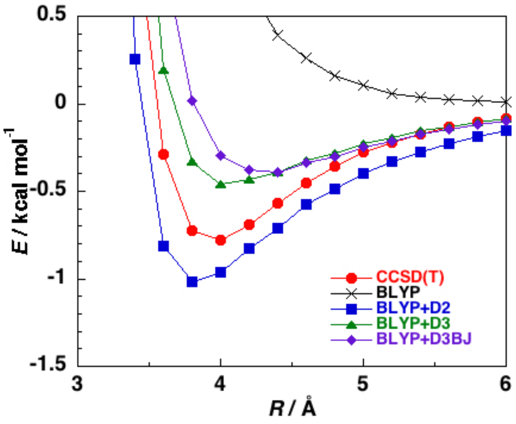

1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M062X
M062X+D3

(v)

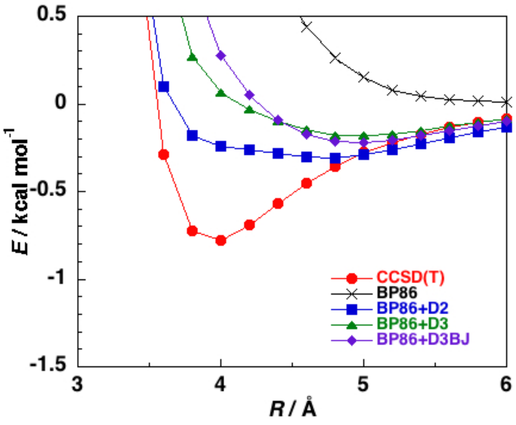

1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

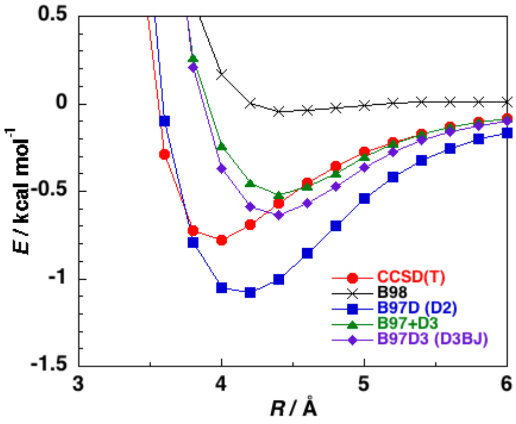
Figure 5S. Intermolecular interaction potentials obtained for C_{3v} benzene-methane complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. R is the distance between the symmetry center of benzene and carbon atom of methane.


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

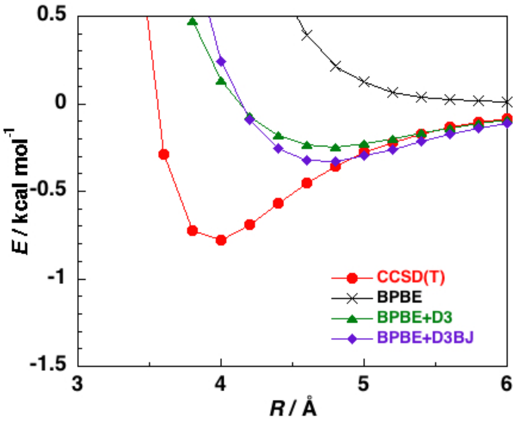
(a)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

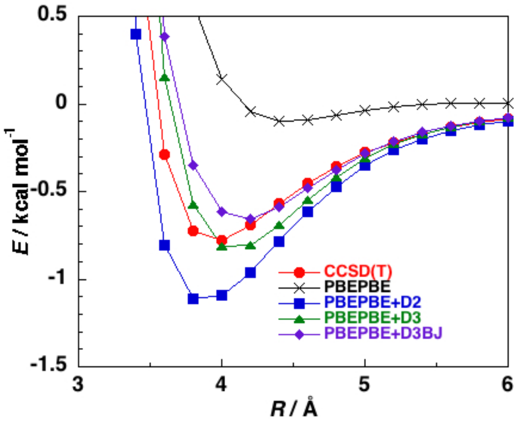
(b)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

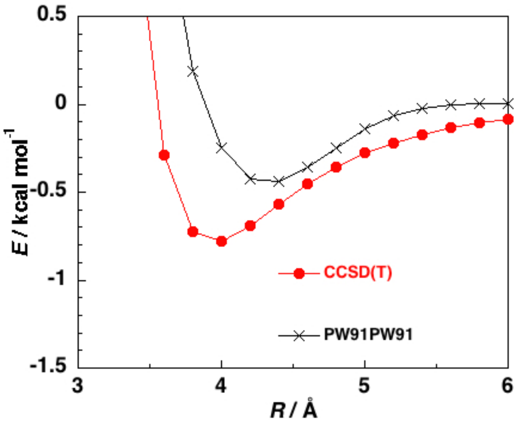
(c)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

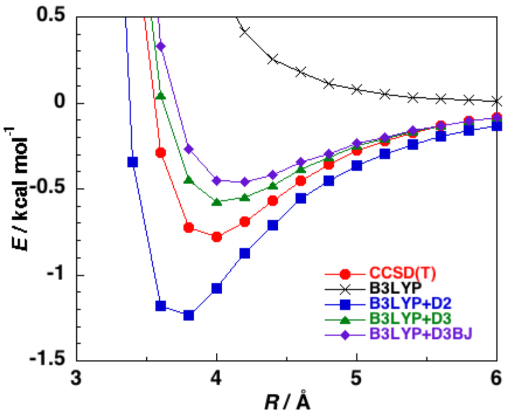
(d)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

(e)

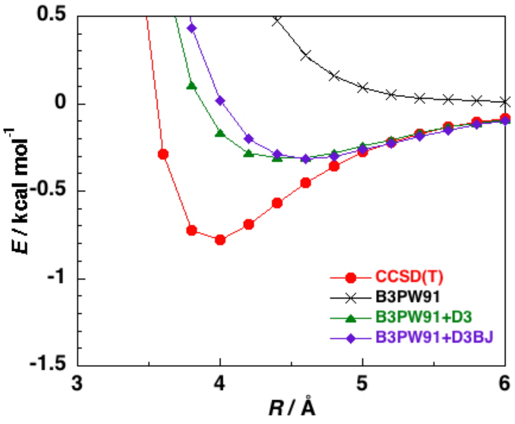

0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
PW91PW91

(f)



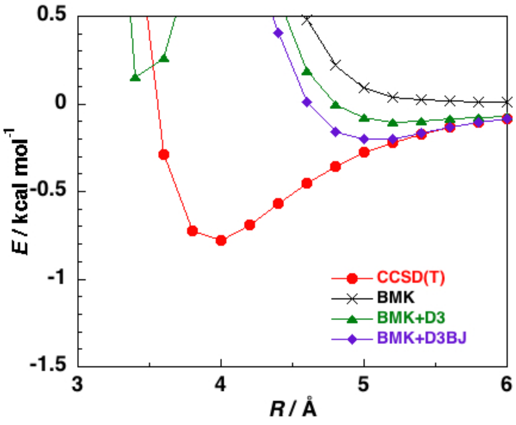
0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

(g)



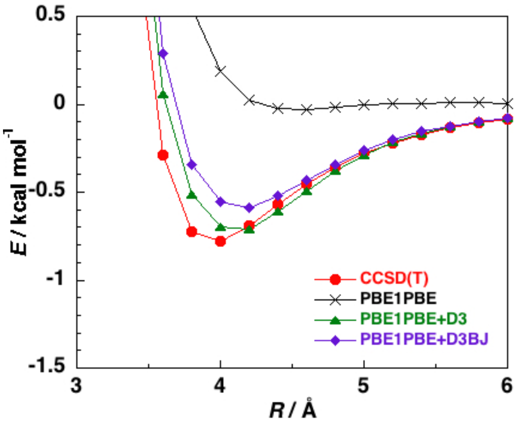
0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

(h)



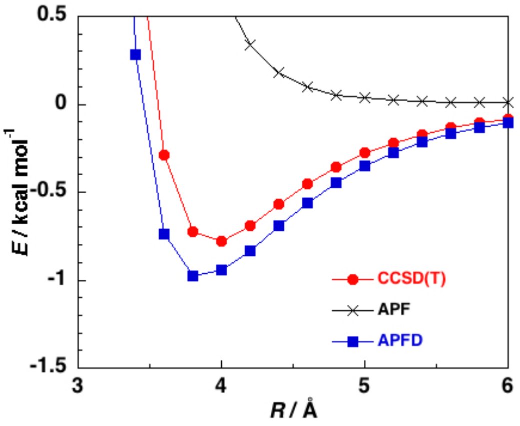
0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

(i)



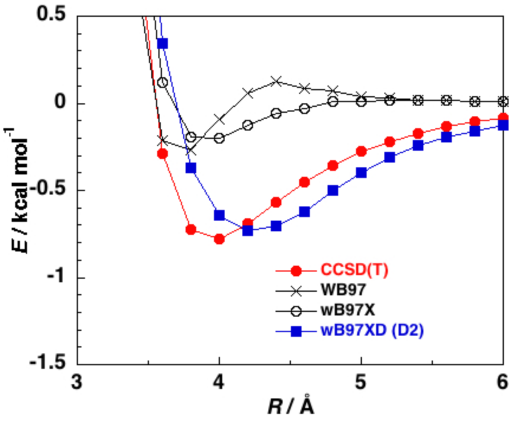
0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

(j)



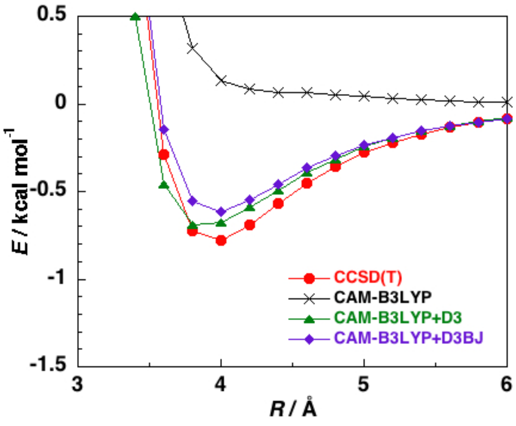
0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
APF
APFD

(k)

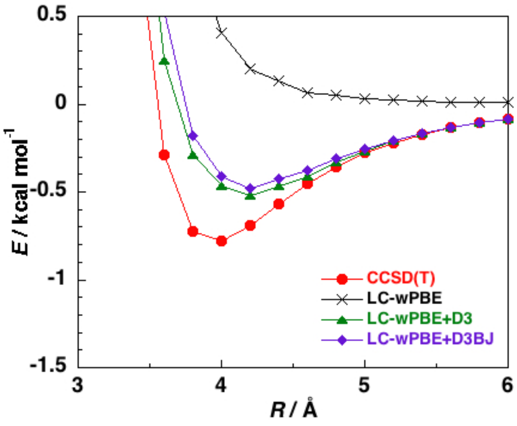


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol^{-1}
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

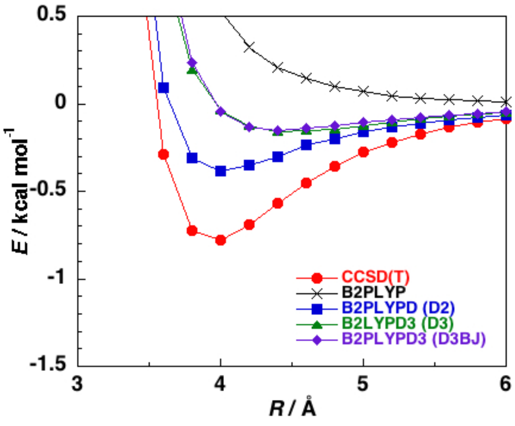
(l)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

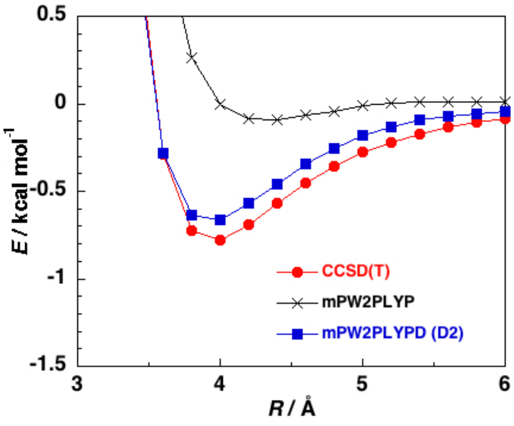
(m)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

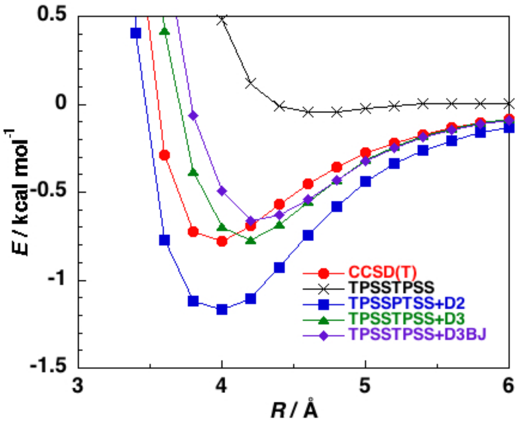
(n)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

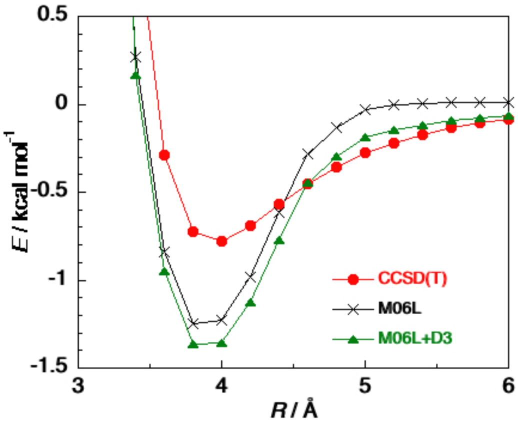
(o)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

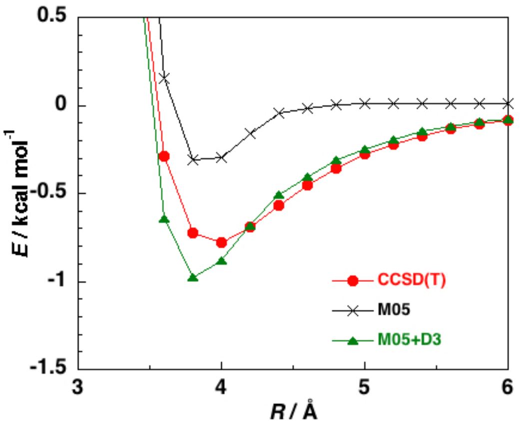
(p)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

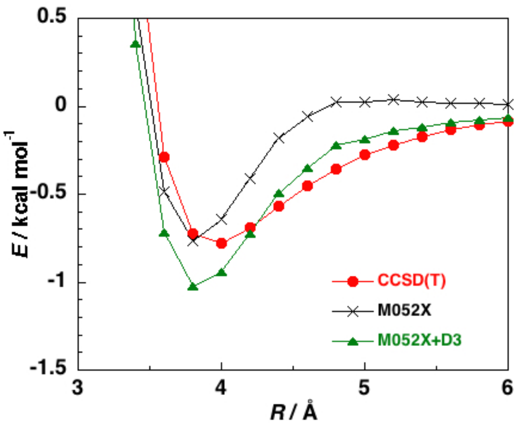
(q)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M06L
M06L+D3

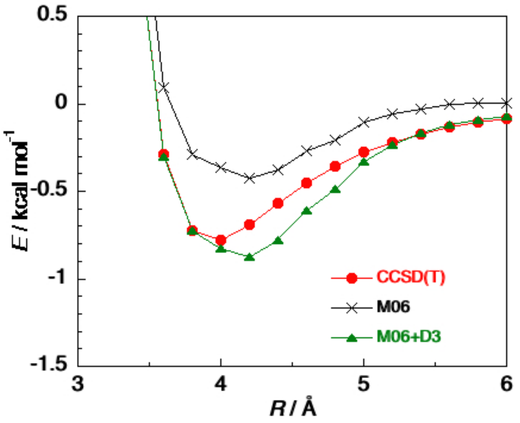
(r)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M05
M05+D3

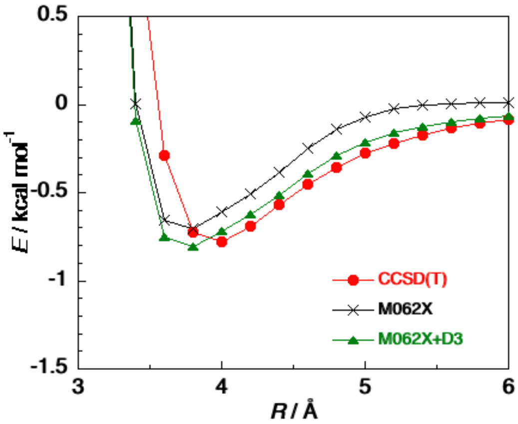
(s)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M052X
M052X+D3

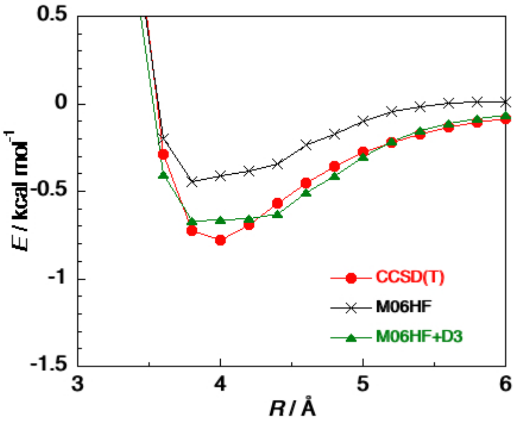
(t)


0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M06
M06+D3

(u)

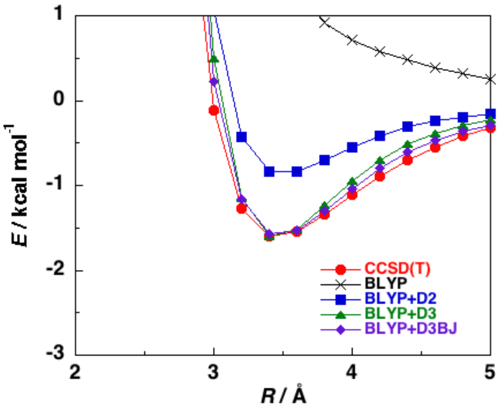

0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M062X
M062X+D3

(v)

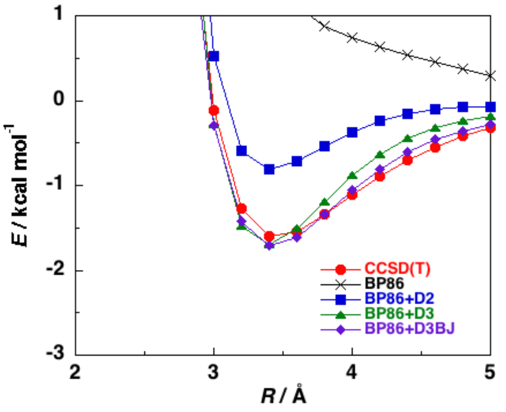

0.5
0
-0.5
-1
-1.5
3
4
5
6
E / kcal mol-1
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

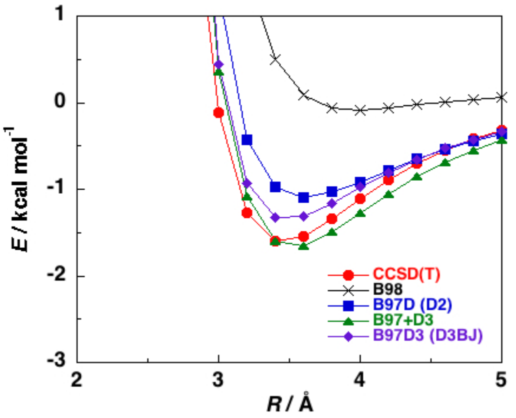
Figure 6S. Intermolecular interaction potentials obtained for D_{3h} perfluoromethane dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. R is the distance between the carbon atoms of perfluoromethanes.


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

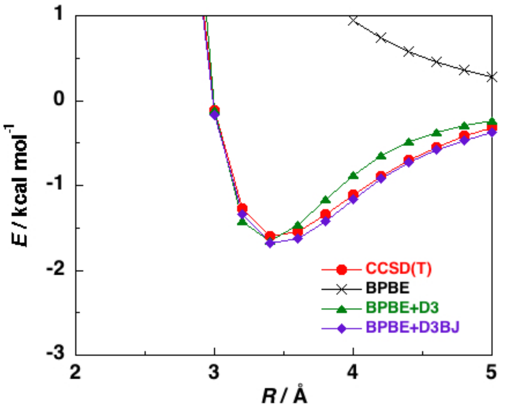
(a)


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

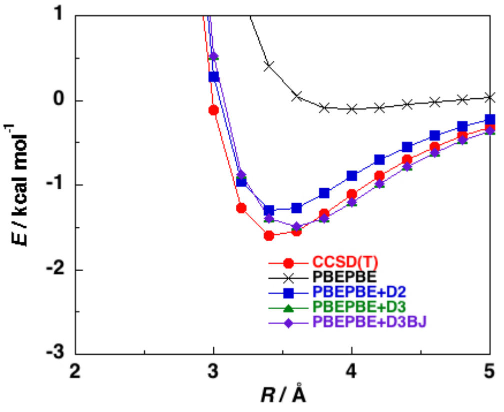
(b)


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

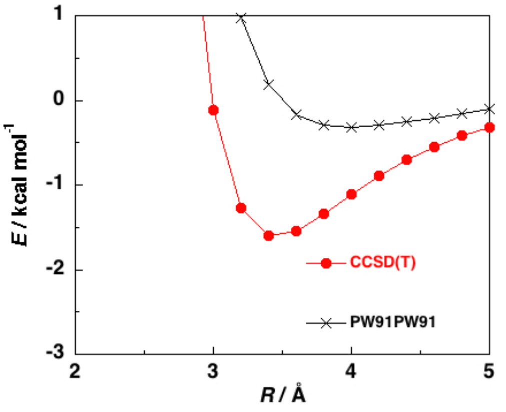
(c)


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

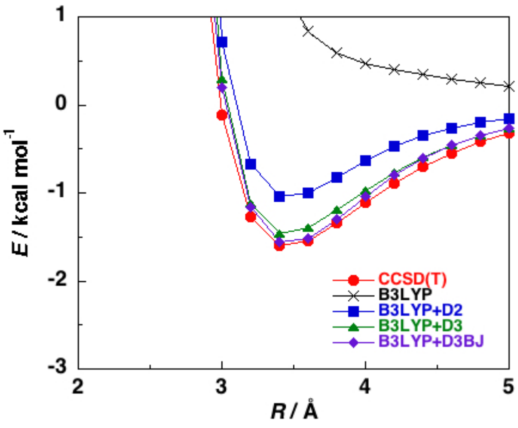
(d)


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

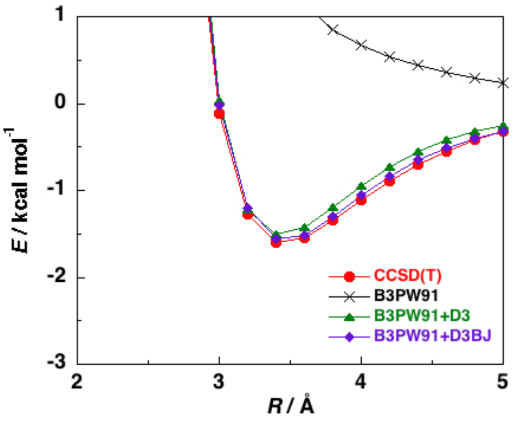
(e)


1
0
-1
-2
-3
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
PW91PW91

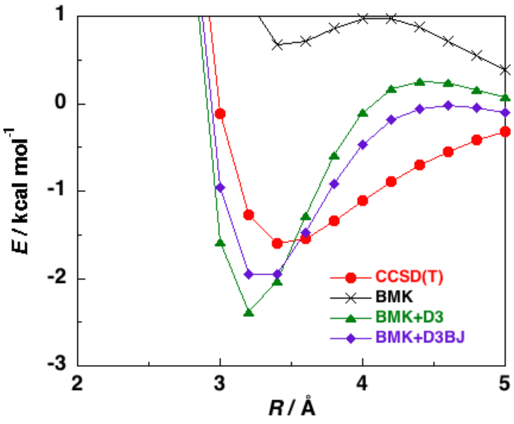
(f)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

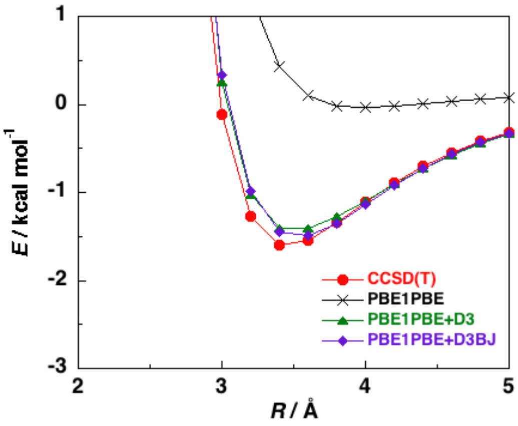
(g)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

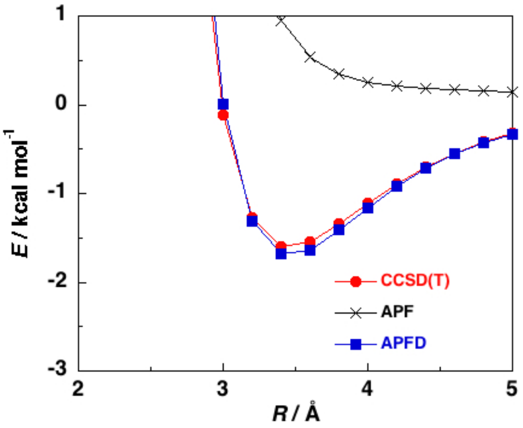
(h)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

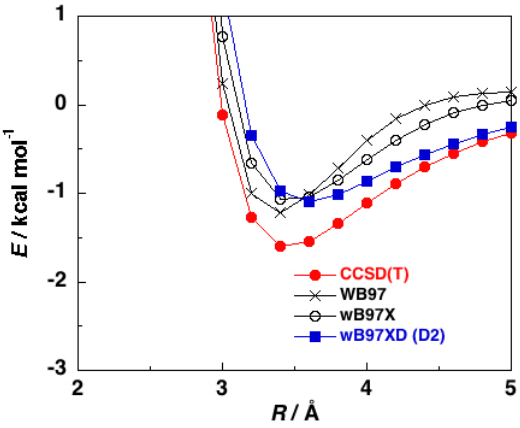
(i)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

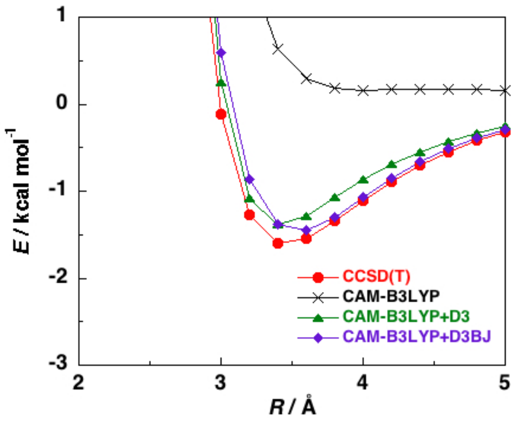
(j)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
APF
APFD

(k)

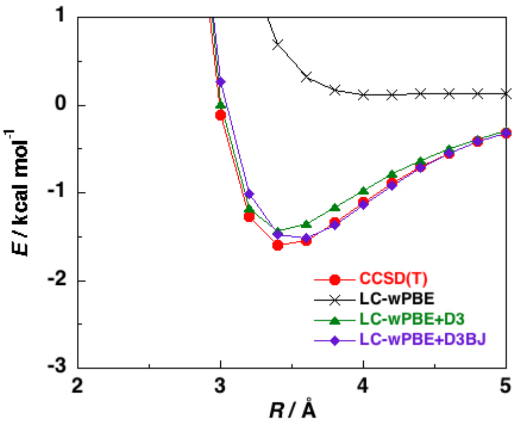

E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
WB97
wB97X
wB97XD (D2)

(l)



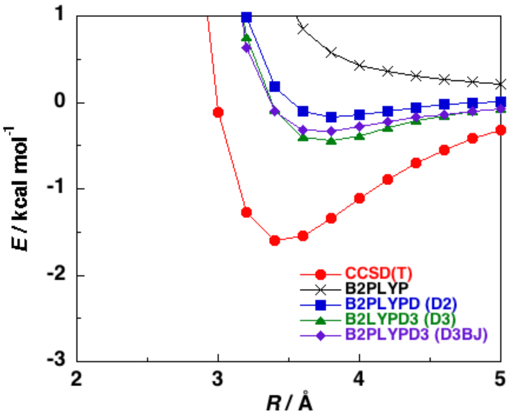
E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

(m)



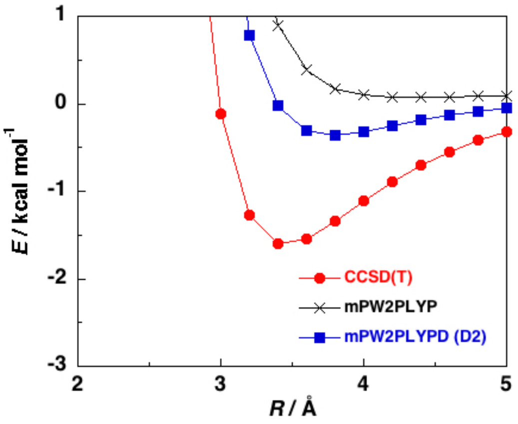
E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

(n)



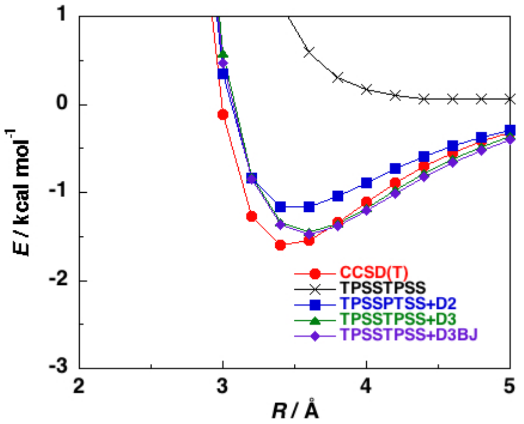
E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

(o)



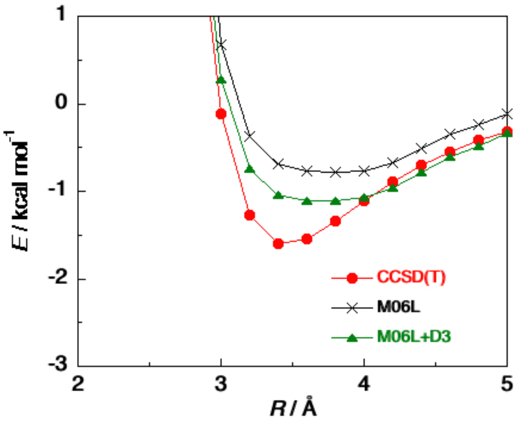
E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

(p)



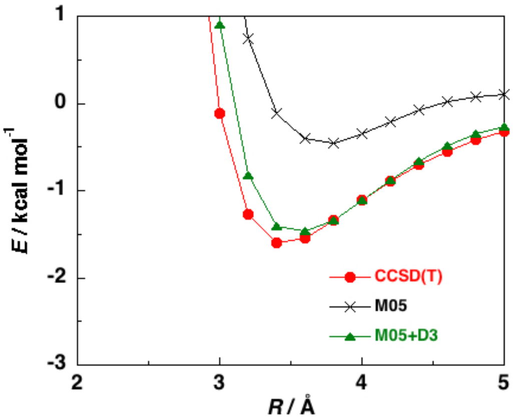
E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

(q)

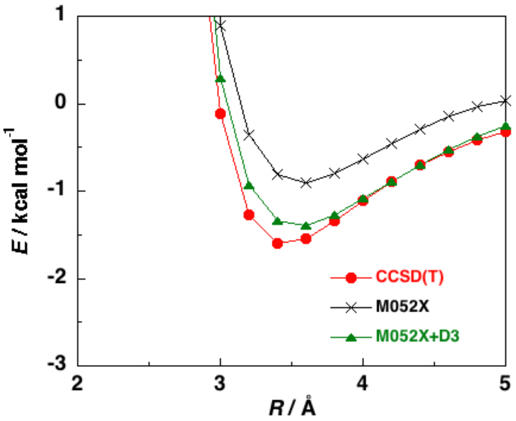


E / kcal mol-1
R / Å
1
0
-1
-2
-3
2
3
4
5
CCSD(T)
M06L
M06L+D3

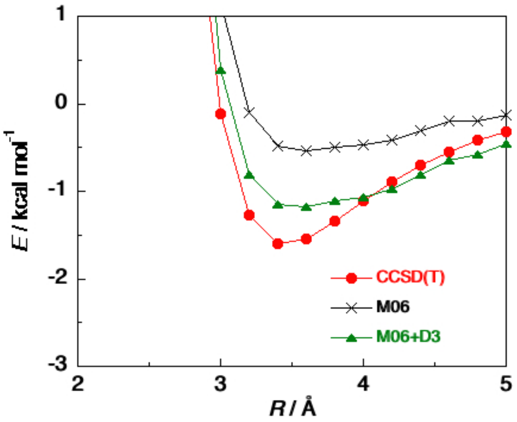
(r)


1
0
-1
-2
-3
2
3
4
5
E / kcal mol-1
R / Å
CCSD(T)
M05
M05+D3

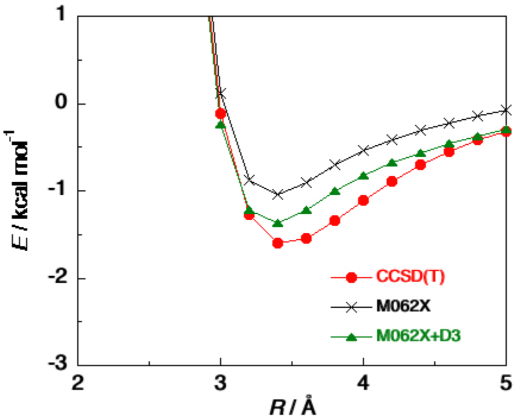
(s)


1
0
-1
-2
-3
2
3
4
5
E / kcal mol-1
R / Å
CCSD(T)
M052X
M052X+D3

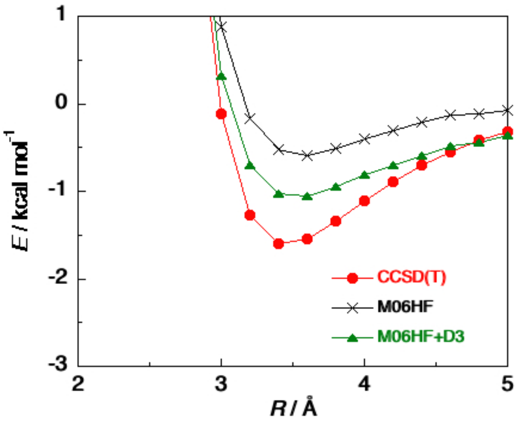
(t)


1
0
-1
-2
-3
2
3
4
5
E / kcal mol-1
R / Å
CCSD(T)
M06
M06+D3

(u)

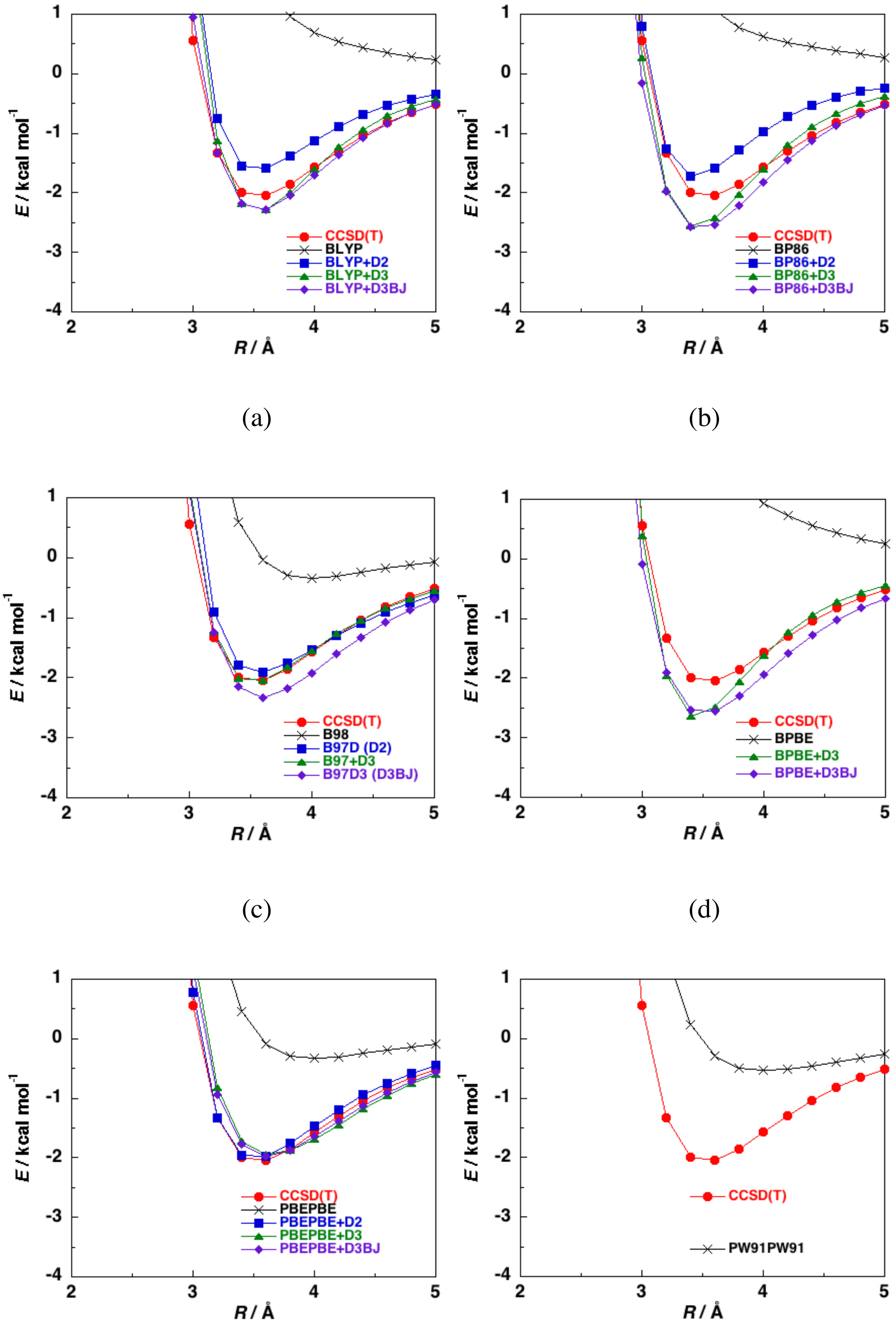

1
0
-1
-2
-3
2
3
4
5
E / kcal mol-1
R / Å
CCSD(T)
M062X
M062X+D3

(v)


1
0
-1
-2
-3
2
3
4
5
E / kcal mol-1
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

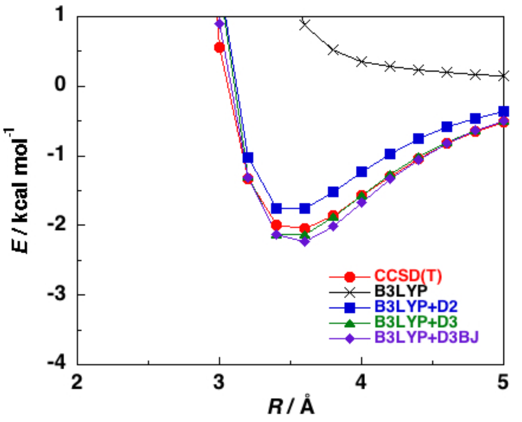
Figure 7S. Intermolecular interaction potentials obtained for benzene-chlorobenzene complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme’s dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry center of benzene and chlorine atom.


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
2
3
4
5
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ
BP86
BP86+D2
BP86+D3
BP86+D3BJ
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)
BPBE
BPBE+D3
BPBE+D3BJ
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ
PW91PW91

(a) (b)

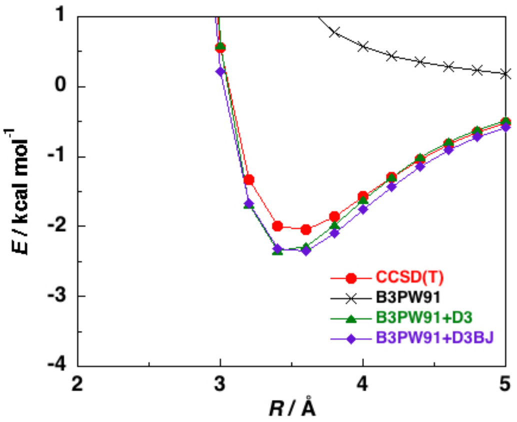
(c) (d)

(e) (f)



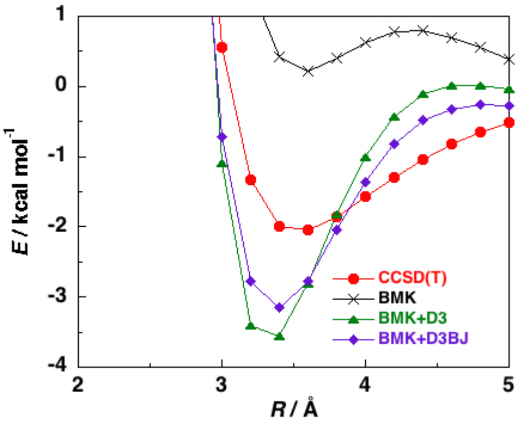
E / kcal mol-1
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

(g)



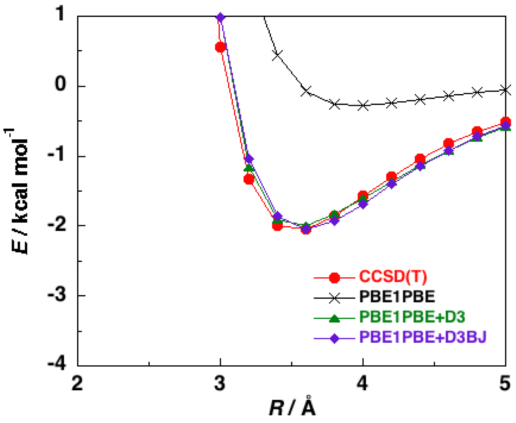
E / kcal mol-1
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

(h)



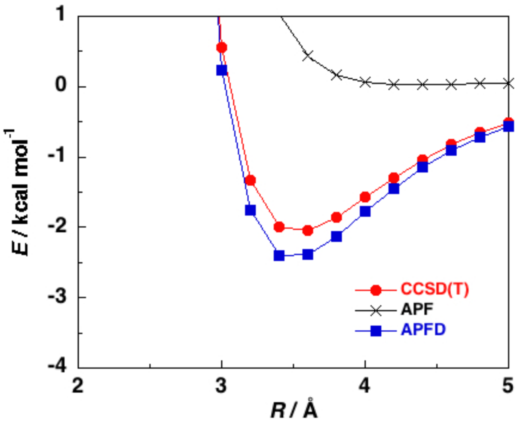
E / kcal mol-1
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

(i)



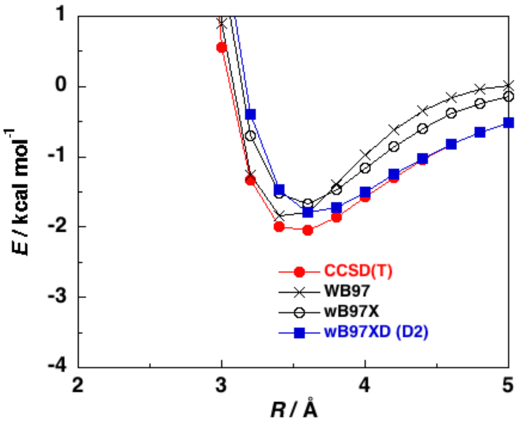
E / kcal mol-1
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

(j)



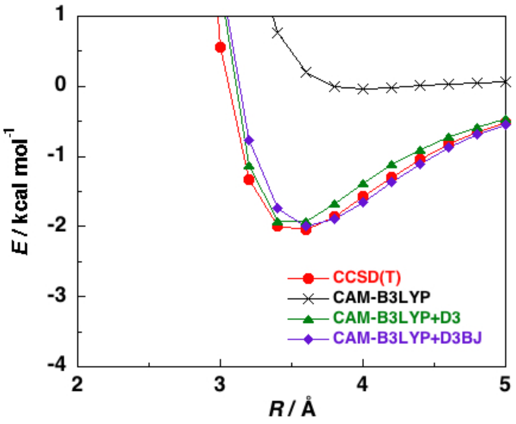
E / kcal mol-1
R / Å
CCSD(T)
APF
APFD

(k)

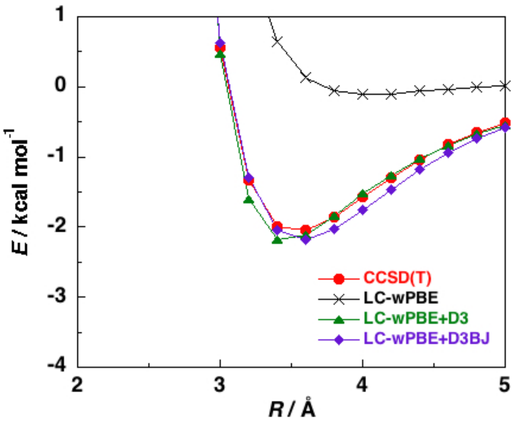


E / kcal mol-1
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

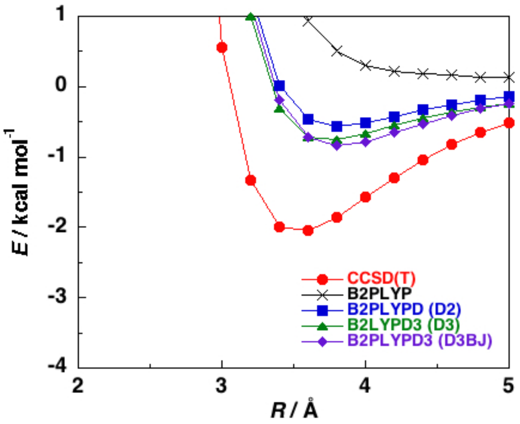
(l)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

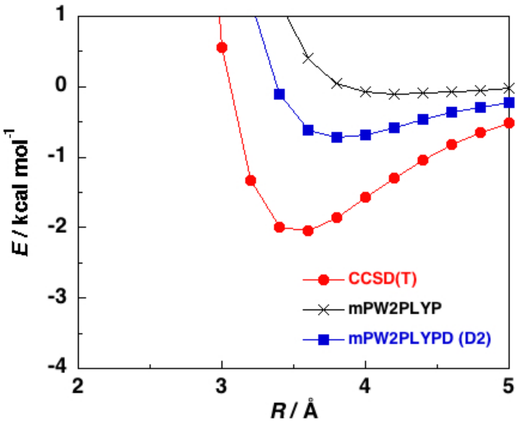
(m)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

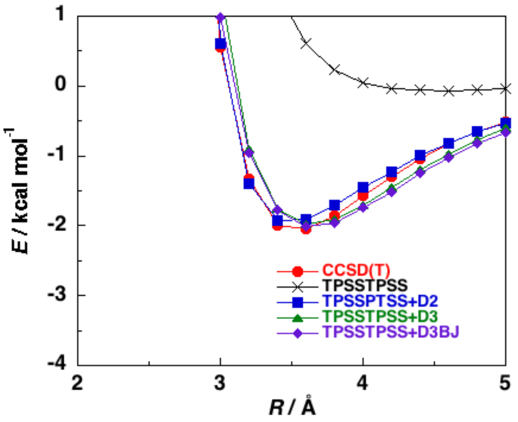
(n)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

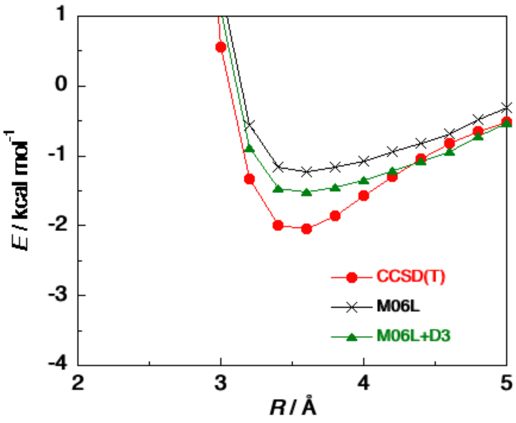
(o)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

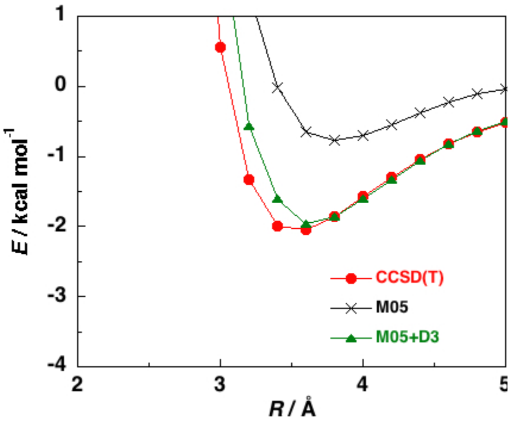
(p)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

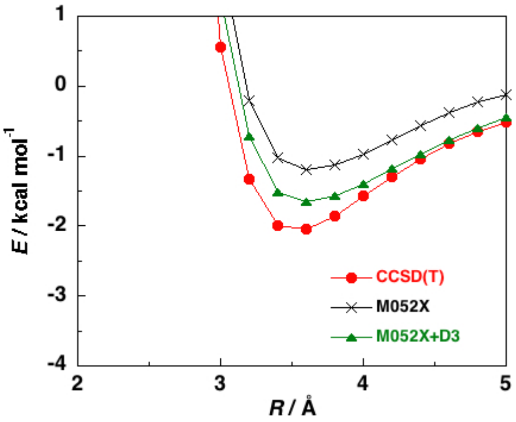
(q)


1
0
-1
-2
-3
-4
E / kcal mol-1
2
3
4
5
R / Å
CCSD(T)
M06L
M06L+D3

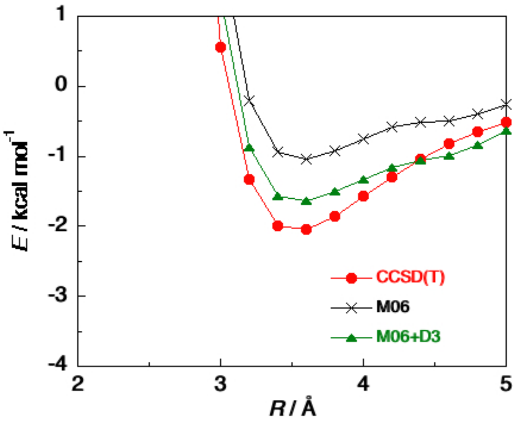
(r)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
2
3
4
5
R / Å
CCSD(T)
M05
M05+D3

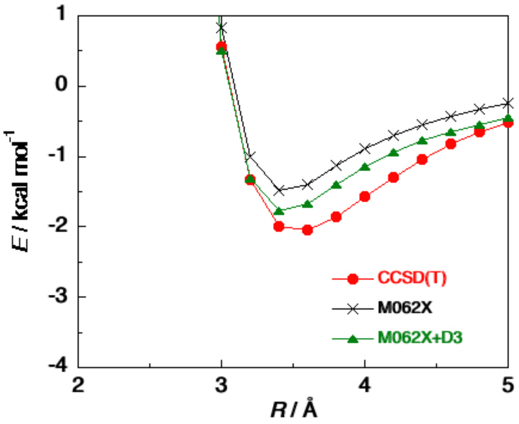
(s)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
2
3
4
5
R / Å
CCSD(T)
M052X
M052X+D3

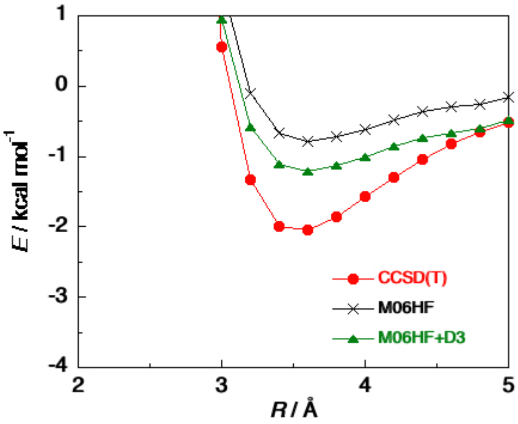
(t)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
2
3
4
5
R / Å
CCSD(T)
M06
M06+D3

(u)

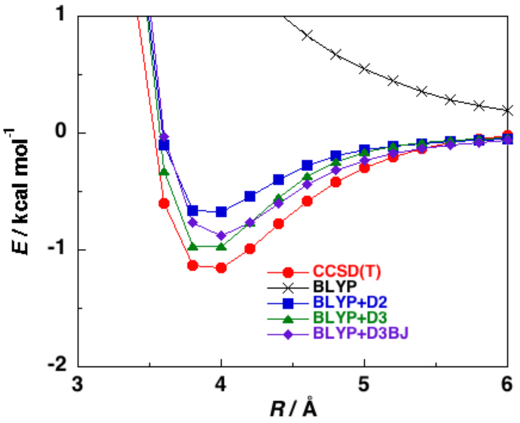

E / kcal mol^{-1}
1
0
-1
-2
-3
-4
2
3
4
5
R / Å
CCSD(T)
M062X
M062X+D3

(v)

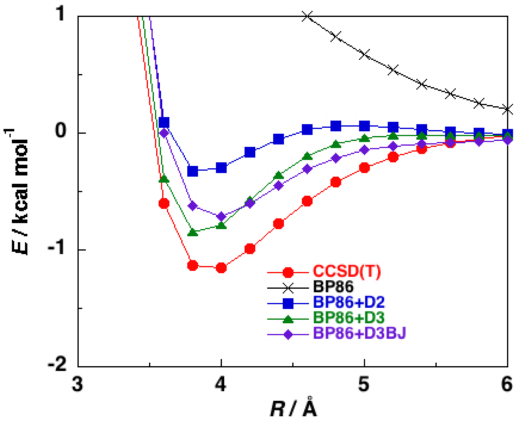

E / kcal mol^{-1}
1
0
-1
-2
-3
-4
2
3
4
5
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

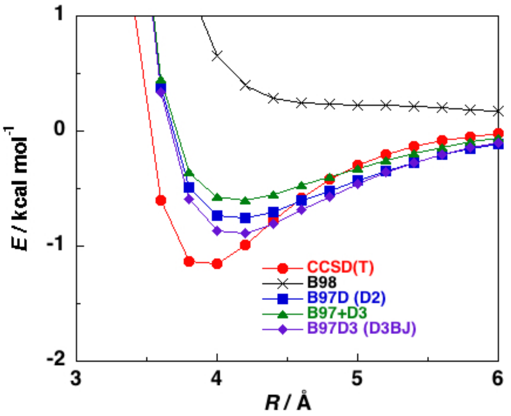
Figure 8S. Intermolecular interaction potentials obtained for benzene-bromobenzene complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry center of benzene and bromine atom.


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

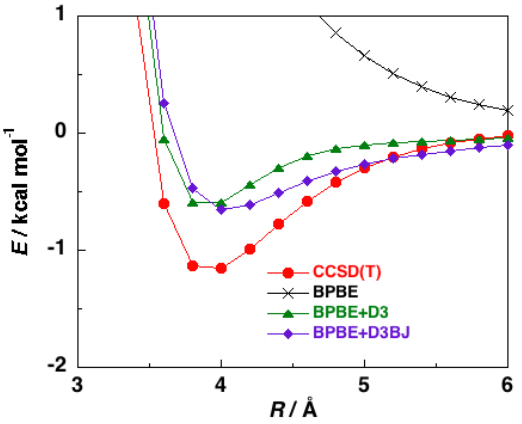
(a)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

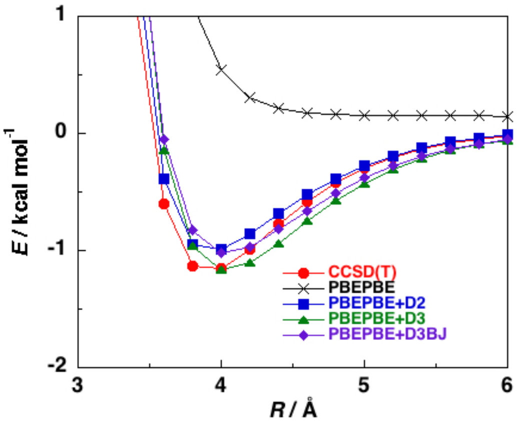
(b)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

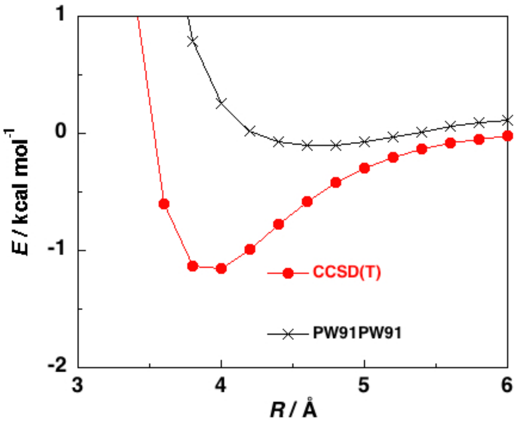
(c)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

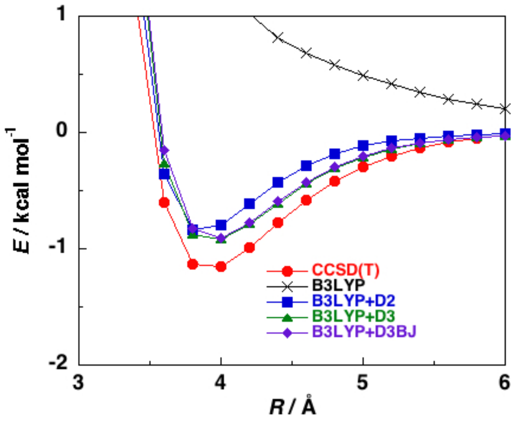
(d)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

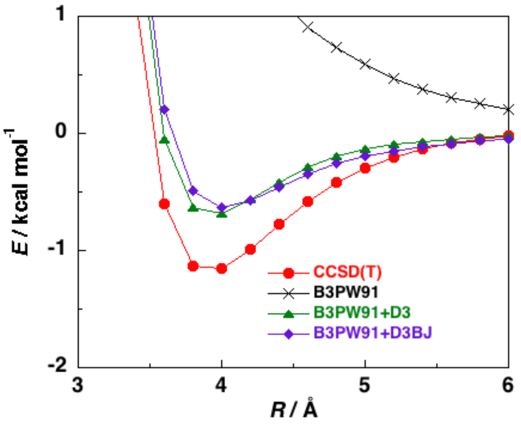
(e)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
PW91PW91

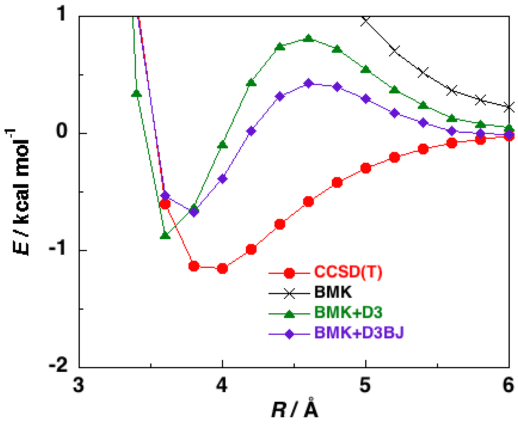
(f)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

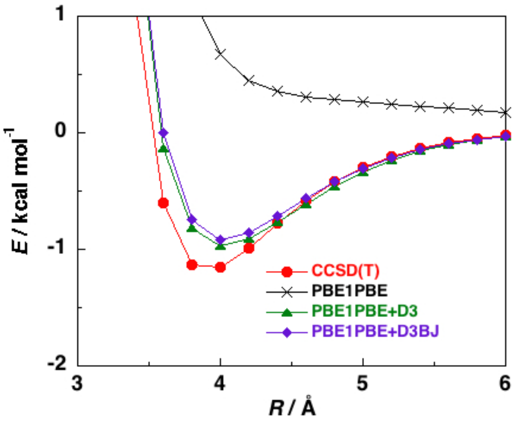
(g)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

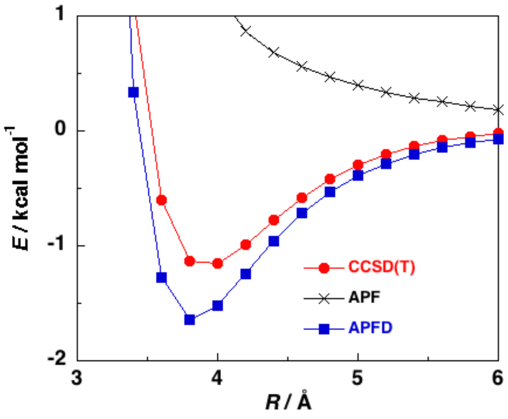
(h)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

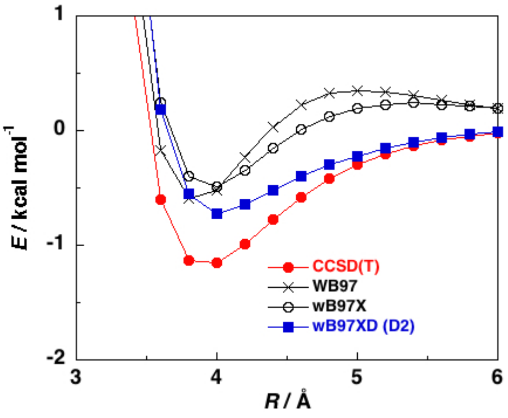
(i)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

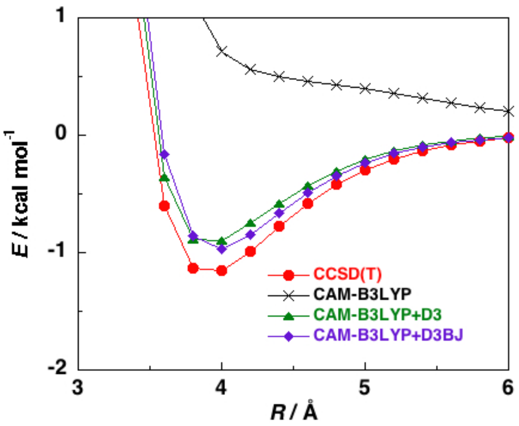
(j)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
APF
APFD

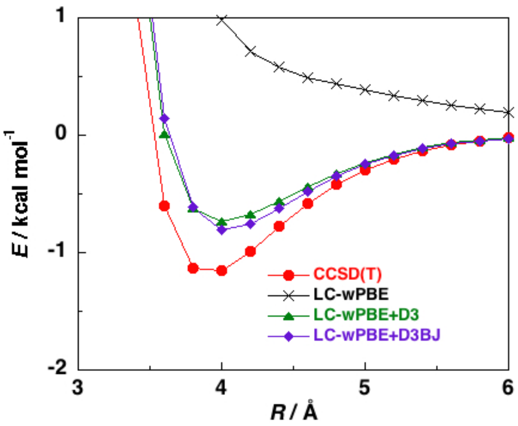
(k)


1
0
-1
-2
E / kcal mol^{-1}
3
4
5
6
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

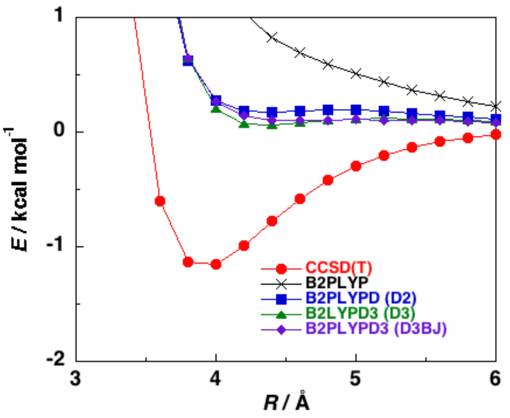
(l)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

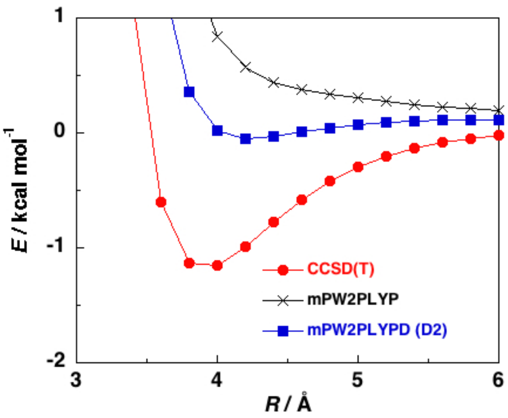
(m)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

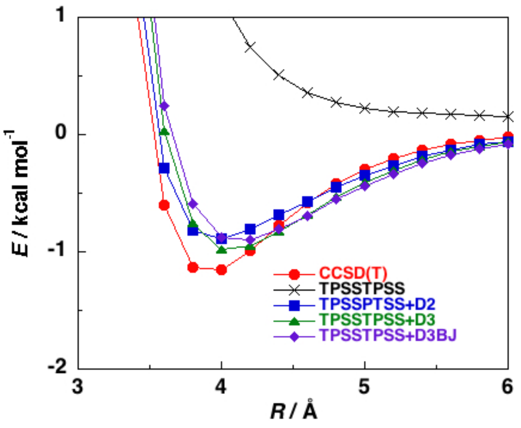
(n)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

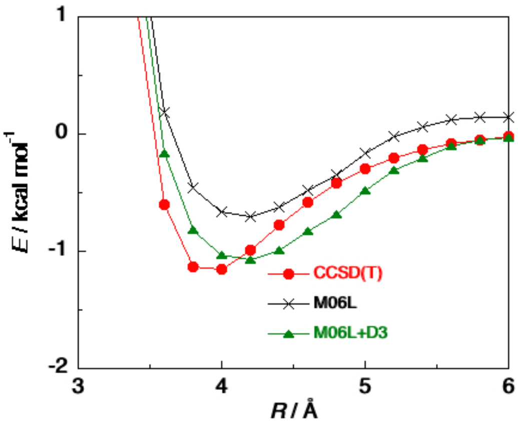
(o)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

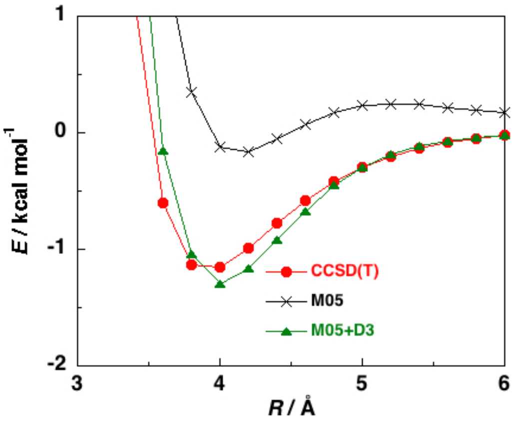
(p)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

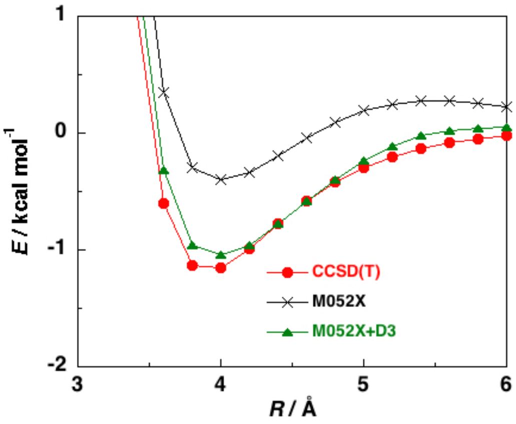
(q)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06L
M06L+D3

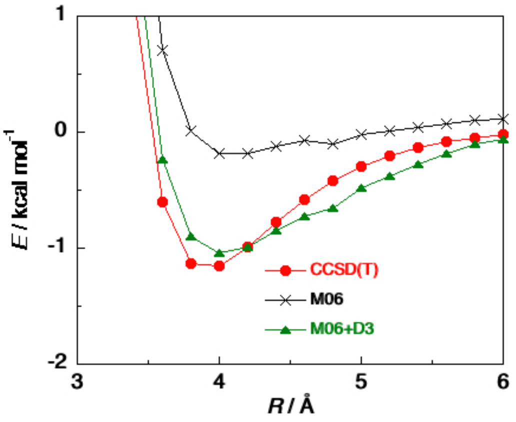
(r)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M05
M05+D3

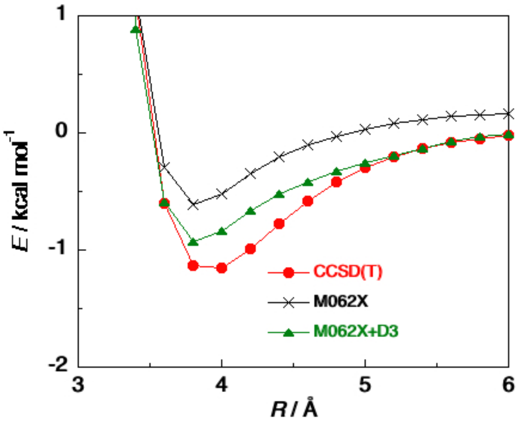
(s)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M052X
M052X+D3

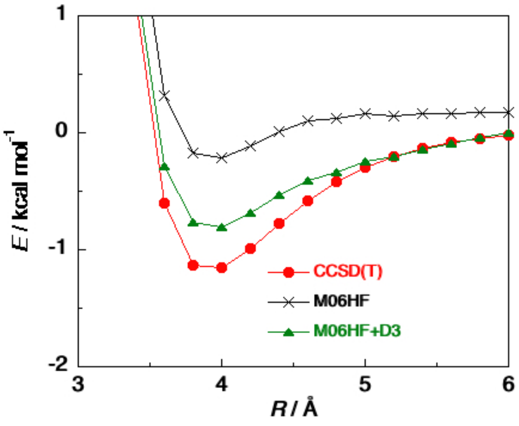
(t)


1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06
M06+D3

(u)

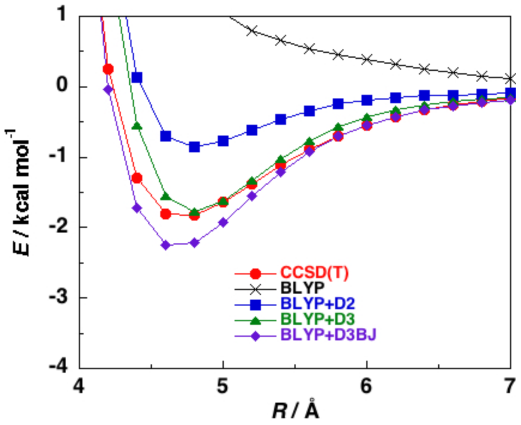

1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M062X
M062X+D3

(v)

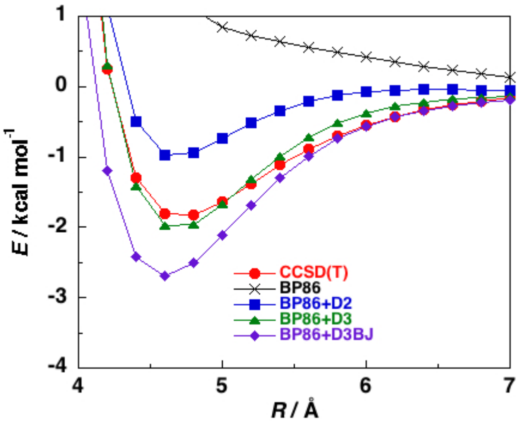

1
0
-1
-2
E / kcal mol-1
3
4
5
6
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

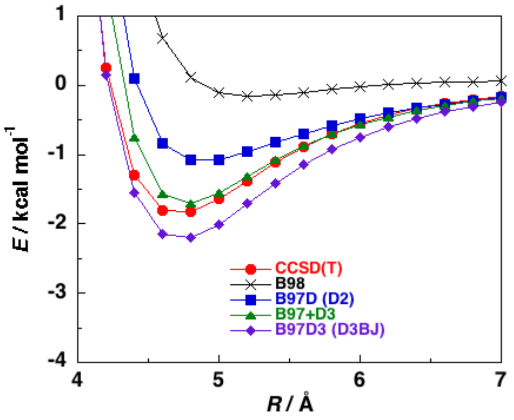
Figure 9S. Intermolecular interaction potentials obtained for C_s furan dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to oxygen atom (C_2 and C_5). R is the distance between X of two furan rings.


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

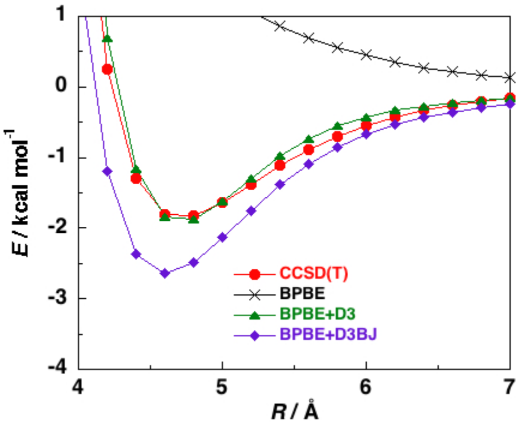
(a)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

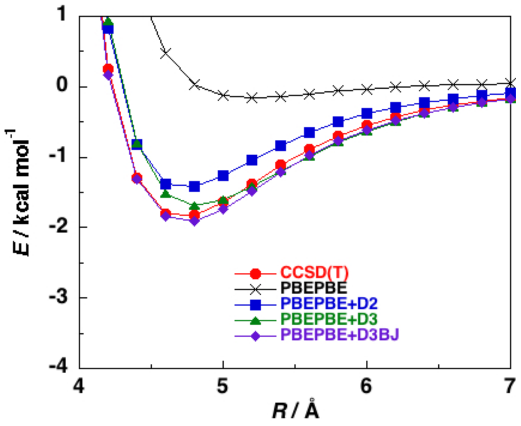
(b)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

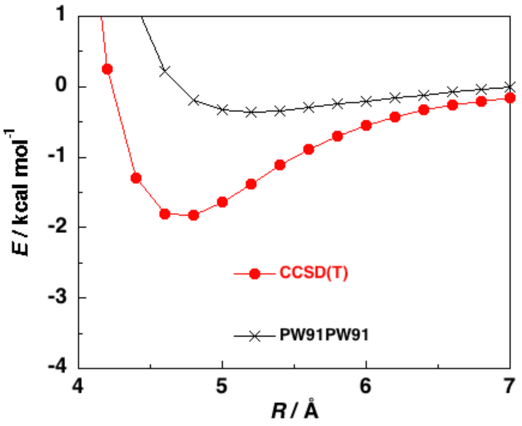
(c)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

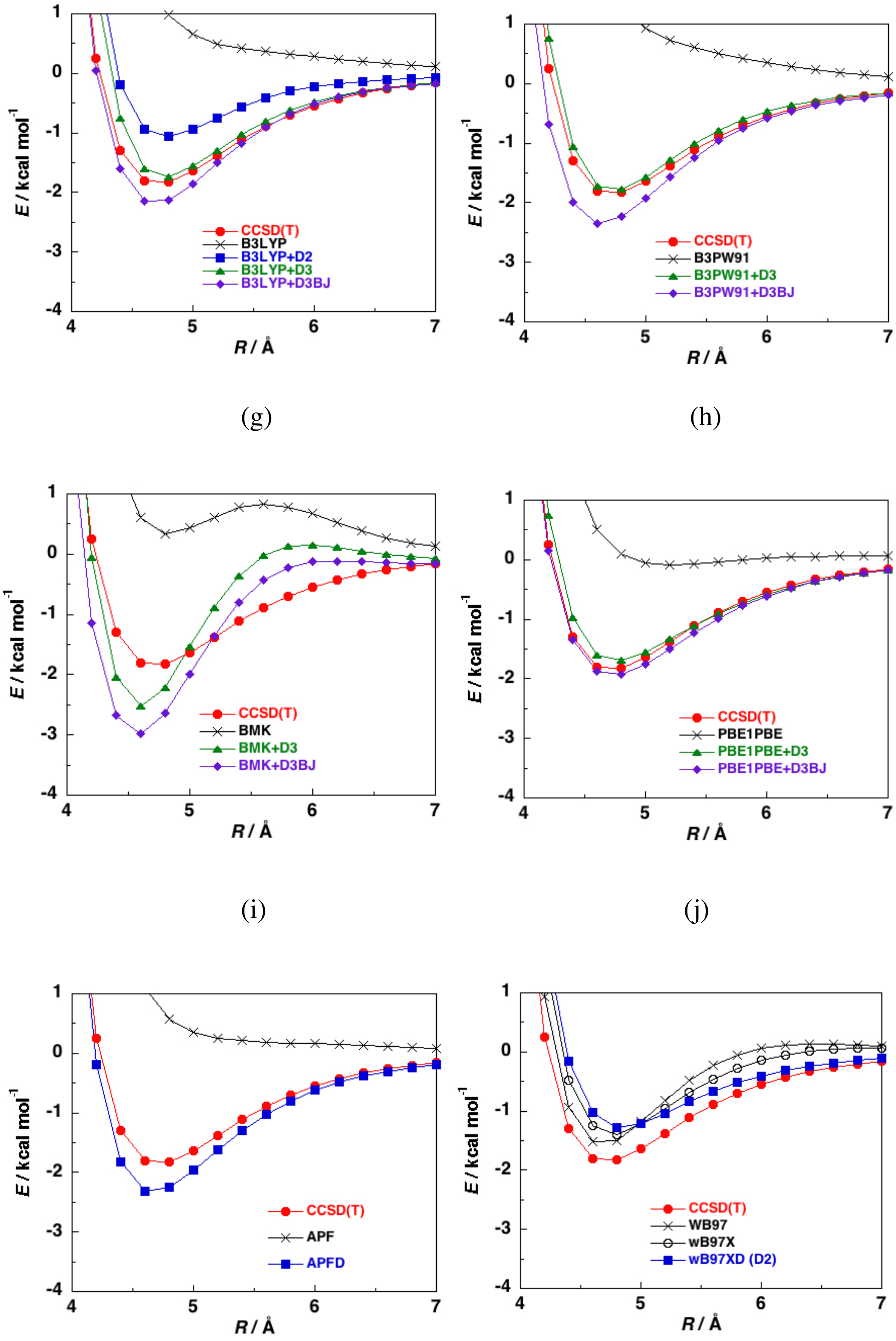
(d)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

(e)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
PW91PW91

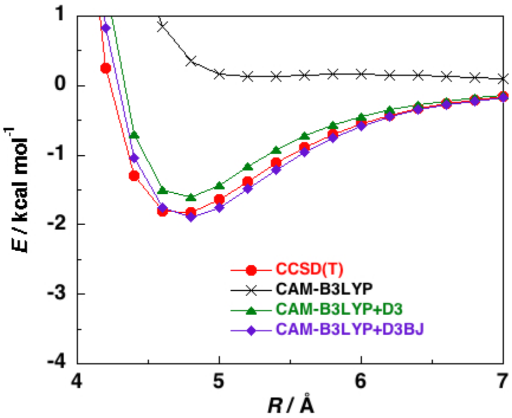
(f)


E / kcal mol^{-1}
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ
B3PW91
B3PW91+D3
B3PW91+D3BJ
BMK
BMK+D3
BMK+D3BJ
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ
APF
APFD
WB97
wB97X
wB97XD (D2)
1
0
-1
-2
-3
-4
4
5
6
7

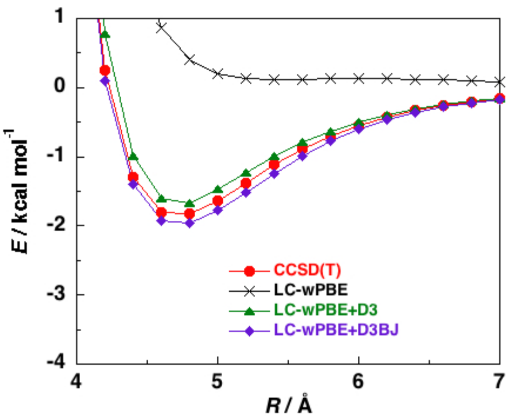
(g) (h)

(i) (j)

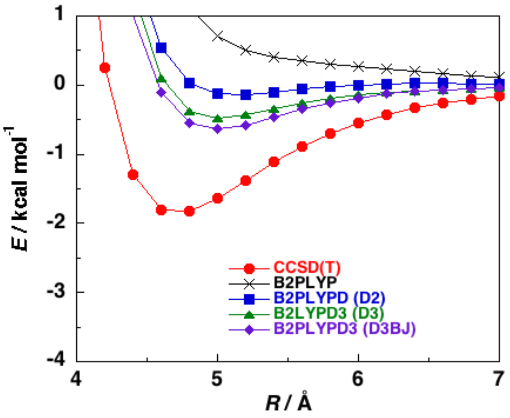
(k) (l)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

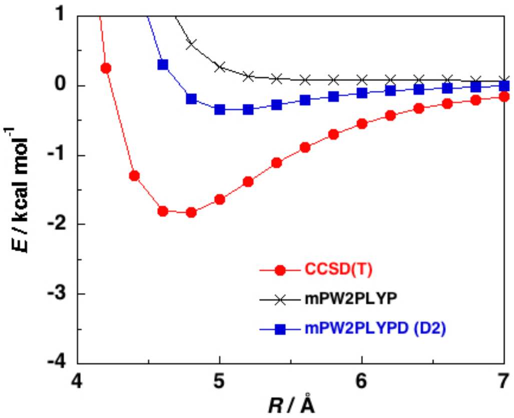
(m)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

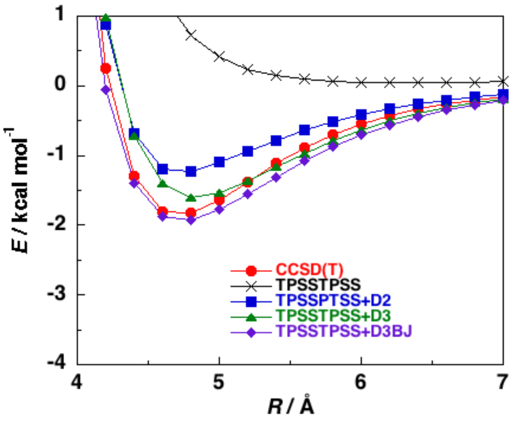
(n)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

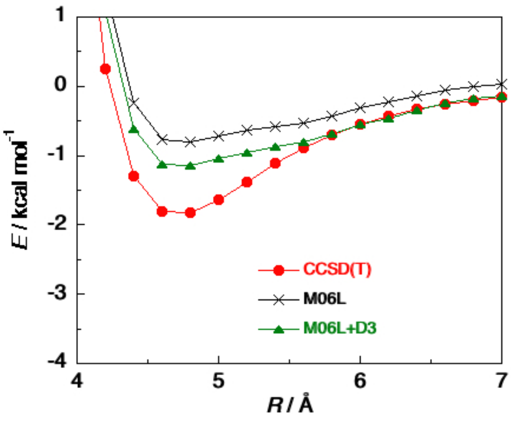
(o)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

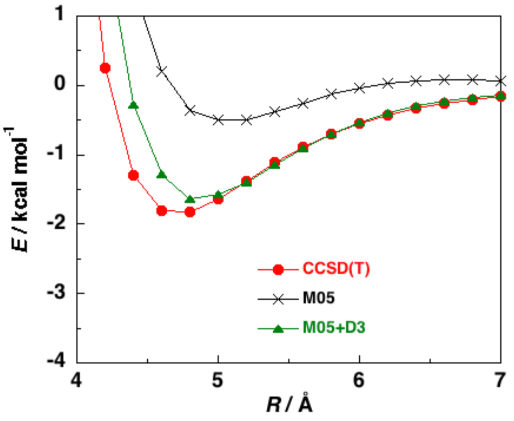
(p)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

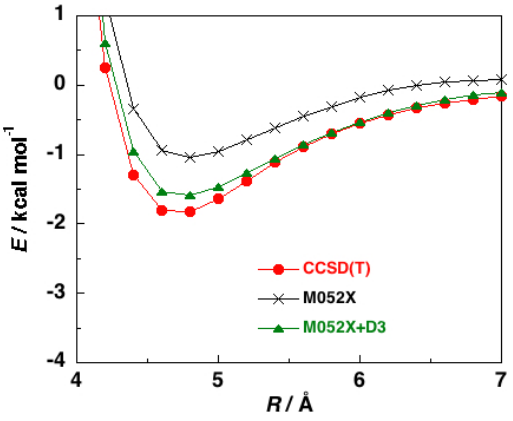
(q)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol-1
R / Å
CCSD(T)
M06L
M06L+D3

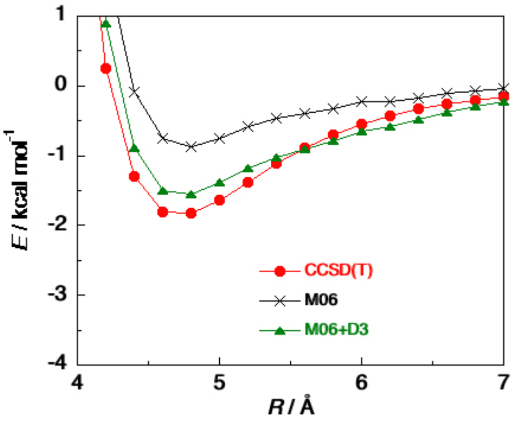
(r)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M05
M05+D3

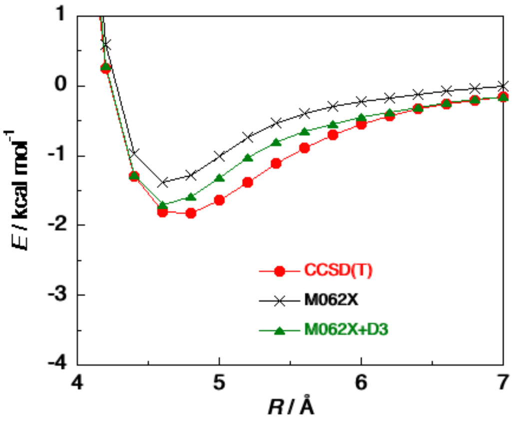
(s)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M052X
M052X+D3

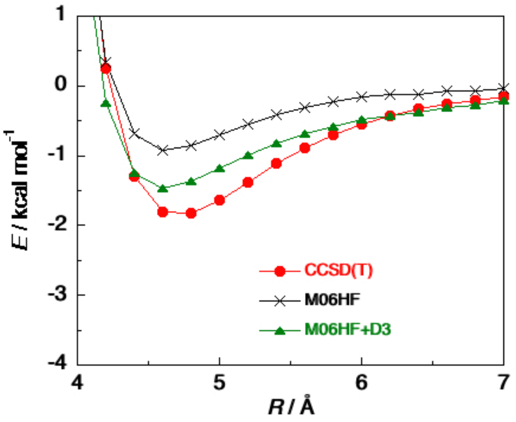
(t)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M06
M06+D3

(u)

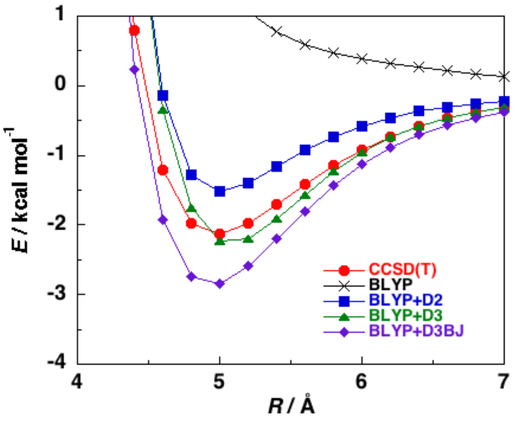

1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M062X
M062X+D3

(v)

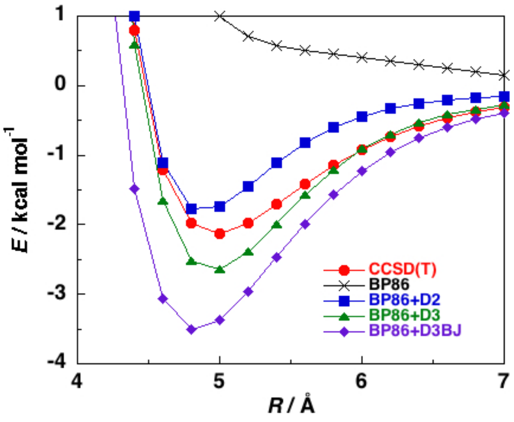

1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

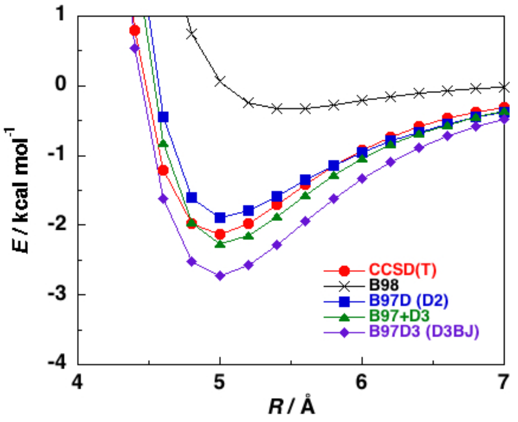
Figure 10S. Intermolecular interaction potentials obtained for C_s thiophene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to sulfur atom (C_2 and C_5). *R* is the distance between X of two thiophene rings.


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

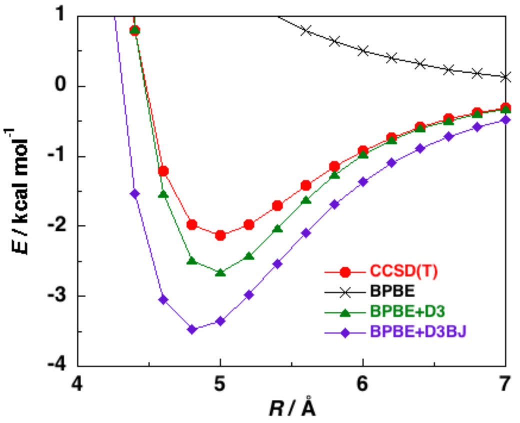
(a)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

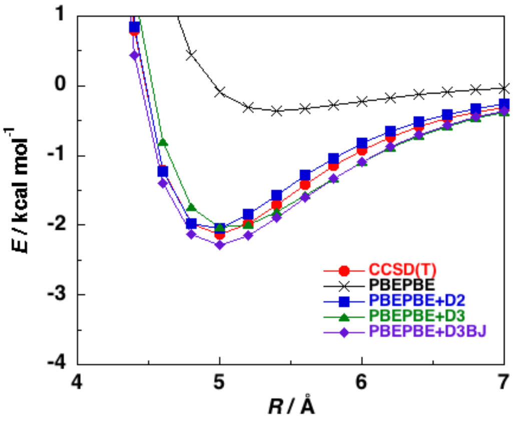
(b)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

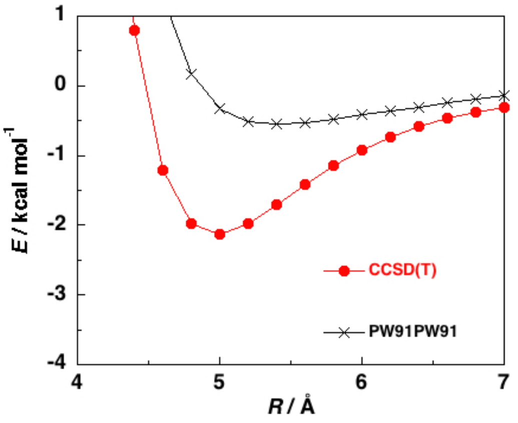
(c)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

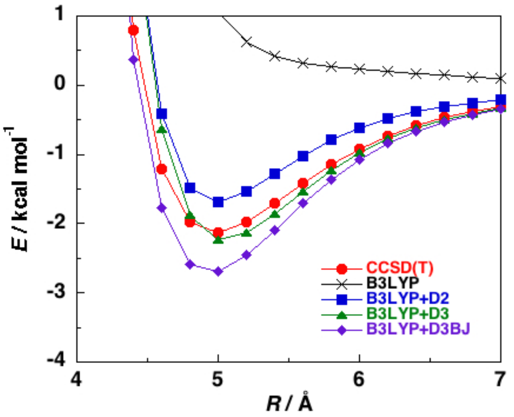
(d)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

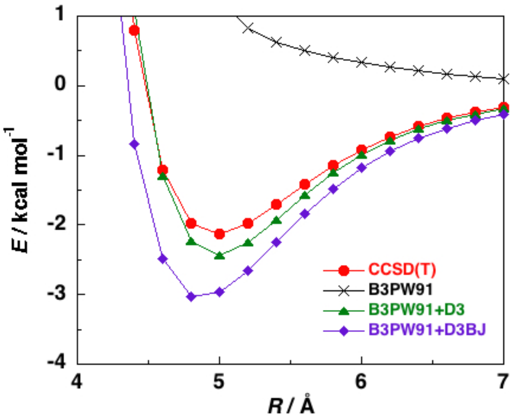
(e)


1
0
-1
-2
-3
-4
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
PW91PW91

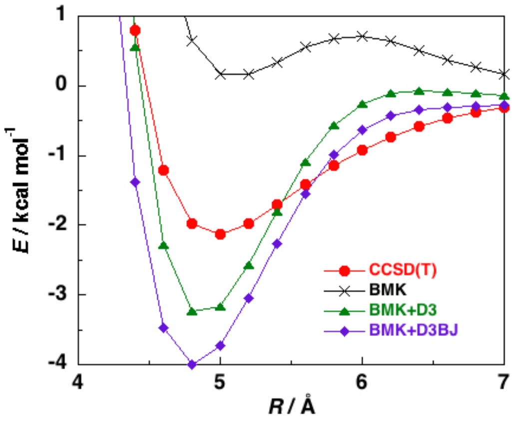
(f)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

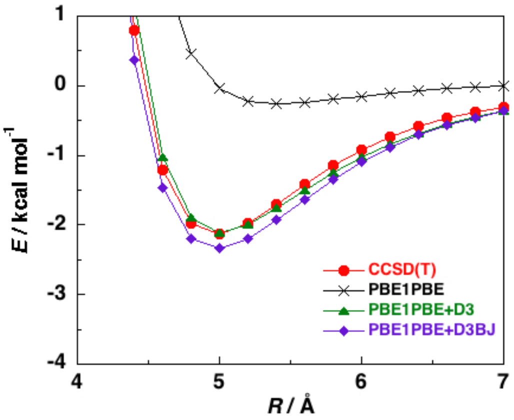
(g)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

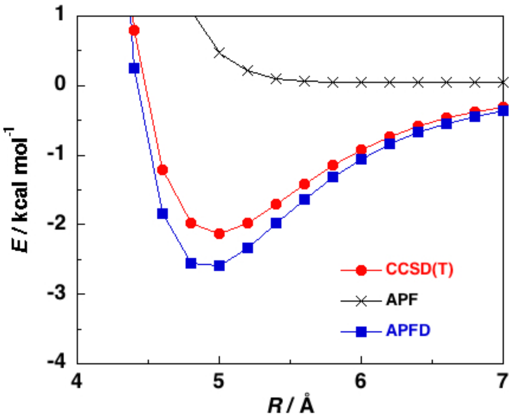
(h)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

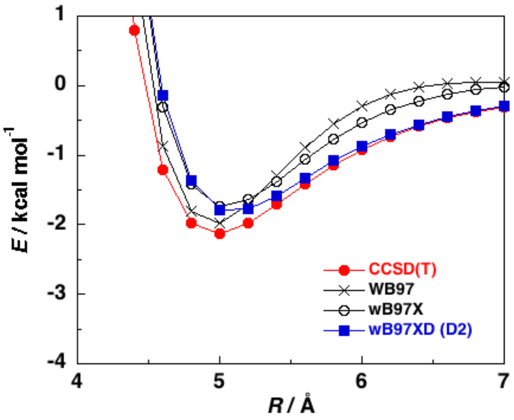
(i)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

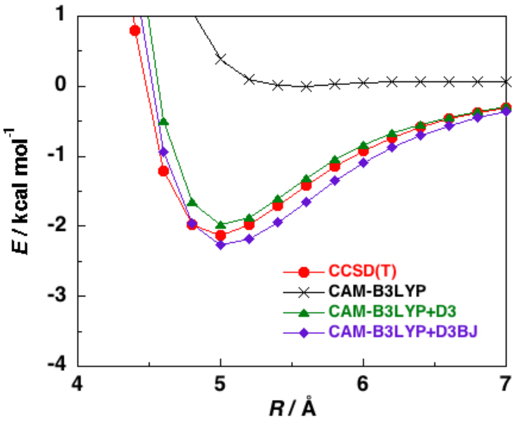
(j)


E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
APF
APFD

(k)

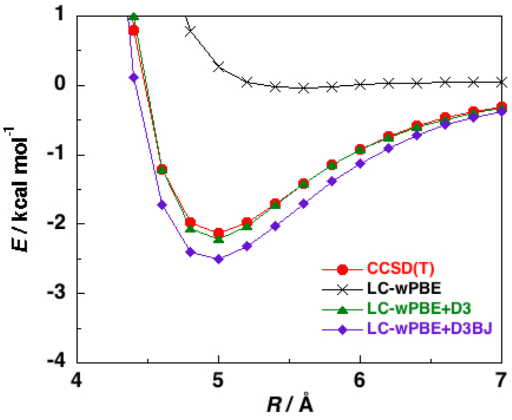

E / kcal mol-1
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
WB97
wB97X
wB97XD (D2)

(l)



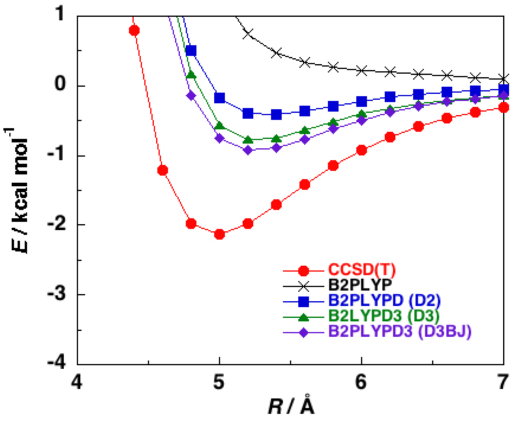
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

(m)



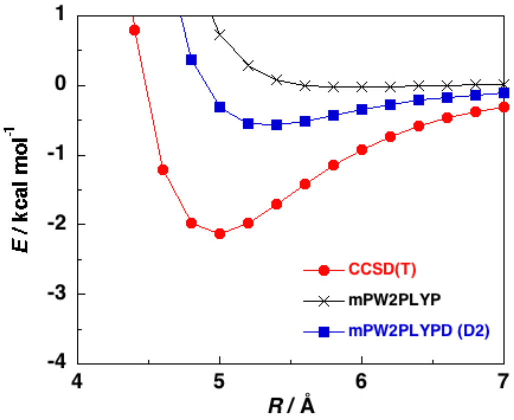
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

(n)



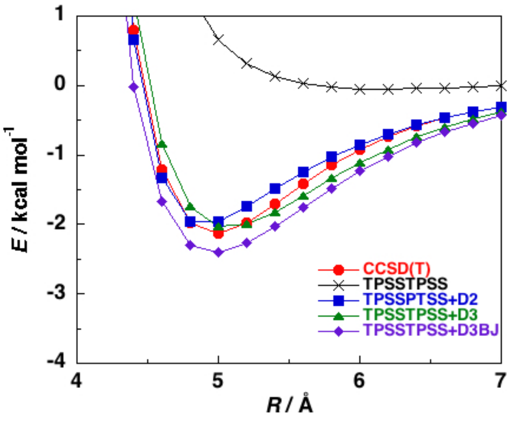
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

(o)



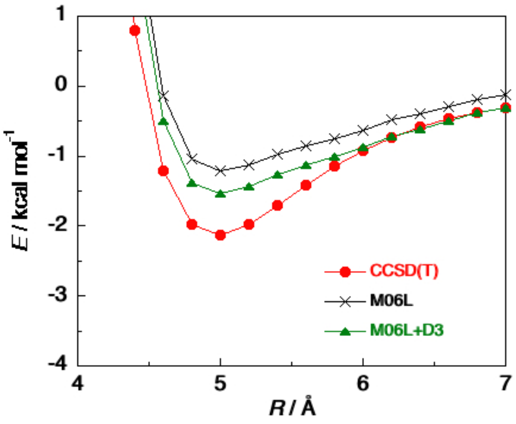
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

(p)



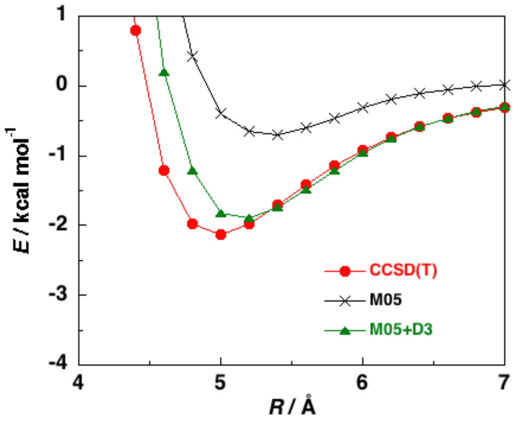
E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

(q)

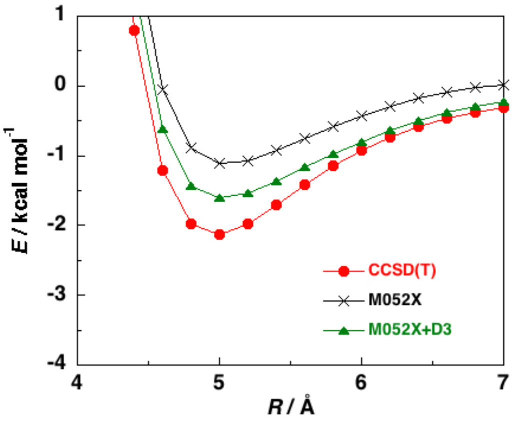


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M06L
M06L+D3

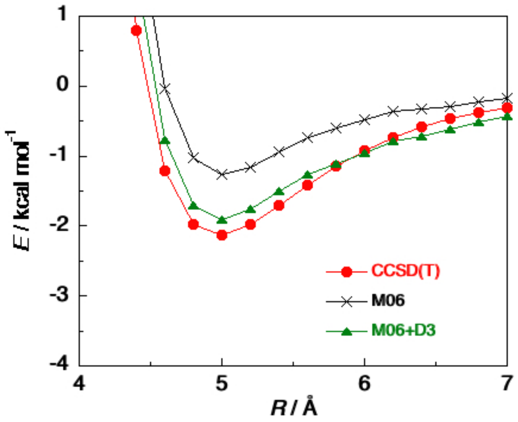
(r)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M05
M05+D3

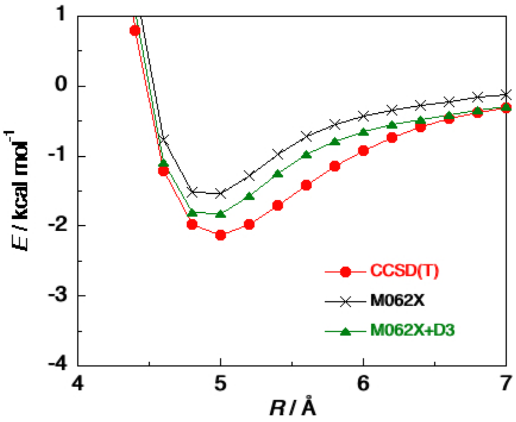
(s)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M052X
M052X+D3

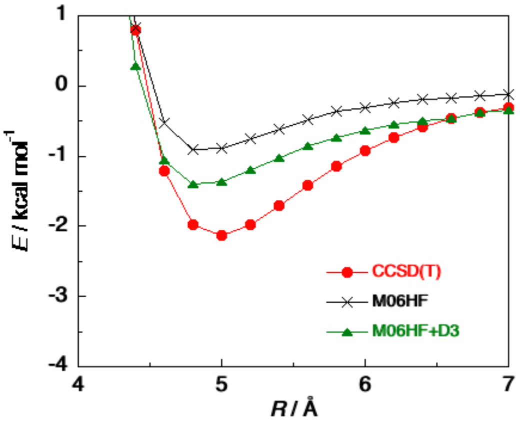
(t)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M06
M06+D3

(u)

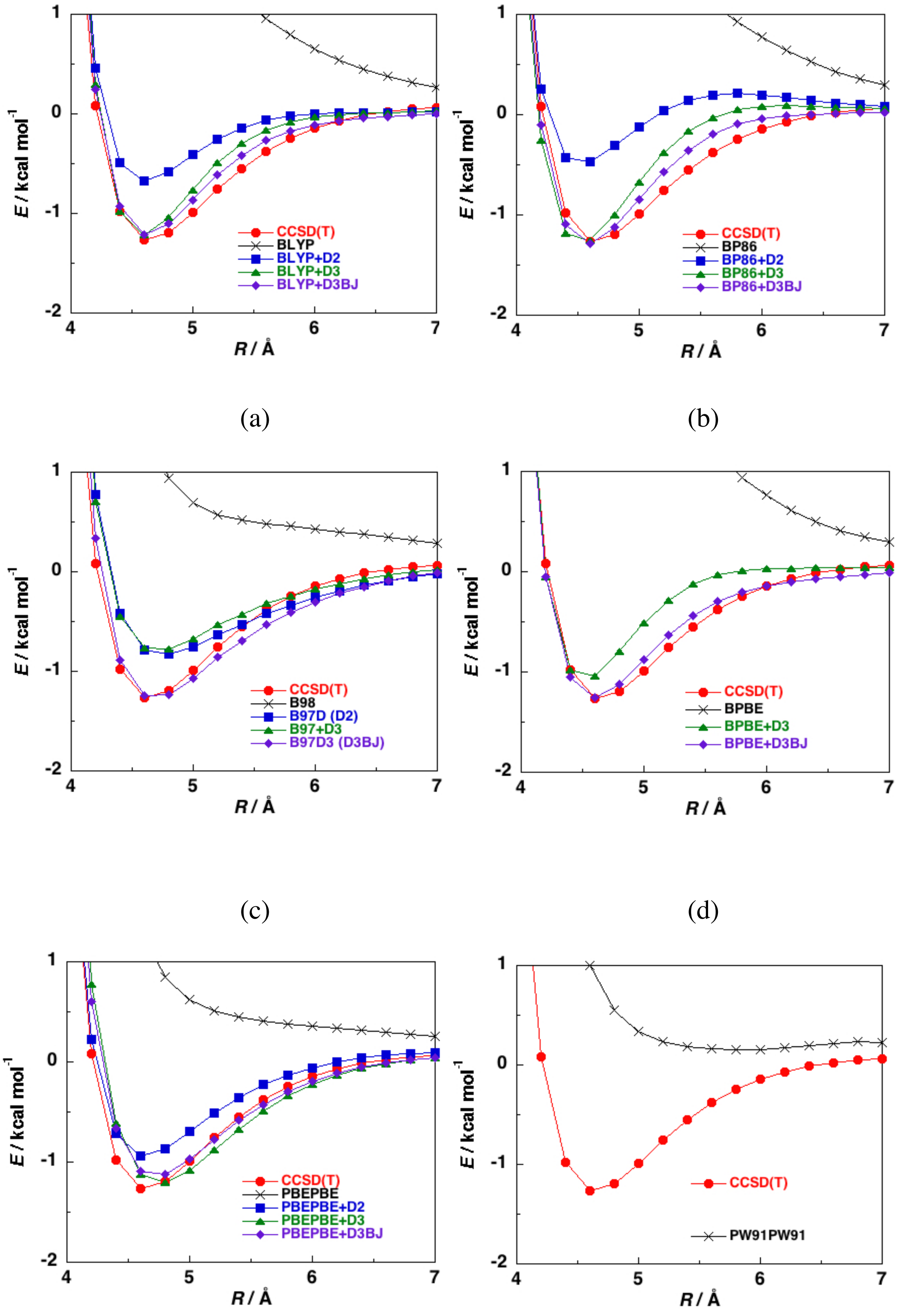

E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M062X
M062X+D3

(v)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
-3
-4
4
5
6
7
CCSD(T)
M06HF
M06HF+D3

(w)

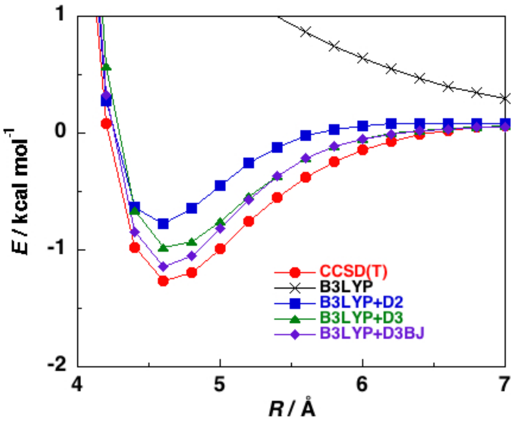
Figure 11S. Intermolecular interaction potentials obtained for C_s selenophene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to selenium atom (C_2 and C_5). *R* is the distance between X of two thiophene rings.


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ
BP86
BP86+D2
BP86+D3
BP86+D3BJ
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)
BPBE
BPBE+D3
BPBE+D3BJ
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ
PW91PW91

(a) (b)

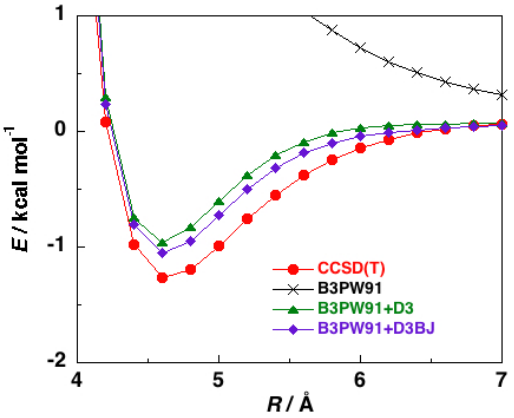
(c) (d)

(e) (f)



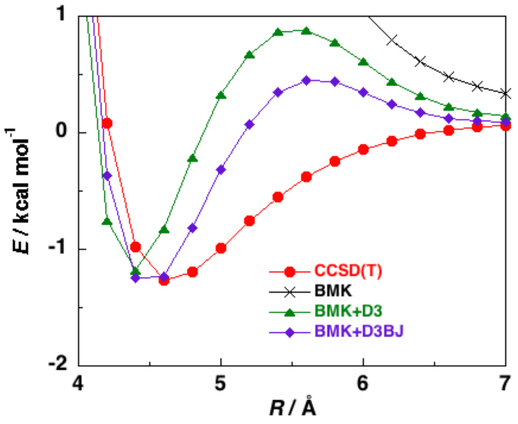
E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

(g)



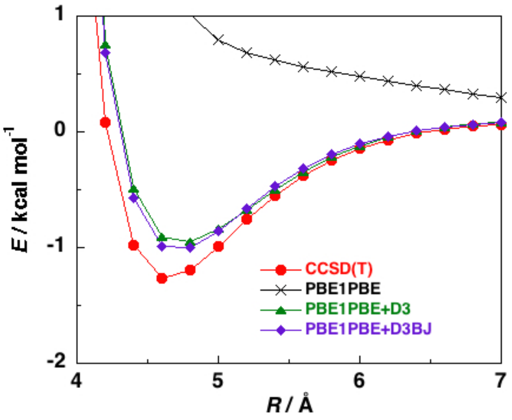
E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

(h)



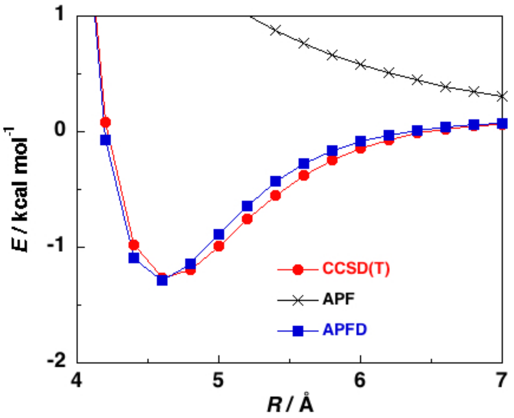
E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

(i)



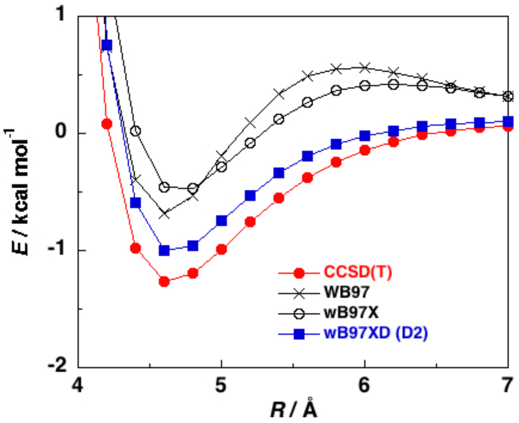
E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

(j)



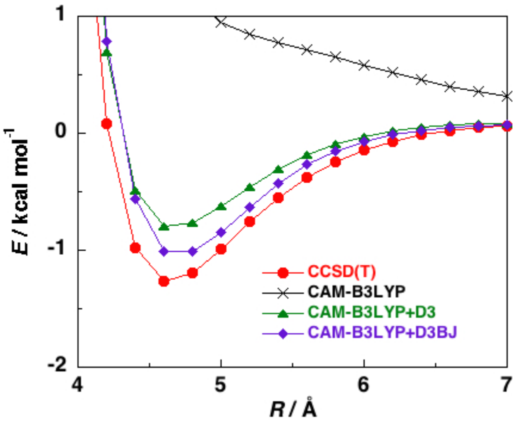
E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
APF
APFD

(k)

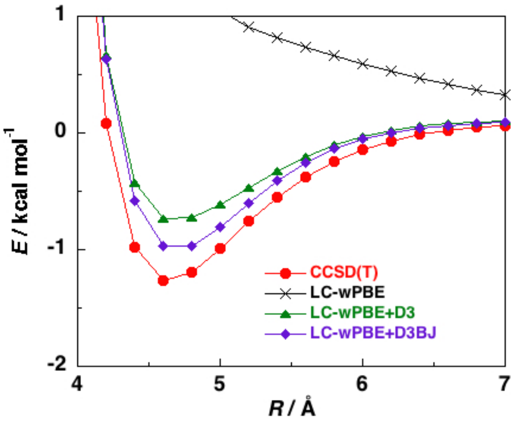


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
WB97
wB97X
wB97XD (D2)

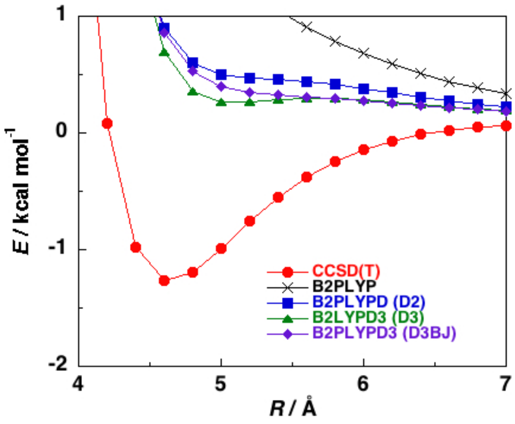
(l)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

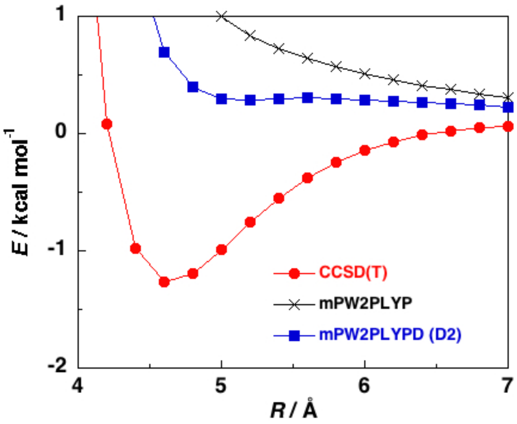
(m)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

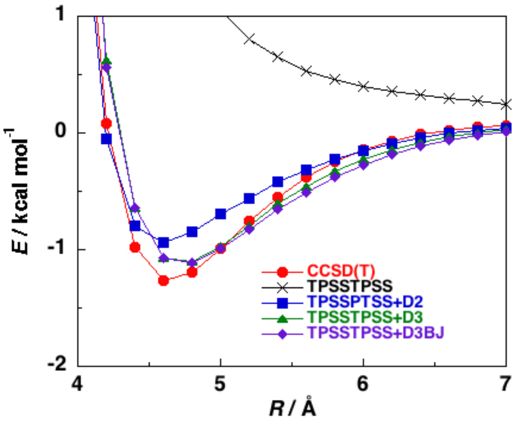
(n)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

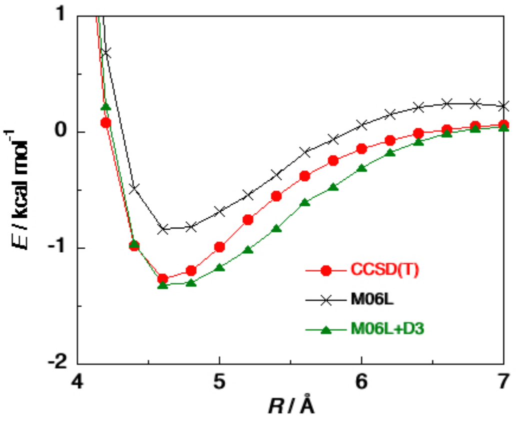
(o)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

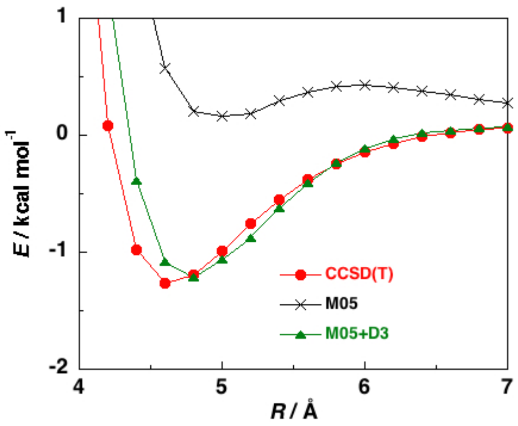
(p)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

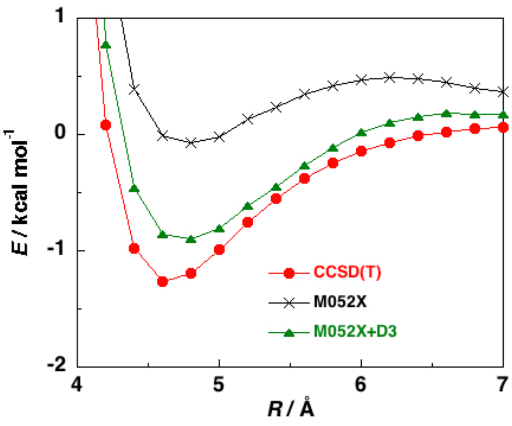
(q)


E / kcal mol^{-1}
R / Å
1
0
-1
-2
4
5
6
7
CCSD(T)
M06L
M06L+D3

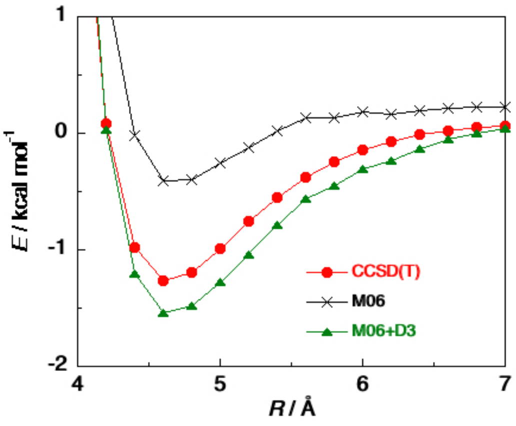
(r)


1
0
-1
-2
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
M05
M05+D3

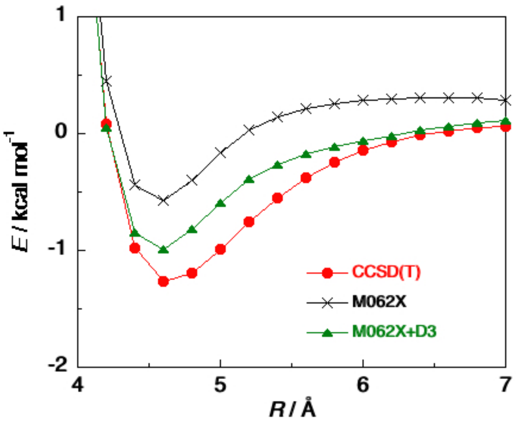
(s)


1
0
-1
-2
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
M052X
M052X+D3

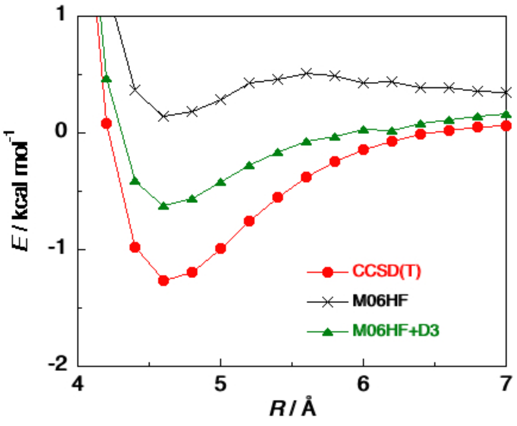
(t)


1
0
-1
-2
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
M06
M06+D3

(u)

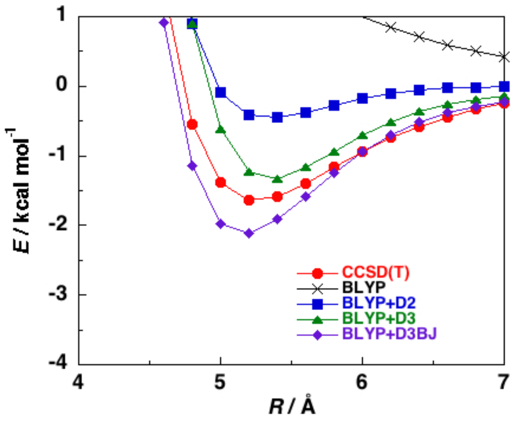

1
0
-1
-2
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
M062X
M062X+D3

(v)

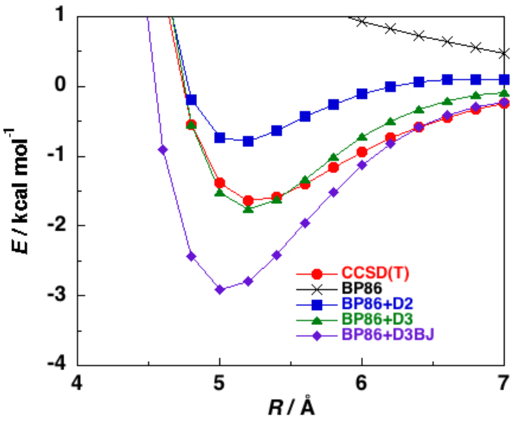

1
0
-1
-2
E / kcal mol-1
4
5
6
7
R / Å
CCSD(T)
M06HF
M06HF+D3

(w)

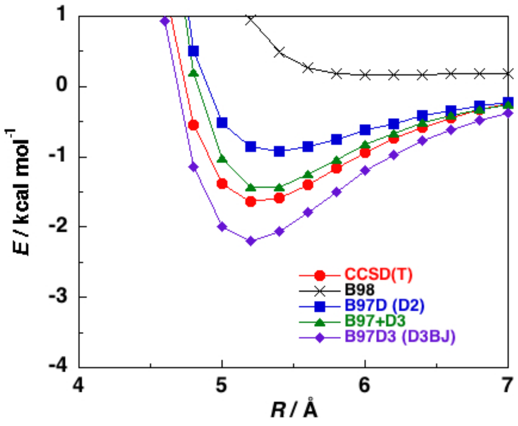
Figure 12S. Intermolecular interaction potentials obtained for C_s pyridine dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. X is the midpoint between N_1 and C_4. R is the distance between X of two pyridine molecules.


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
BLYP
BLYP+D2
BLYP+D3
BLYP+D3BJ

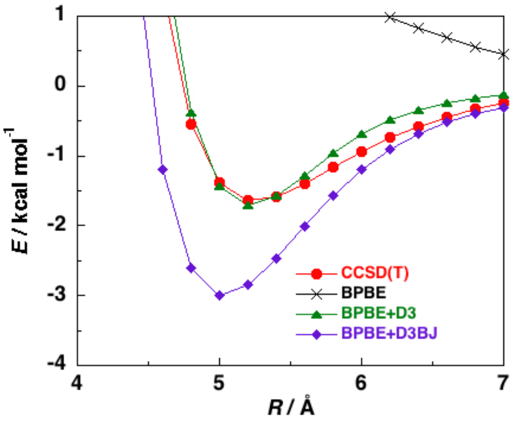
(a)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
BP86
BP86+D2
BP86+D3
BP86+D3BJ

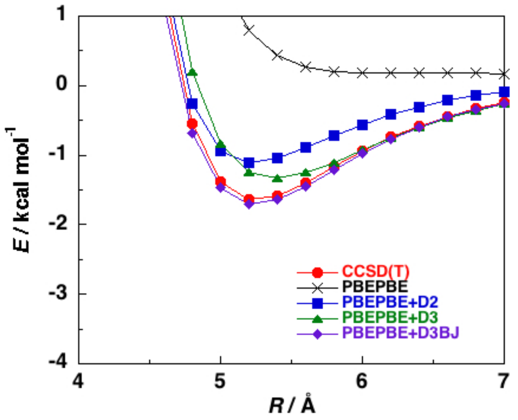
(b)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
B98
B97D (D2)
B97+D3
B97D3 (D3BJ)

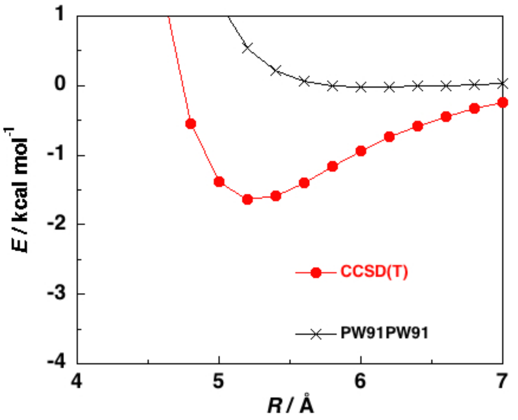
(c)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
BPBE
BPBE+D3
BPBE+D3BJ

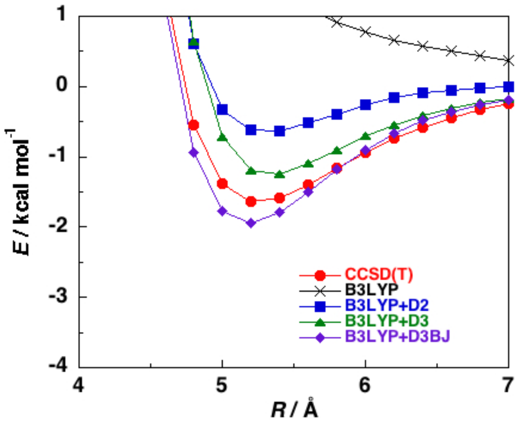
(d)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
PBEPBE
PBEPBE+D2
PBEPBE+D3
PBEPBE+D3BJ

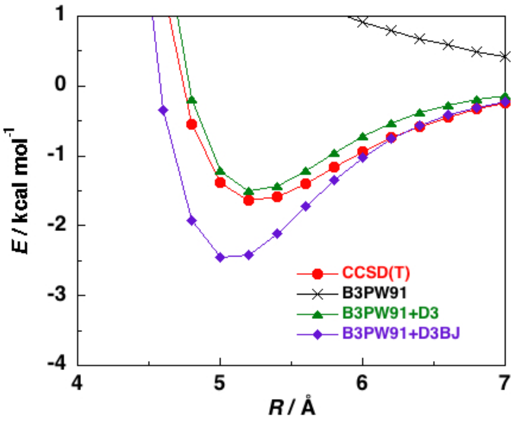
(e)


1
0
-1
-2
-3
-4
4
5
6
7
E / kcal mol^{-1}
R / Å
CCSD(T)
PW91PW91

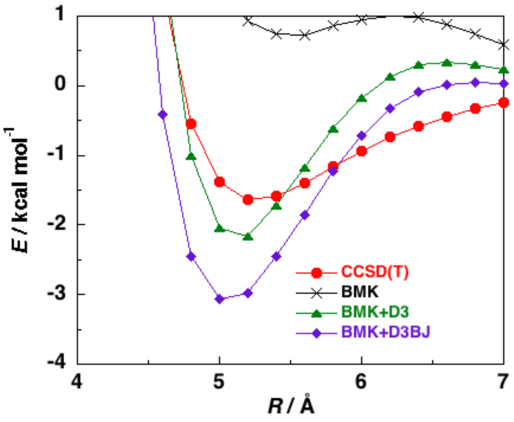
(f)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
B3LYP
B3LYP+D2
B3LYP+D3
B3LYP+D3BJ

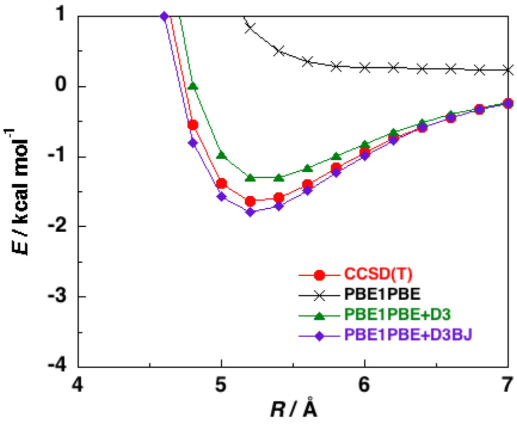
(g)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
B3PW91
B3PW91+D3
B3PW91+D3BJ

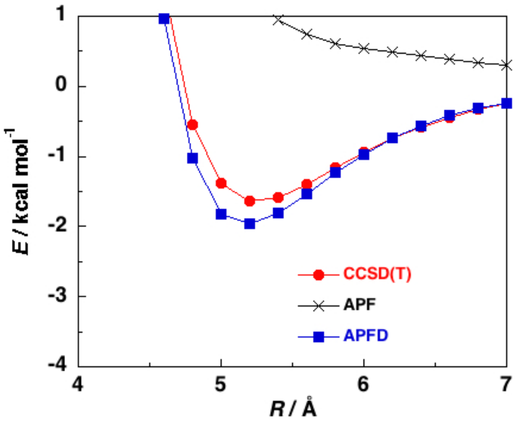
(h)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
BMK
BMK+D3
BMK+D3BJ

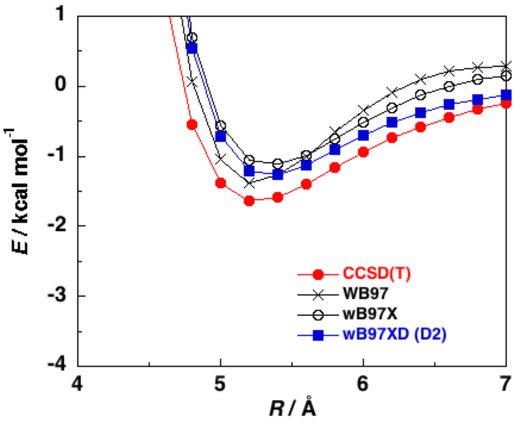
(i)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
PBE1PBE
PBE1PBE+D3
PBE1PBE+D3BJ

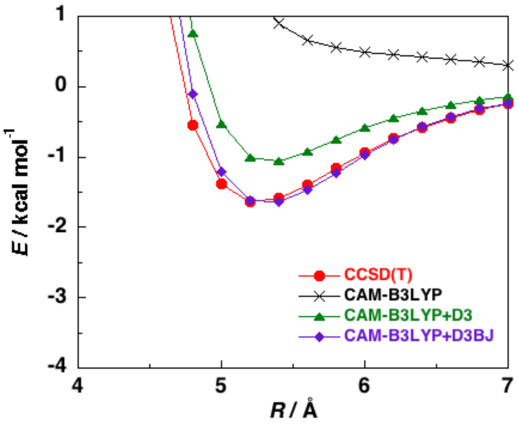
(j)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
APF
APFD

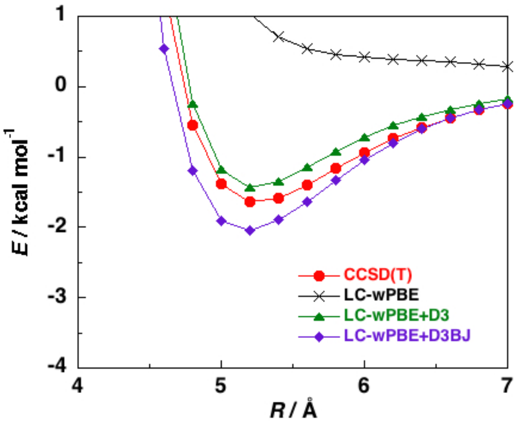
(k)


E / kcal mol^{-1}
1
0
-1
-2
-3
-4
4
5
6
7
R / Å
CCSD(T)
WB97
wB97X
wB97XD (D2)

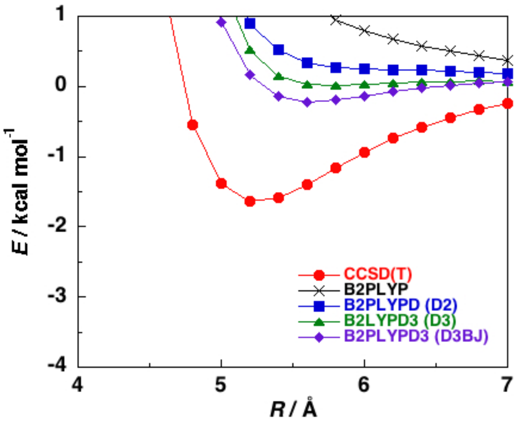
(l)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
CAM-B3LYP
CAM-B3LYP+D3
CAM-B3LYP+D3BJ

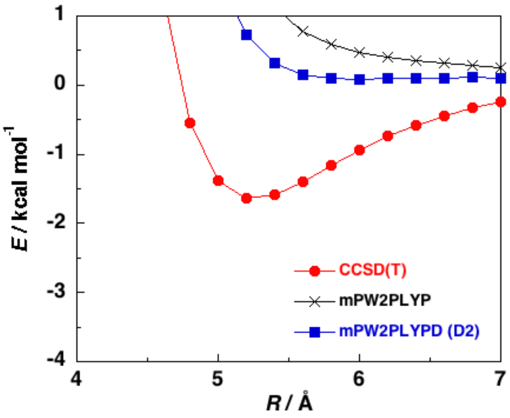
(m)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
LC-wPBE
LC-wPBE+D3
LC-wPBE+D3BJ

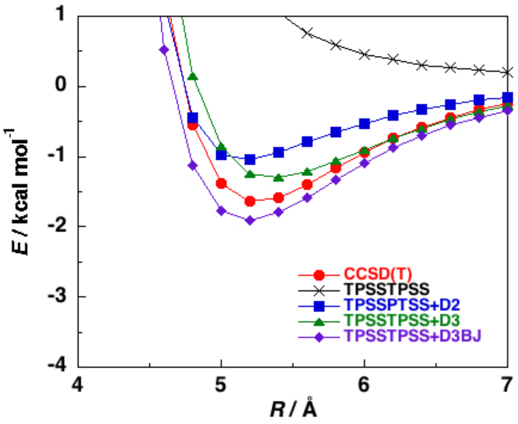
(n)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
B2PLYP
B2PLYPD (D2)
B2LYPD3 (D3)
B2PLYPD3 (D3BJ)

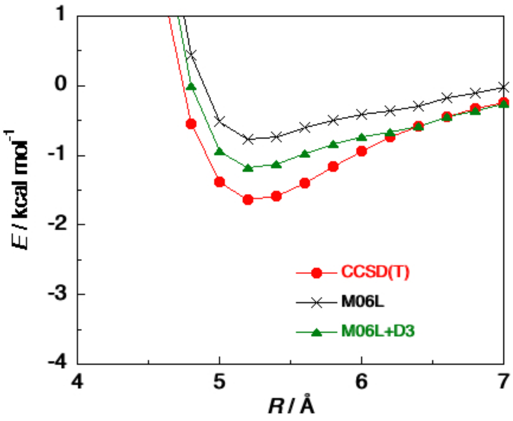
(o)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
mPW2PLYP
mPW2PLYPD (D2)

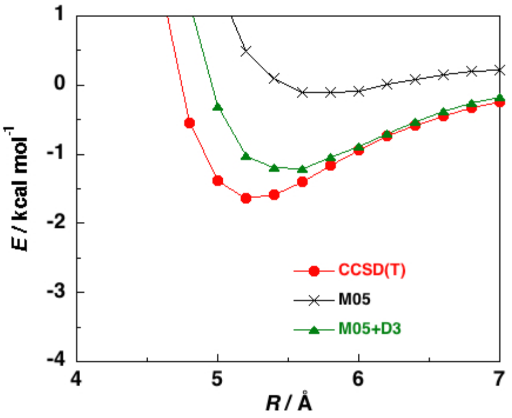
(p)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
TPSSTPSS
TPSSPTSS+D2
TPSSTPSS+D3
TPSSTPSS+D3BJ

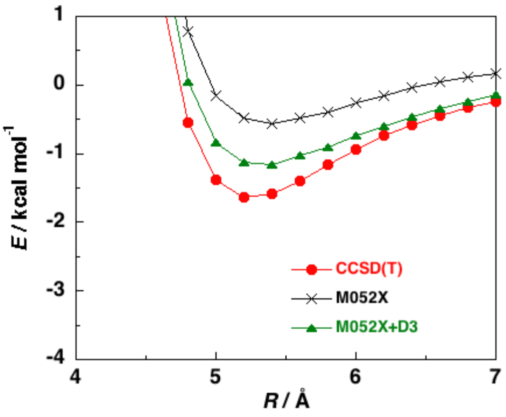
(q)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M06L
M06L+D3

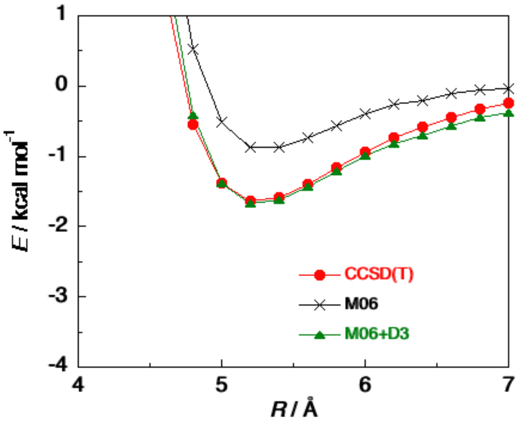
(r)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M05
M05+D3

(s)


1
0
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M052X
M052X+D3

(t)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-1
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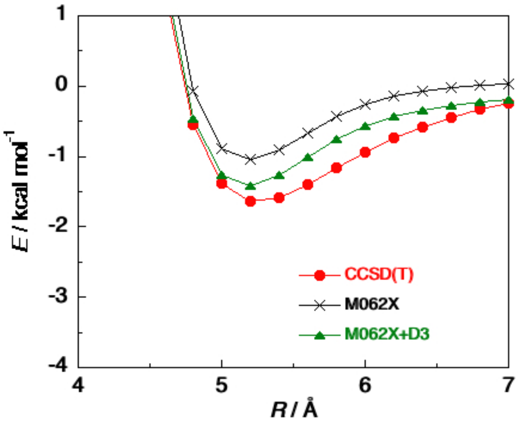
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M06
M06+D3

(u)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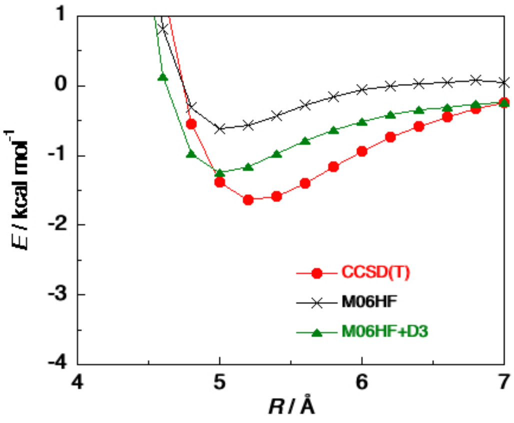
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M062X
M062X+D3

(v)


1
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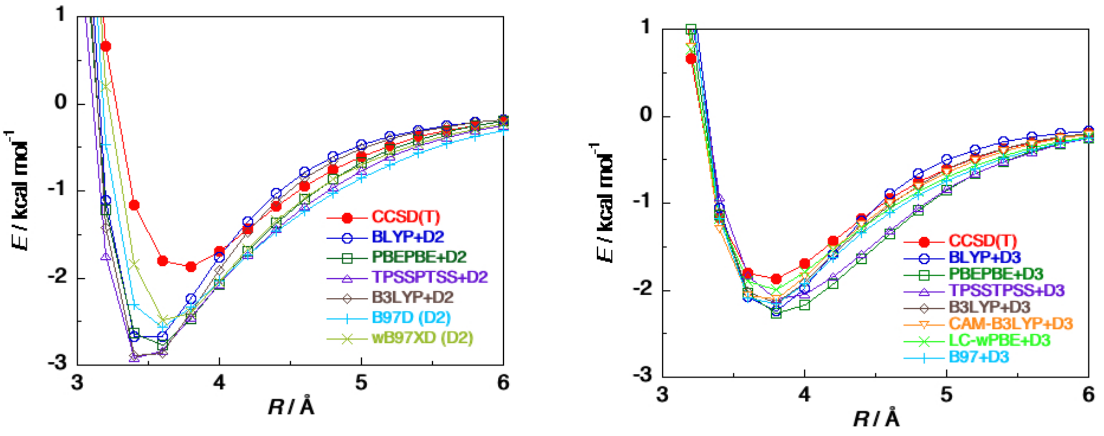
-1
-2
-3
-4
E / kcal mol^{-1}
4
5
6
7
R / Å
CCSD(T)
M06HF
M06HF+D3

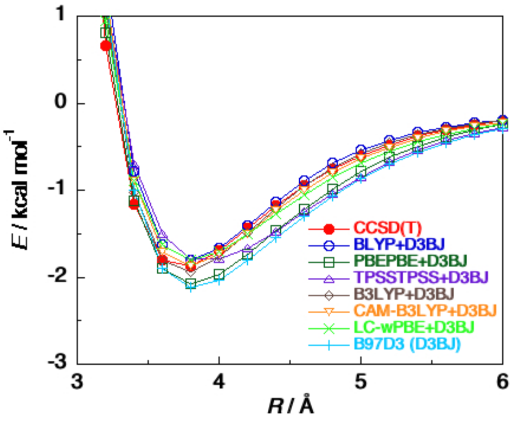
(w)

Figure 13S. Intermolecular interaction potentials obtained for C_s phosphorine dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods are compared with the estimated CCSD(T) level interaction potential at the basis set limit. The geometry of complex is shown in Figure 1. X is the midpoint between P_1 and C_4. *R* is the distance between X of two phosphorene molecules.



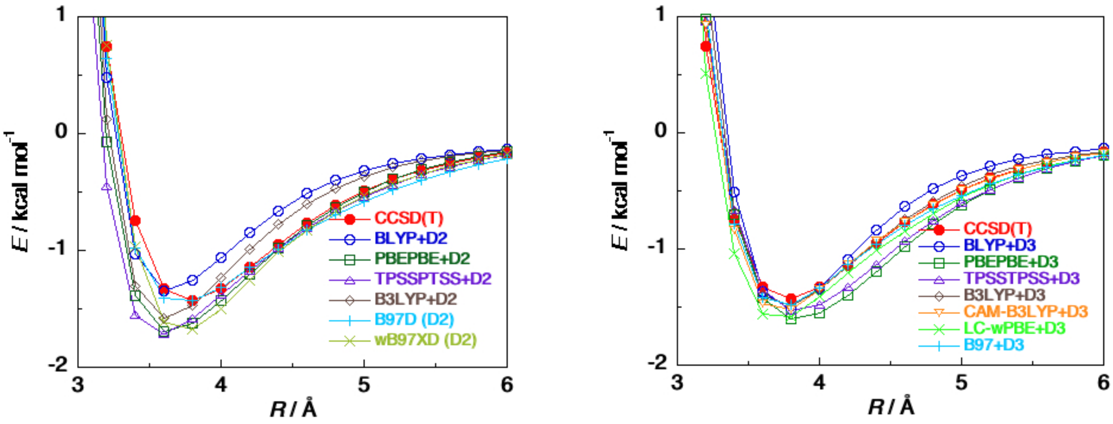
(a) D2 correction

(b) D3 correction



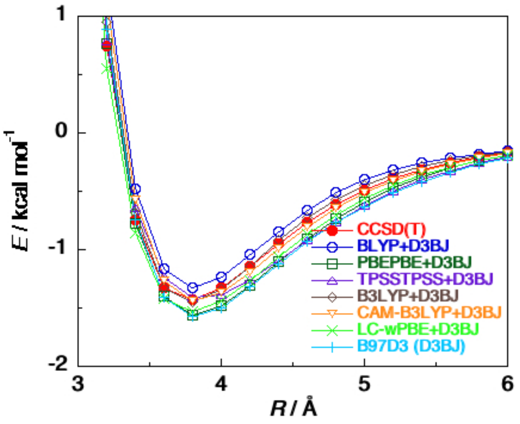
(c) D3BJ correction

Figure 14S. Intermolecular interaction potentials calculated for C_{2h} propane dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. *R* is the distance between the central carbon atoms of two propanes.



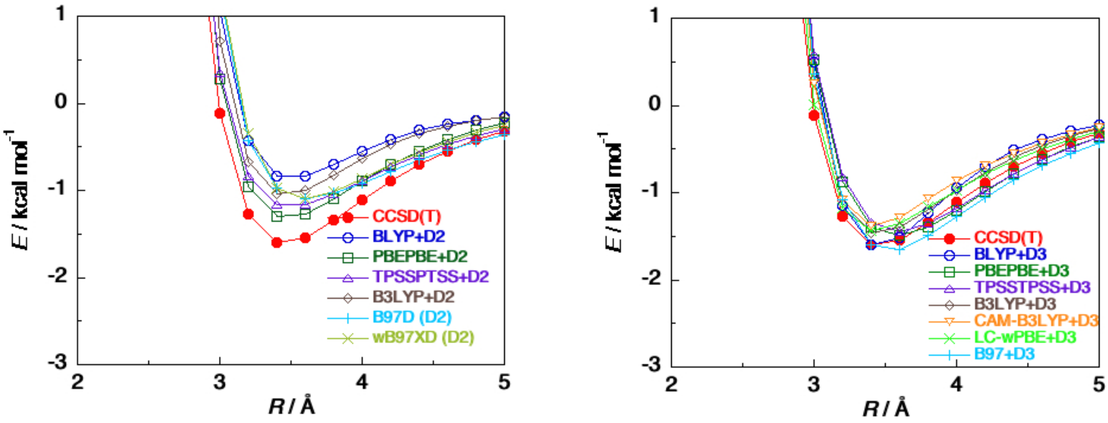
(a) D2 correction

(b) D3 correction



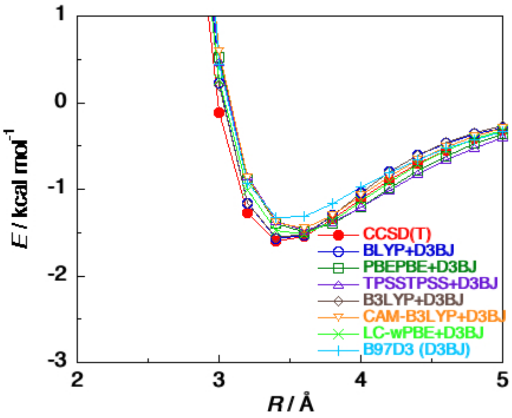
(c) D3BJ correction

Figure 15S. Intermolecular interaction potentials calculated for C_{3v} benzene-methane complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry center of benzene and carbon atom of methane.



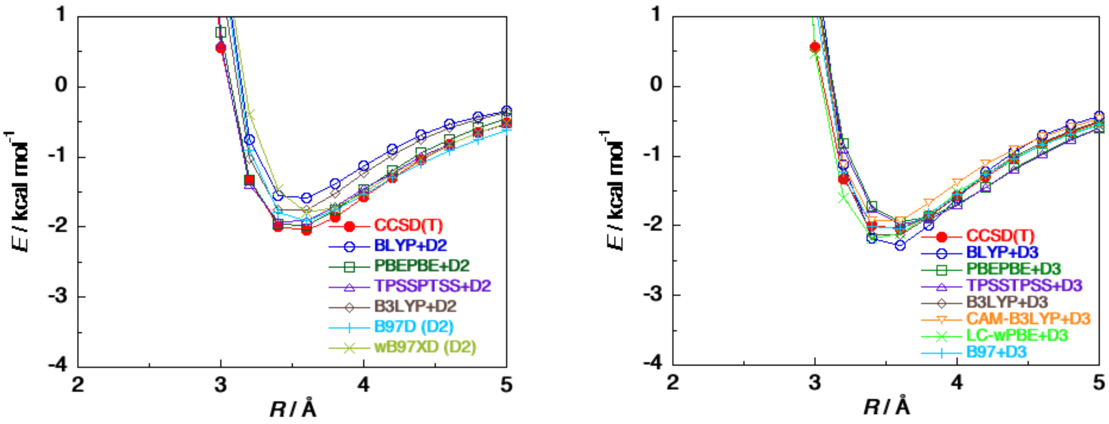
(a) D2 correction

(b) D3 correction

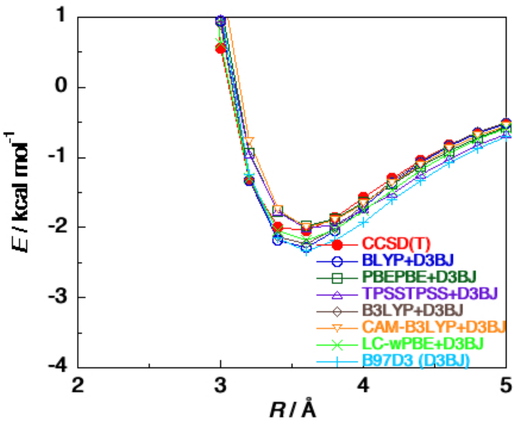


(c) D3BJ correction

Figure 16S. Intermolecular interaction potentials calculated for benzene-chlorobenzene complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry center of benzene and chlorine atom.

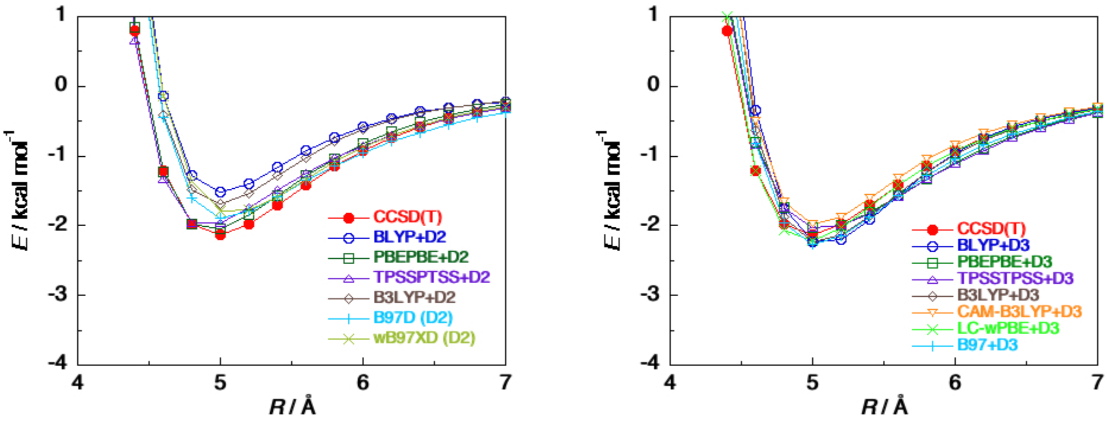


(a) D2 correction (b) D3 correction

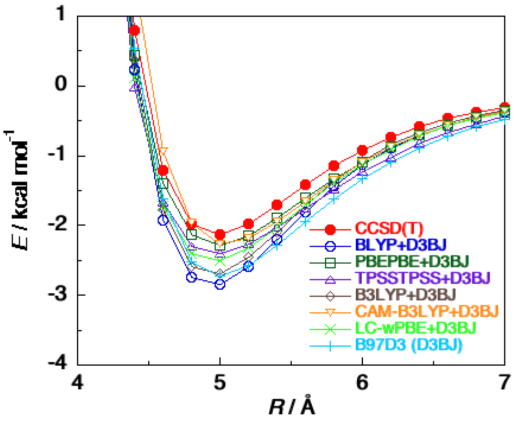


(c) D3BJ correction

Figure 17S. Intermolecular interaction potentials calculated for benzene-bromobenzene complex by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry center of benzene and bromine atom.

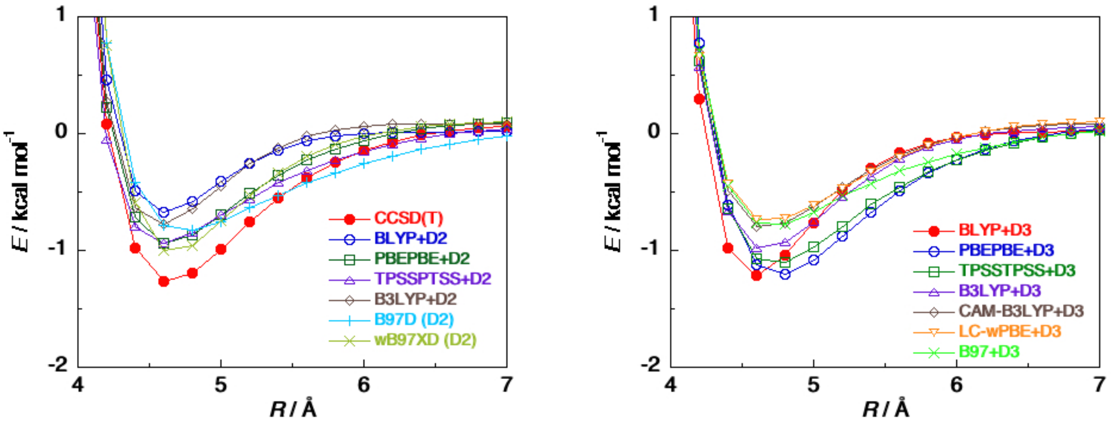


(a) D2 correction (b) D3 correction



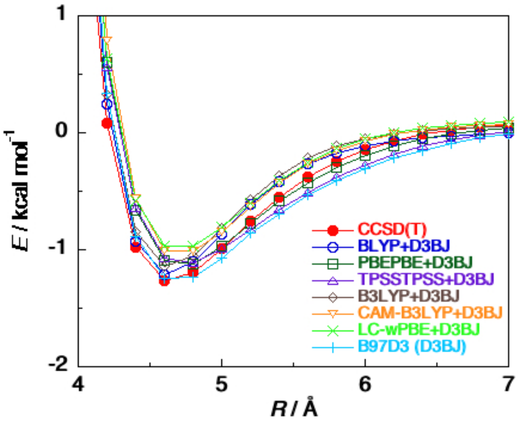
(c) D3BJ correction

Figure 18S. Intermolecular interaction potentials calculated for C_s selenophene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to selenium atom (C_2 and C_5). *R* is the distance between X of two thiophene rings.



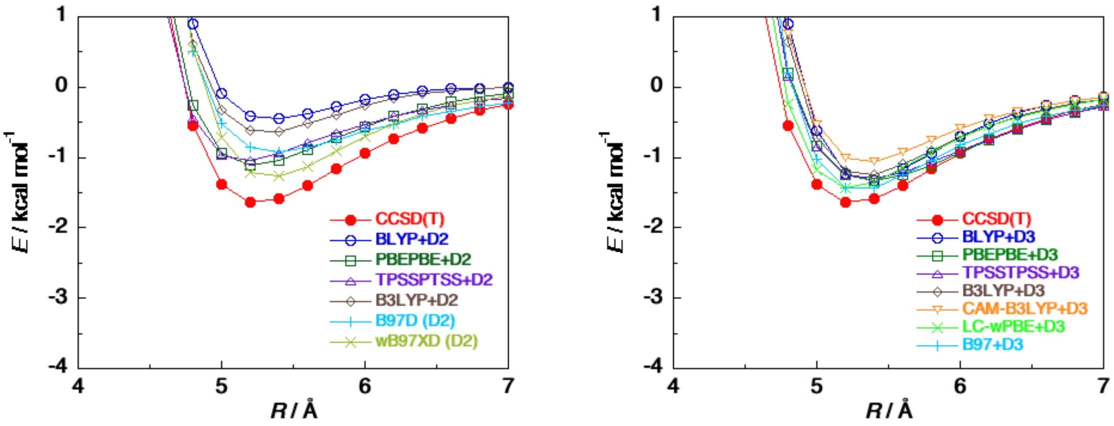
(a) D2 correction

(b) D3 correction



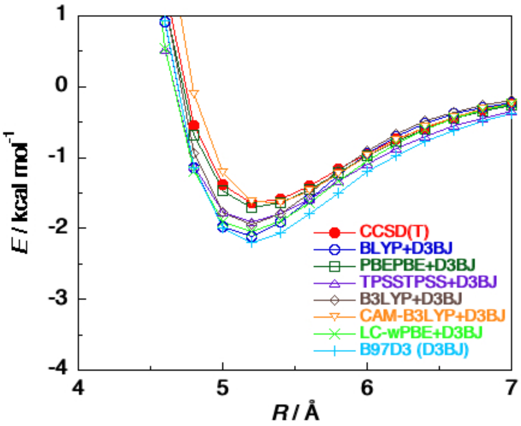
(c) D3BJ correction

Figure 19S. Intermolecular interaction potentials calculated for C_s pyridine dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. X is the midpoint between N_1 and C_4. *R* is the distance between X of two pyridine molecules.



(a) D2 correction

(b) D3 correction



(c) D3BJ correction

Figure 20S. Intermolecular interaction potentials calculated for C_s phosphorine dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. X is the midpoint between P_1 and C_4. *R* is the distance between X of two phosphorine molecules.