Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information to

Ordering of monomers, dimers and polymers of deposited Br_2I_2Py molecules: a modeling study

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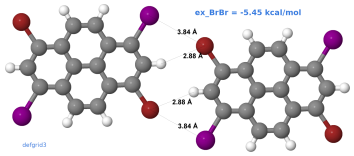
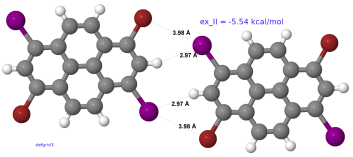
Types of e_X interaction

Br_2I_2Py



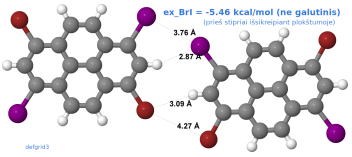
e_{X1} = -5.45 kcal/mol

$e_{X1} \approx 2e_{X(Br\text{-}I)} + 2e_{X(Br\text{-}H)}$ (1x)



e_{X2} = -5.54 kcal/mol

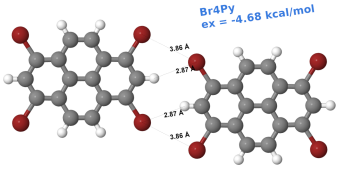
$e_{X2} \approx 2e_{X(Br\text{-}I)} + 2e_{X(I\text{-}H)}$ (2x)



e_{X3} = -5.46 kcal/mol

$e_{X3} \approx e_{X(I\text{-}I)} + e_{X(Br\text{-}Br)} + e_{X(I\text{-}H)} + e_{X(Br\text{-}H)}$ (3x)

Br_4Py



e_X = -4.68 kcal/mol

$e_{XBr} \approx 2e_{X(Br\text{-}Br)} + 2e_{X(Br\text{-}H)}$ (4x)

(2x) - (1x)
$e_{X(I\text{-}H)} - e_{X(Br\text{-}H)}$ = -0.05 kcal/mol ~ 0

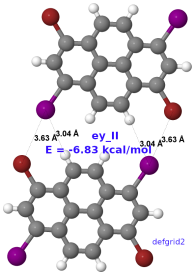
[(1x) + (2x)] / 2 – (3x)
$2e_{X(Br\text{-}I)} - e_{X(I\text{-}I)} - e_{X(Br\text{-}Br)}$ = -0.04 kcal/mol ~ 0 (5x)

(1x) - (4x)
$e_{X(Br\text{-}I)} - e_{X(Br\text{-}Br)}$ = -0.39 kcal/mol (6x)

(6x) - (5x)
$e_{X(I\text{-}I)} - e_{X(Br\text{-}I)}$ = -0.35 kcal/mol

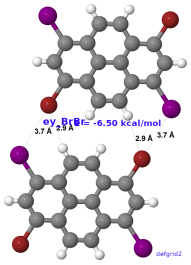
Types of e_Y interaction

Br_2I_2Py



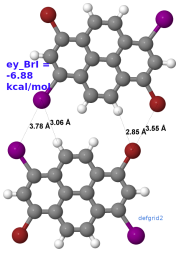
e_{Y1} = -6.83 kcal/mol

$e_{Y1} \approx 2e_{Y(Br\text{-}I)} + 2e_{Y(I\text{-}H)}$ (1y)



e_{Y2} = -6.50 kcal/mol

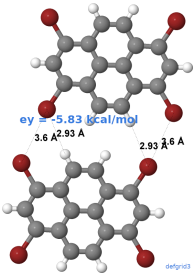
$e_{Y2} \approx 2e_{Y(Br\text{-}I)} + 2e_{Y(Br\text{-}H)}$ (2y)



e_{Y3} = -6.88 kcal/mol

$e_{Y3} \approx e_{Y(I\text{-}I)} + e_{Y(Br\text{-}Br)} + e_{Y(I\text{-}H)} + e_{Y(Br\text{-}H)}$ (3y)

Br_4Py



e_Y = -5.83 kcal/mol

$e_{YBr} \approx 2e_{Y(Br\text{-}Br)} + 2e_{Y(Br\text{-}H)}$ (4y)

(1y) – (2y)
$e_{Y(I\text{-}H)} - e_{Y(Br\text{-}H)}$ = -0.16 kcal/mol

[(1y) + (2y)] / 2 – (3y)
$2e_{Y(Br\text{-}I)} - e_{Y(I\text{-}I)} - e_{Y(Br\text{-}Br)}$ = 0.22 kcal/mol (5y)

(2y) – (4y)
$e_{Y(Br\text{-}I)} - e_{Y(Br\text{-}Br)}$ = -0.34 kcal/mol (6y)

(6y) – (5y)
$e_{Y(I\text{-}I)} - e_{Y(Br\text{-}I)}$ = -0.56 kcal/mol

Fig. S1: DFT-optimized molecular pairs corresponding to configurations $i = 1, 2, 3$ of the monomeric phase built of Br_2I_2Py and Br_4Py molecules. Interaction energies e_{xi}, e_{yi} obtained by DFT are shown for each case, along with equations for rough estimation of differences between X-X and X-H components of e_{xi} and e_{yi}.

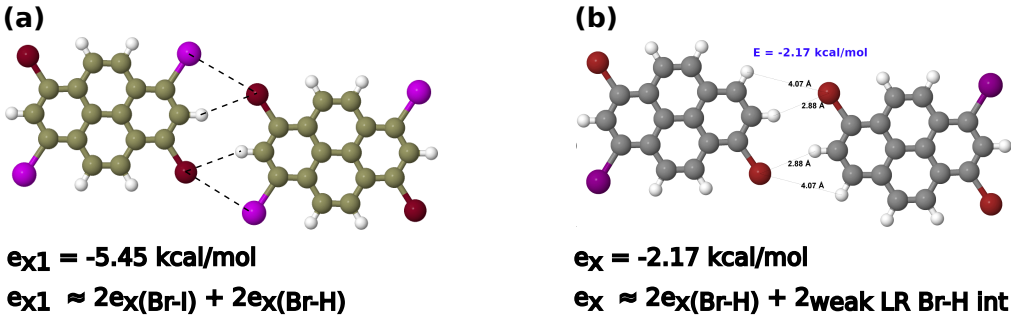


Fig. S2: DFT-optimized two-molecule clusters corresponding to (a) e_{x1} and (b) derivative of e_{x1} with both I atoms substituted by H atoms. The difference of -3.28 kcal/mol between energies of (a) and (b) configurations can be attributed mainly to the the Br - I bonding, amounting approximately to 60% of e_{x1}.

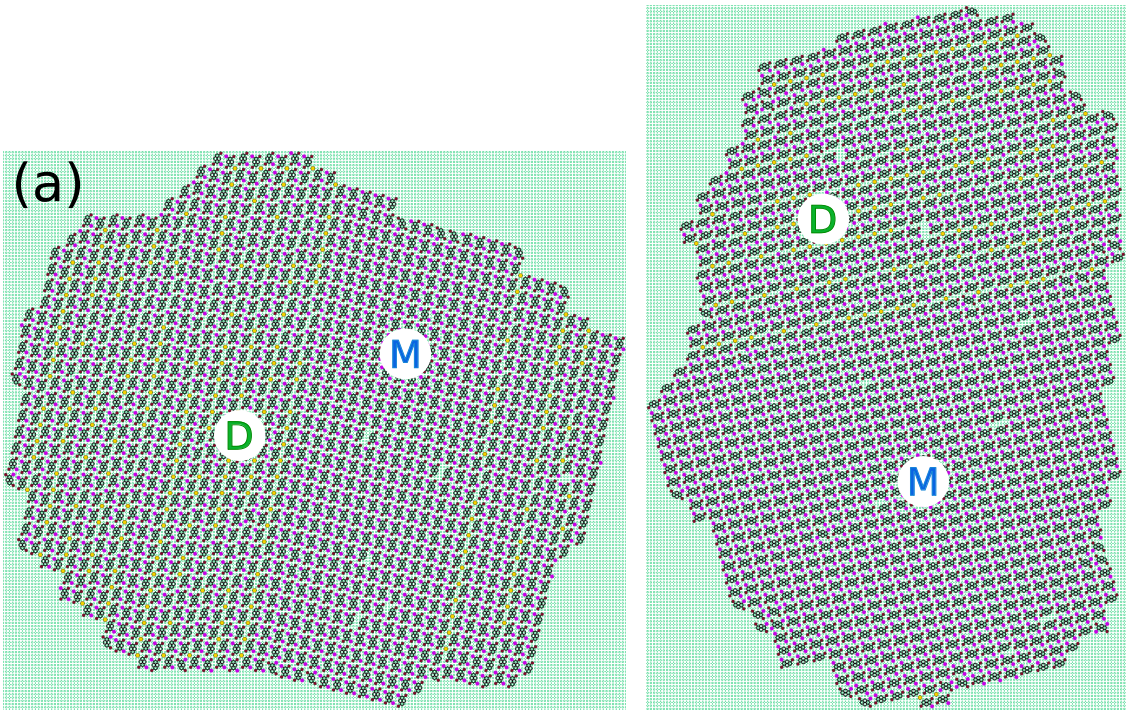


Fig. S3: Snapshots of MC simulation, illustrating phase separation and mixing in monomeric-dimeric system consisting of intact and singly deiodinated molecules when organometallic interaction is weak ($e_{Au}/e_y = 0.3$). Here (a) $c_2/c_1 = 1$ and (b) $c_2/c_1 = 2$. The letters M and D mark monomeric and dimeric regions, respectively.