

SUPPORTING INFORMATION

DFT study of Host-Dopant systems of DPVBi with Organophosphorus π-Conjugated materials

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Contents

Table S1. Selected bond lengths (Å), torsional angles (Φ, °) and dipole moments (Debye) of ground state (GS) and excited state (ES) geometries of **DPVBi**, Phospholes **A** and **B** at B3LYP/6-31+G(d,p) level in dichloromethane solvent in comparison with X-ray data.....(2)

Figure S1. Frontier molecular Orbitals (Energies in eV) of homodimers **DPVBi**, **A** and **B** calculated at B3LYP/6-31+g(d,p) level of theory in gas phase (isovalue=0.02).....(3)

Figure S2. Frontier molecular Orbitals (Energies in eV) of heterodimers **DPVBi-A(DA)** and **DPVBi-B(DB)** calculated at B3LYP/6-31+G(d,p)//B97D/6-31G(d) level of theory (isovalue=0.02).....(5)

Figure S3. Scheme to calculate reorganization energy(eV).....(9)

Table S2. Selected bond lengths (Å) and torsional angles (°) of **DPVBi**, Phospholes **A** and **B** at B3LYP/6-31+g(d,p) level in gas phase along with respective cation and anion optimized geometries.....(10)

Table S3. The calculated Interaction energies ($\Delta E_{\text{int}}^{\text{cp}}$, in kcal/mol), Effective charge transfer integrals ($(J_{\text{eff}})_{ij}$ in eV), for hole and electron transfer of heterodimers DPVBi-A (**DA**) and DPVBi-B(**DB**).....(12)

Figure S4. Frontier molecular Orbitals (Energies in eV) of **DPVBi**, Phospholes **A** and **B** calculated at B3LYP/6-31+G(d,p) level of theory in dichloromethane solvent (isovalue=0.02).....(16)

Figure S5. Natural Transition Orbitals (Energies in eV) of **DPVBi**, Phospholes **A** and **B** calculated at CAM-B3LYP and M06-2X functionals and 6-31+G(d,p) level of theory in dichloromethane solvent (isovalue=0.02).....(17)

Table S1. Selected bond lengths (\AA), torsional angles (Φ , ($^{\circ}$)) and dipole moments (Debye) of ground state (GS) and excited state (ES) geometries of **DPVBi**, Phospholes **A** and **B** at B3LYP/6-31+G(d,p) level in dichloromethane solvent in comparison with X-ray data.

DPVBi

Phosphole A, $R_3 =$

Phosphole B, $R_3 =$

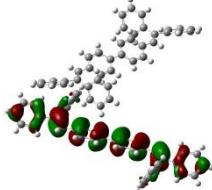
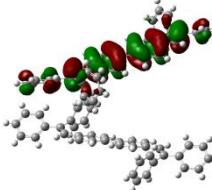
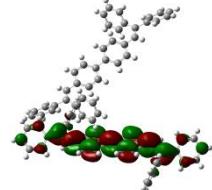
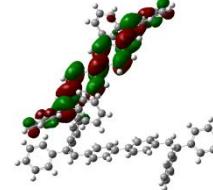
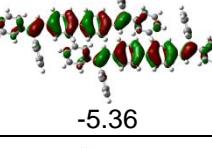
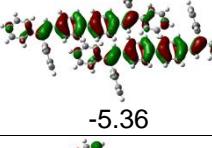
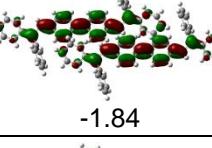
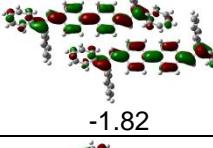
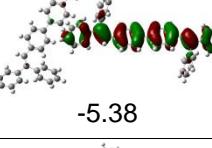
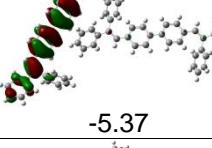
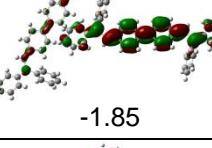
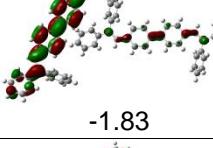
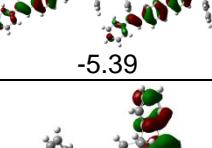
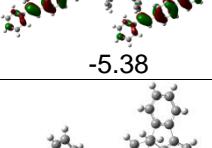
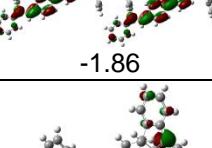
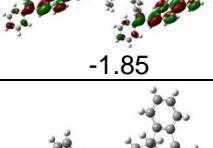
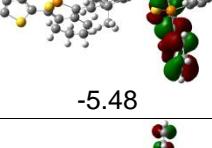
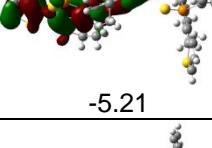
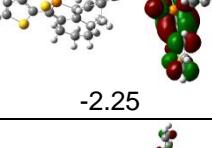
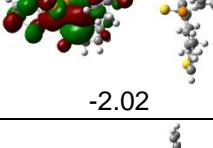
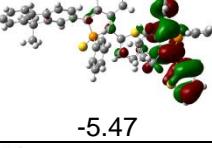
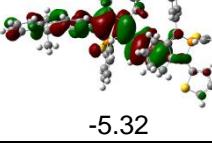
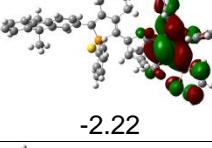
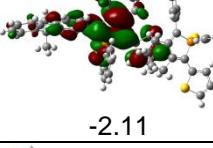
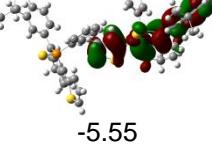
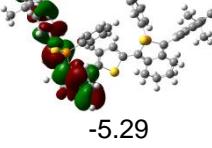
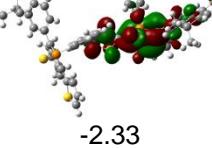
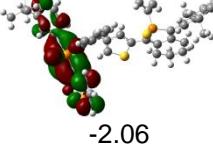
in A and B, $R_1 = \text{Phenyl}$, $R_2 = \text{Fluorenyl}$

Phospholes A and B

Bond	DPVBi			Bond	A			B		
	GS	ES	Exp ^a .		GS	ES	Exp ^b .	GS	ES	Exp ^b .
1	1.483	1.438	1.481	P-S	1.993	2.025	1.953	1.995	2.028	1.953
2, 2'	1.407, 1.409	1.436, 1.435	1.387, 1.393	P-C ₁	1.838	1.843	1.818	1.836	1.842	1.816
3, 3'	1.409, 1.408	1.435, 1.436	1.393, 1.387	P-C ₂	1.839	1.815	1.814	1.843	1.814	1.820
4, 4'	1.392, 1.392	1.374, 1.375	1.373, 1.368	P-C ₅	1.828	1.810	1.799	1.823	1.810	1.800
5, 5'	1.392, 1.392	1.375, 1.374	1.368, 1.373	C ₃ -C ₂	1.369	1.438	1.358	1.37	1.436	1.361
6, 6'	1.410, 1.410	1.433, 1.433	1.393, 1.383	C ₃ -C ₄	1.489	1.409	1.479	1.491	1.409	1.491
7, 7'	1.410, 1.410	1.433, 1.433	1.383, 1.393	C ₄ -C ₅	1.362	1.440	1.355	1.359	1.440	1.350
8, 8'	1.470, 1.471	1.426, 1.426	1.465, 1.465	C ₂ -C ₇	1.448	1.418	1.45	1.446	1.416	1.452
9, 9'	1.360, 1.360	1.400, 1.400	1.352, 1.352	C ₅ -C ₆	1.476	1.432	1.479	1.480	1.435	1.481
10, 10'	1.491, 1.491	1.470, 1.470	1.482, 1.482							
11, 11'	1.495, 1.495	1.478, 1.478	1.484, 1.484							
Φ_1	-33.6	-3.0	0.8	Φ_1	17.1	-5.4	17.7	-5.4	-11.2	1.2
Φ_2	8.6	19.5	3.3	Φ_2	53.6	20.4	52.4	64.1	27.9	62
Φ_3	-8.4	-19.6	-3.3							
Dipole moment	0.21	0.04			6.45	6.22		8.02	7.87	

^aSee ref no.66, ^bSee ref no. 11

Figure S1. Frontier molecular Orbitals (Energies in eV) of homodimers **DPVBi**, **A** and **B** calculated at B3LYP/6-31+g(d,p) level of theory in gas phase (isovalue=0.02).

	HOMO-1	HOMO	LUMO	LUMO+1
DD1	 -5.4	 -5.37	 -1.87	 -1.84
DD2	 -5.36	 -5.36	 -1.84	 -1.82
DD3	 -5.38	 -5.37	 -1.85	 -1.83
DD4	 -5.39	 -5.38	 -1.86	 -1.85
AA1	 -5.48	 -5.21	 -2.25	 -2.02
AA2	 -5.47	 -5.32	 -2.22	 -2.11
AA3	 -5.55	 -5.29	 -2.33	 -2.06

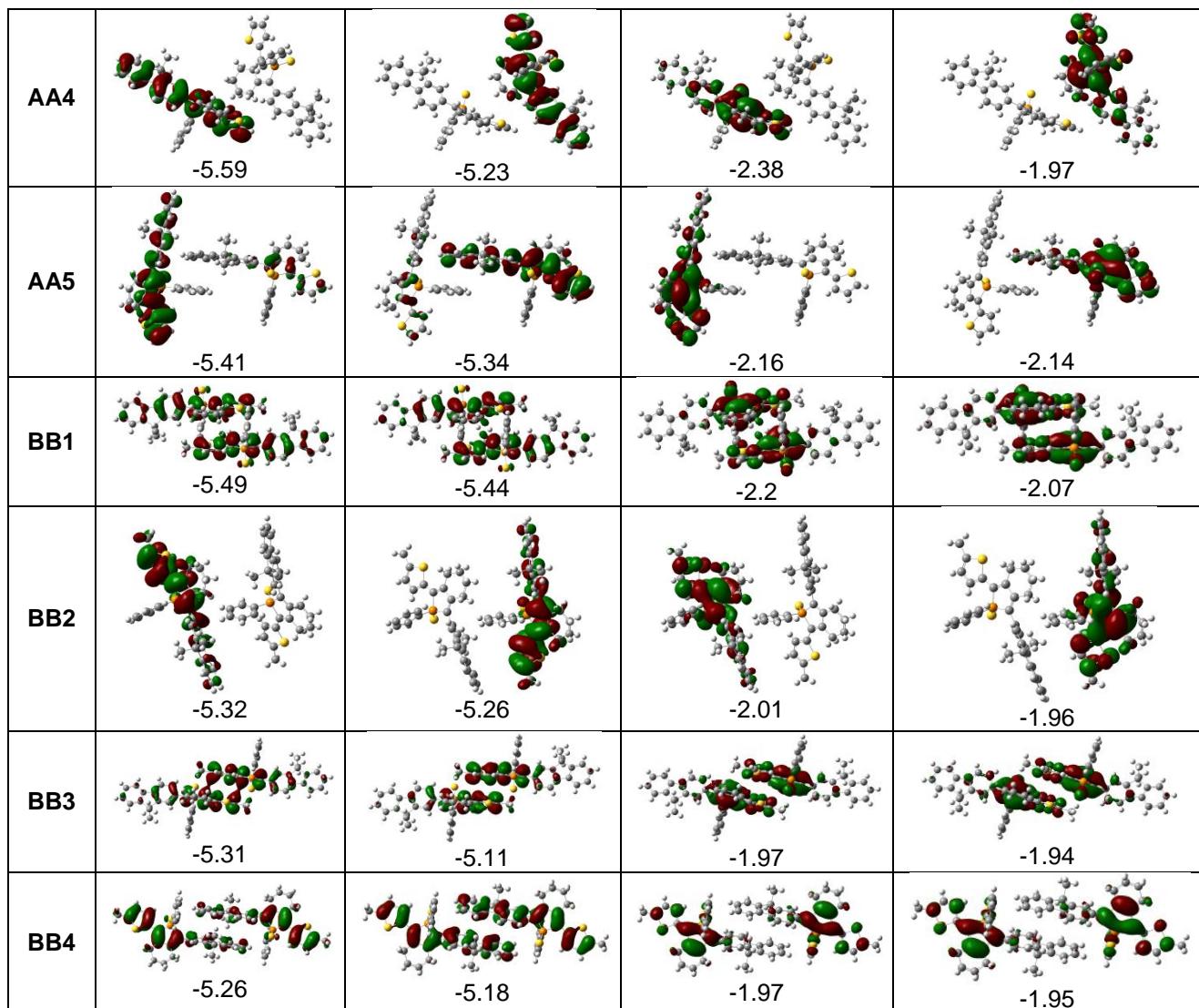
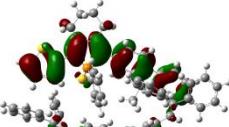
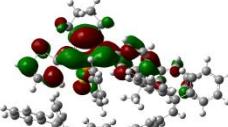
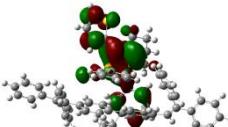
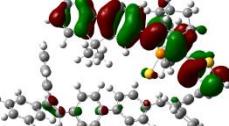
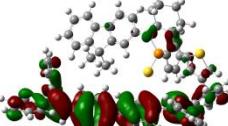
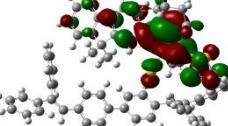
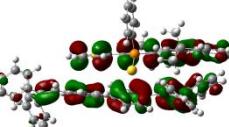
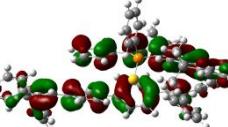
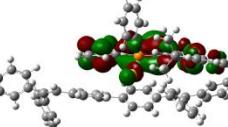
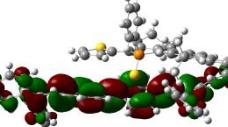
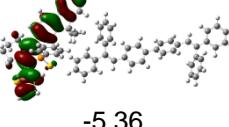
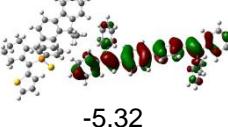
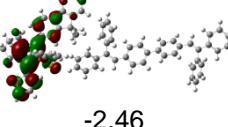
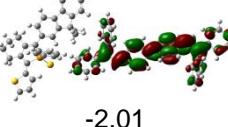
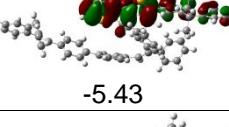
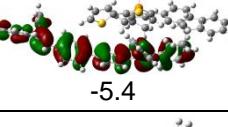
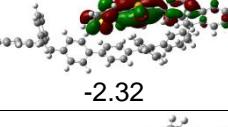
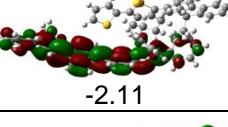
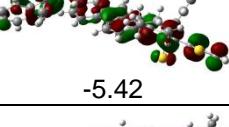
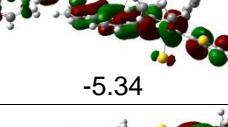
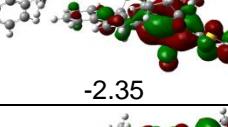
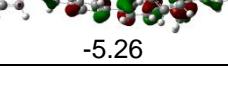
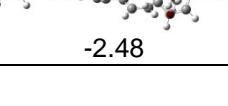
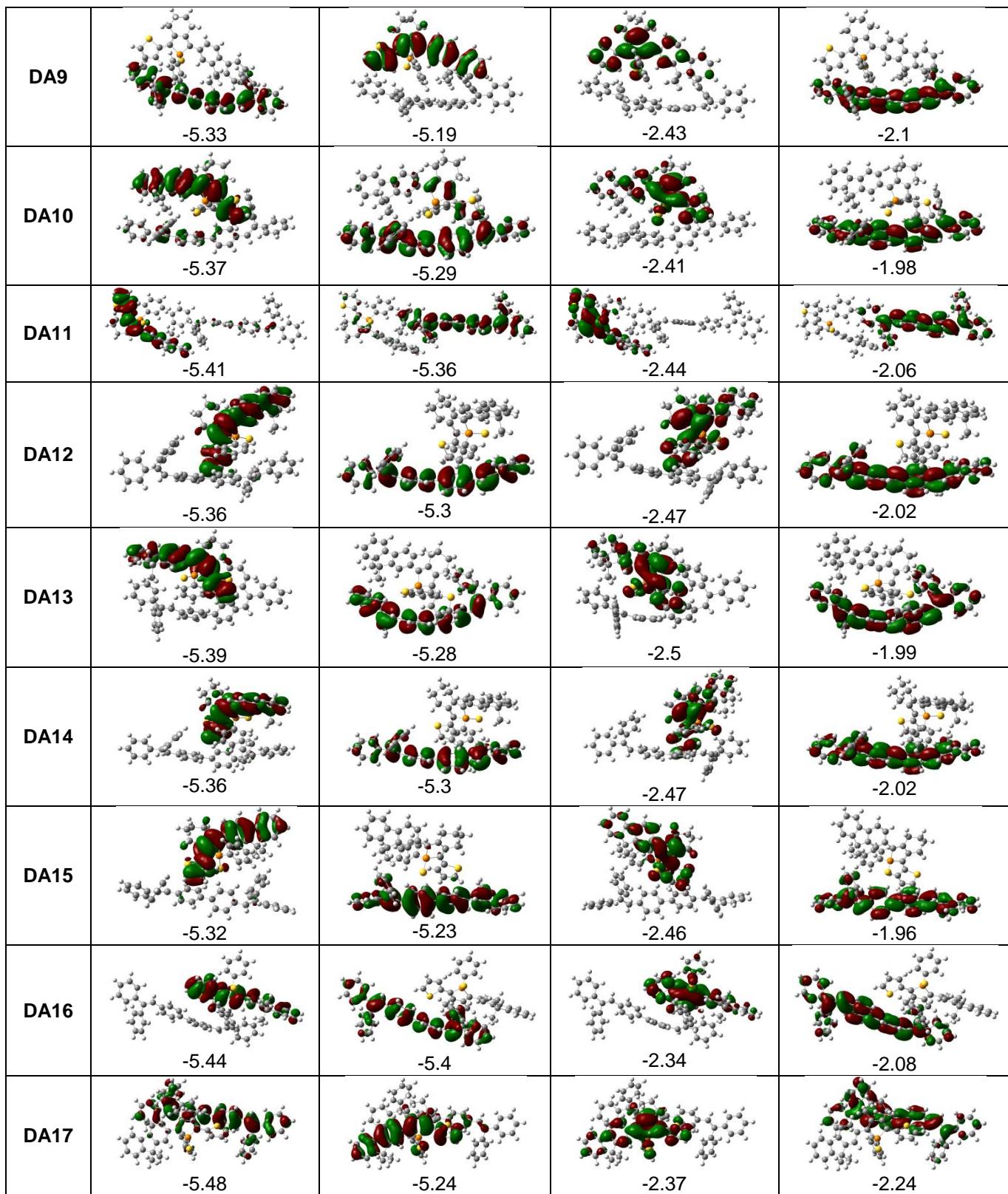
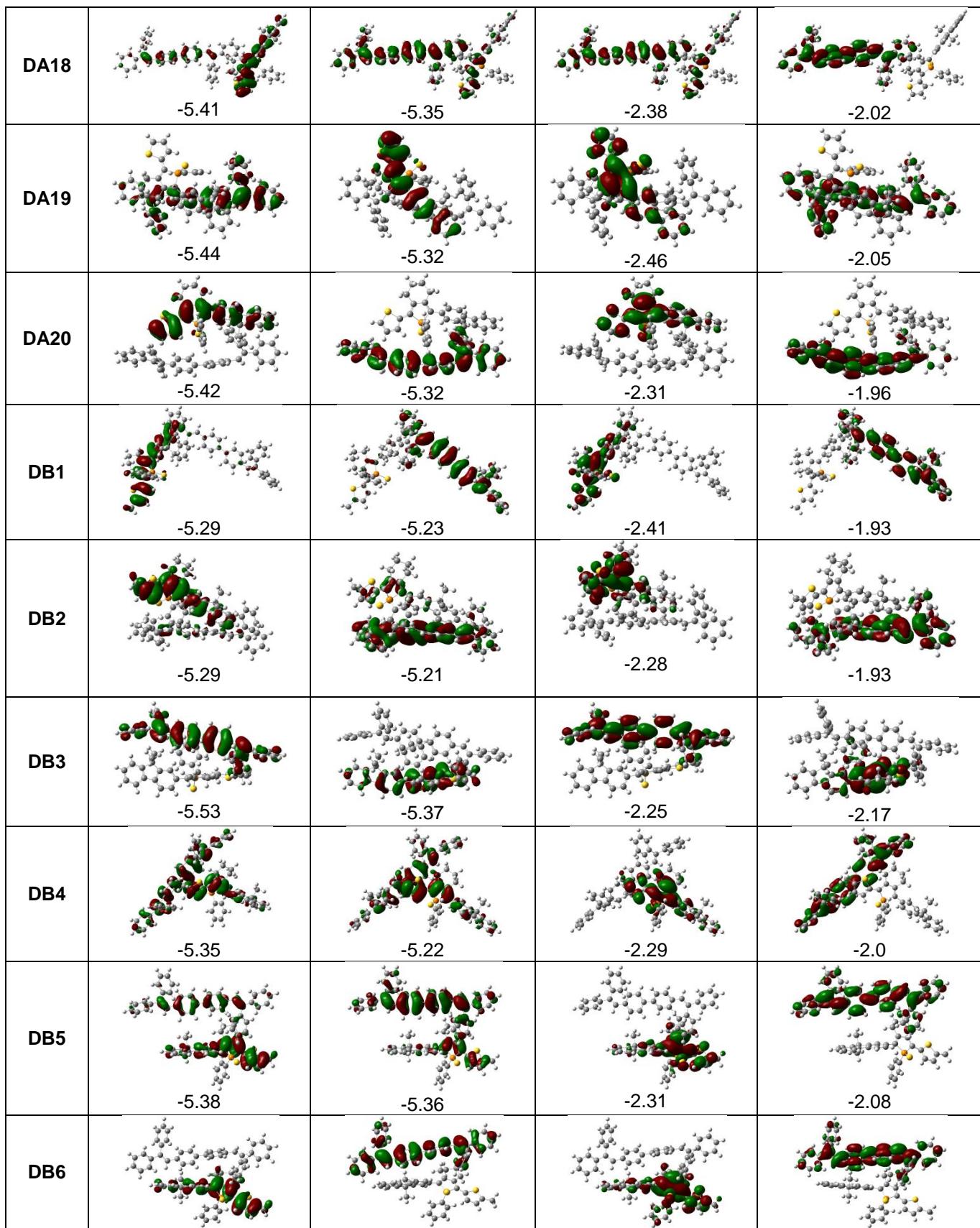


Figure S2. Frontier molecular Orbitals (Energies in eV) of heterodimers **DPVBi-A(DA)** and **DPVBi-B(DB)** calculated at B3LYP/6-31+G(d,p)//B97D/6-31G(d) level of theory (isovalue=0.02).

	HOMO-1	HOMO	LUMO	LUMO+1
DA1	 -5.35	 -5.33	 -2.37	 -2.02
DA2	 -5.41	 -5.25	 -2.43	 -1.96
DA3	 -5.35	 -5.31	 -2.39	 -1.96
DA4	 -5.25	 -5.16	 -2.45	 -1.97
DA5	 -5.36	 -5.32	 -2.46	 -2.01
DA6	 -5.43	 -5.4	 -2.32	 -2.11
DA7	 -5.42	 -5.34	 -2.35	 -2.11
DA8	 -5.43	 -5.26	 -2.48	 -2.04





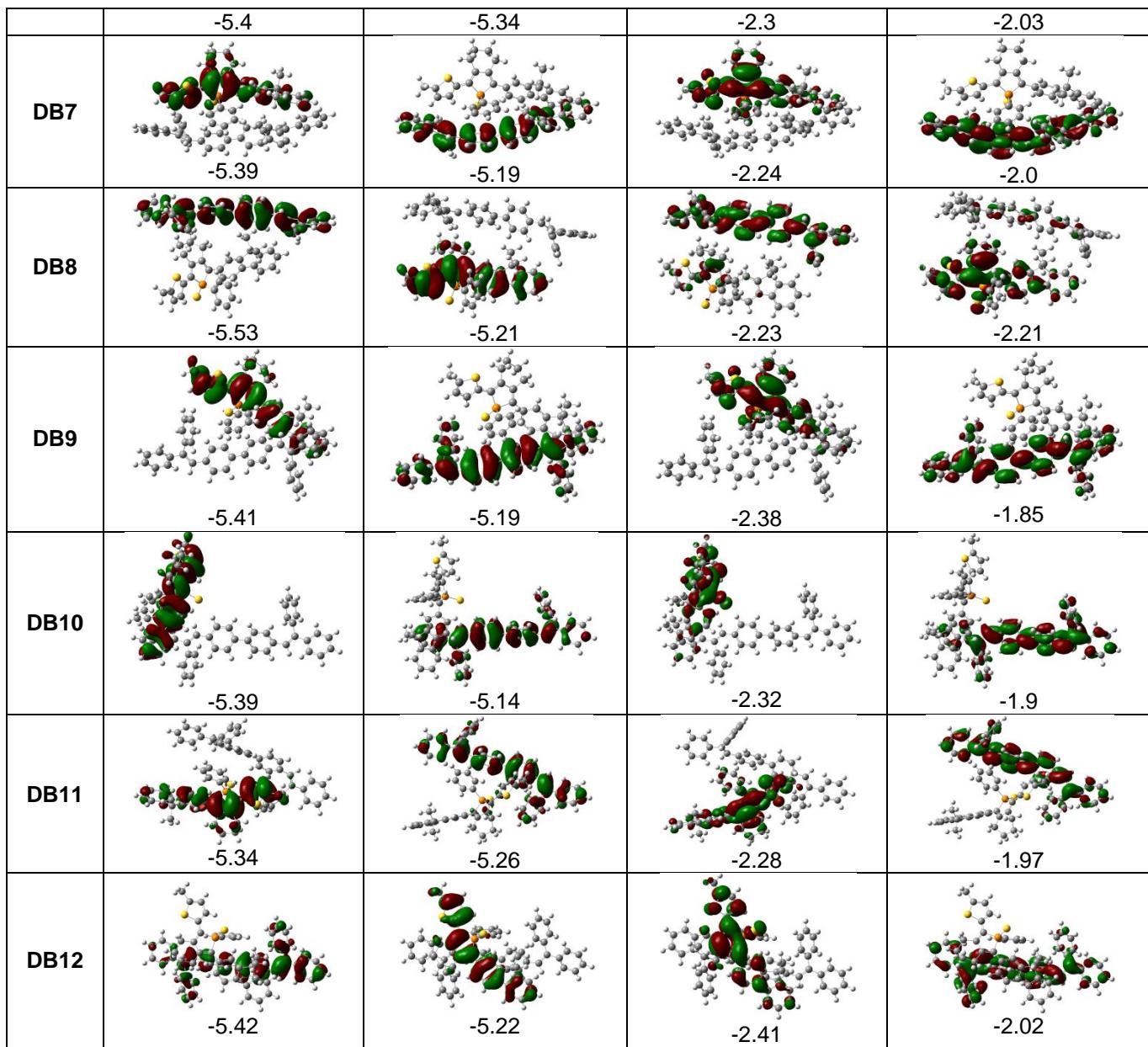
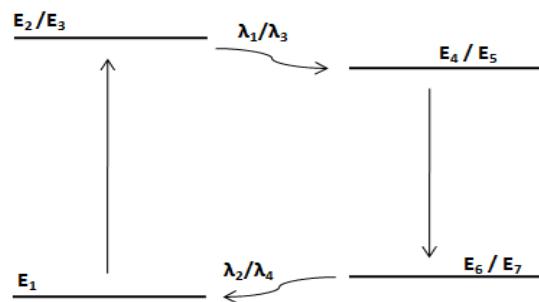


Figure S3. Scheme to calculate reorganization energy (eV).



E_1 - energy of the neutral optimized geometry
 E_2, E_3 - energy of the cation/anion state at neutral optimized geometry
 E_4, E_5 - energy of the cation/anion optimized geometry
 E_6, E_7 - energy of the neutral state at cation/anion optimized geometry.

$$\begin{array}{ll} \lambda_1 = E_2 - E_4 & \lambda_3 = E_3 - E_5 \\ \lambda_2 = E_6 - E_1 & \lambda_4 = E_7 - E_1 \end{array}$$

$$\text{hole reorganization energy}(\lambda_+) = \lambda_1 + \lambda_2$$

$$\text{electron reorganization energy}(\lambda_-) = \lambda_3 + \lambda_4$$

Table S2.a. Selected bond lengths (\AA) and torsional angles ($^\circ$) of DPVBi at B3LYP/6-31+g(d,p) level in gas phase along with respective cation and anion optimized geometries. (Values in parentheses are experimental measures from X-ray diffraction studies)

DPVBi

Bond	DPVBi			
	GS	Optimized cation	Optimized anion	Exp. ^a
1	1.482	1.457	1.456	1.481
2, 2'	1.407, 1.408	1.420, 1.422	1.424, 1.424	1.387, 1.393
3, 3'	1.408, 1.407	1.421, 1.420	1.424, 1.423	1.393, 1.387
4, 4'	1.392, 1.391	1.380, 1.379	1.382, 1.383	1.373, 1.368
5, 5'	1.391, 1.392	1.379, 1.379	1.382, 1.383	1.368, 1.373
6, 6'	1.410, 1.410	1.423, 1.423	1.425, 1.424	1.393, 1.383
7, 7'	1.410, 1.410	1.423, 1.423	1.425, 1.424	1.383, 1.393
8, 8'	1.470, 1.470	1.442, 1.442	1.442, 1.441	1.465, 1.465
9, 9'	1.359, 1.359	1.383, 1.383	1.386, 1.387	1.352, 1.352
10, 10'	1.490, 1.490	1.475, 1.475	1.476, 1.476	1.482, 1.482
11, 11'	1.494, 1.494	1.483, 1.484	1.487, 1.487	1.484, 1.484
Φ_1	143.9	-158.2	-161.7	180.0
Φ_2	-174.0	-168.6	-168.7	-179.4
Φ_3	173.8	168.5	168.6	179.4

^a See ref no. 66

Table S2.b. Selected bond lengths (\AA) and torsional angles ($^\circ$) of Phospholes **A** and **B** at B3LYP/6-31+g(d,p) level in gas phase along with respective cation and anion optimized geometries. (Values in parentheses are experimental measures from X-ray diffraction studies)

Phosphole A, $R_3 =$

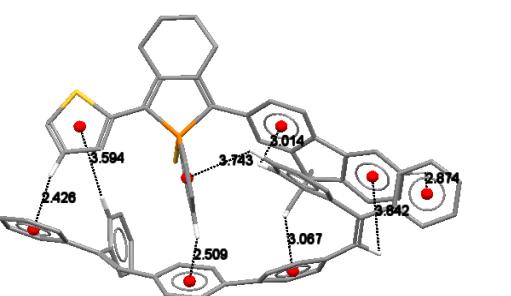
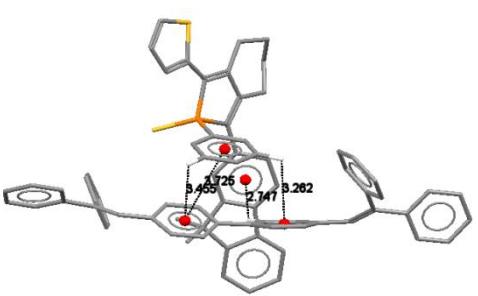
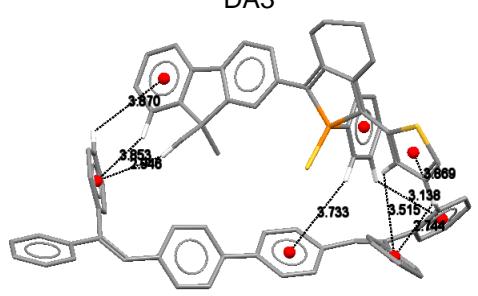
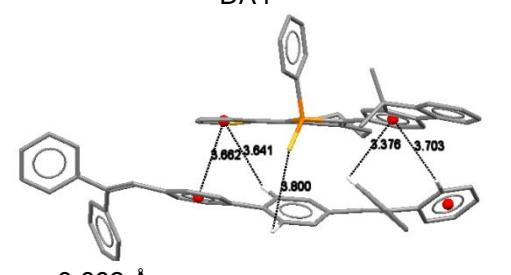
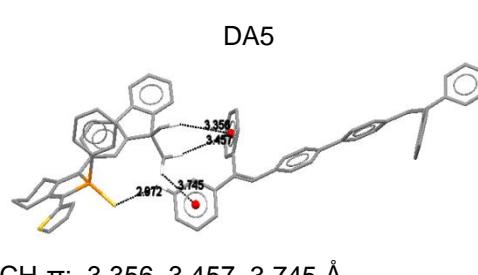
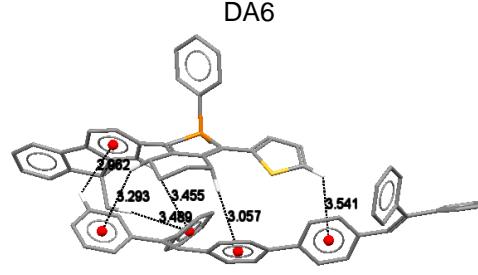
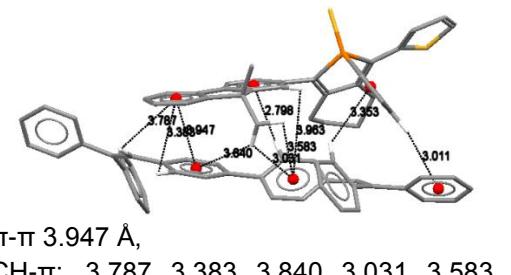
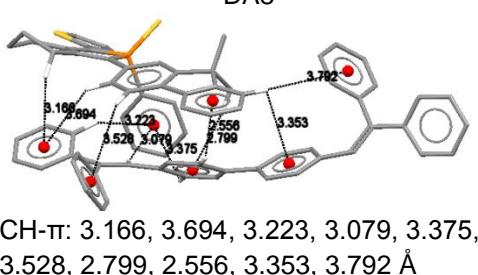
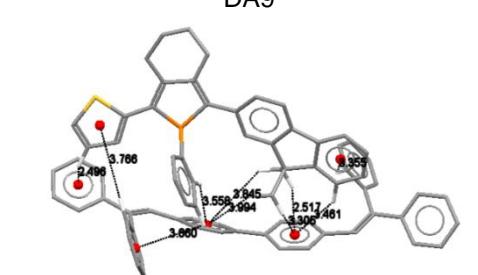
Phosphole B, $R_3 =$

in A and B, $R_1 = \text{Phenyl}$, $R_2 = \text{Fluorenyl}$

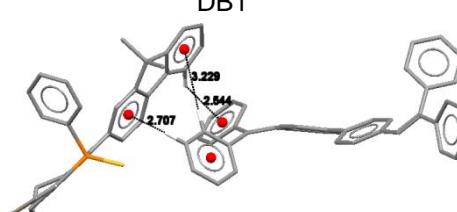
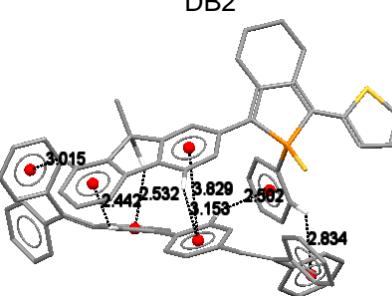
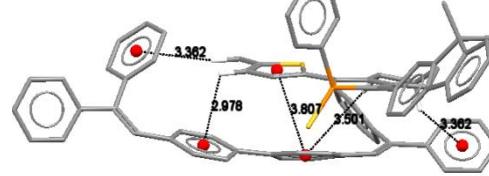
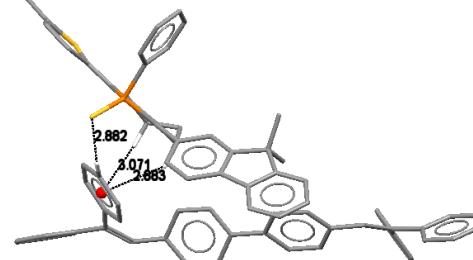
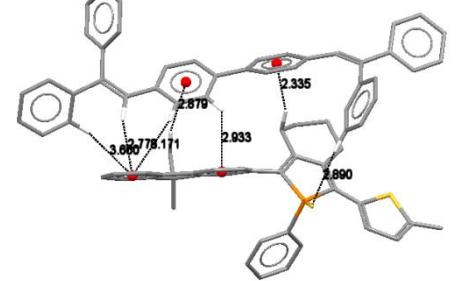
Phospholes A and B								
Bond	A				B			
	GS	Optimized cation	Optimized anion	Exp ^a .	GS	Optimized cation	Optimized anion	Exp ^a .
P=S	1.978	1.969	2.015	1.953	1.980	1.969	2.018	1.953
P-C ₁	1.842	1.829	1.858	1.818	1.840	1.828	1.856	1.816
P-C ₂	1.844	1.850	1.819	1.814	1.846	1.852	1.818	1.820
P-C ₅	1.830	1.848	1.811	1.799	1.829	1.85	1.811	1.800
C ₃ -C ₂	1.369	1.403	1.414	1.358	1.368	1.402	1.411	1.361
C ₃ -C ₄	1.488	1.443	1.429	1.479	1.490	1.446	1.431	1.491
C ₄ -C ₅	1.362	1.403	1.415	1.355	1.359	1.398	1.413	1.350
C ₂ -C ₇	1.446	1.417	1.432	1.450	1.447	1.413	1.433	1.452
C ₅ -C ₆	1.475	1.437	1.449	1.479	1.478	1.443	1.453	1.481
Φ_1	-166.0	-176.5	-180.0	-162.6	163.4	172.4	159.8	-177.1
Φ_2	-132.0	-155.9	-155.3	-130.9	-116.4	-145.3	-145.6	-121.4

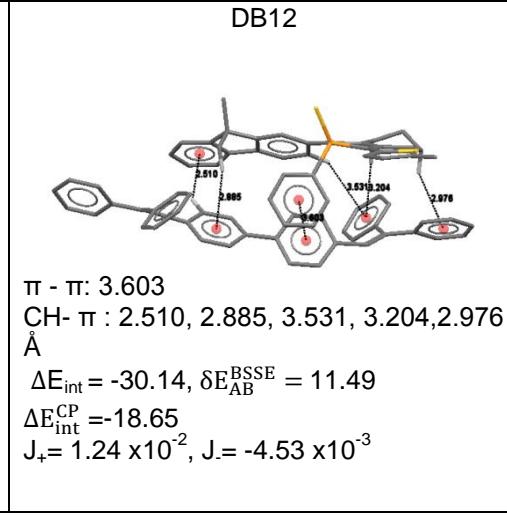
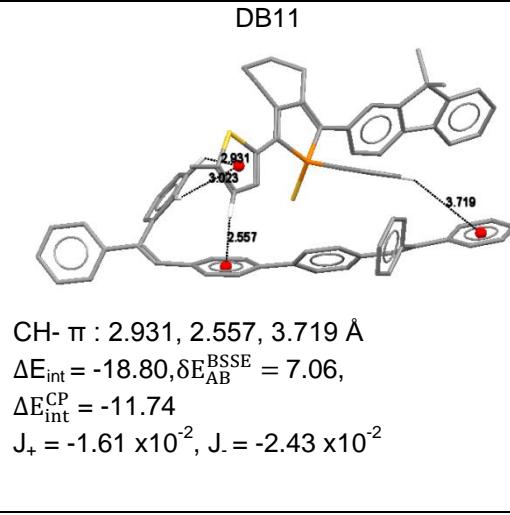
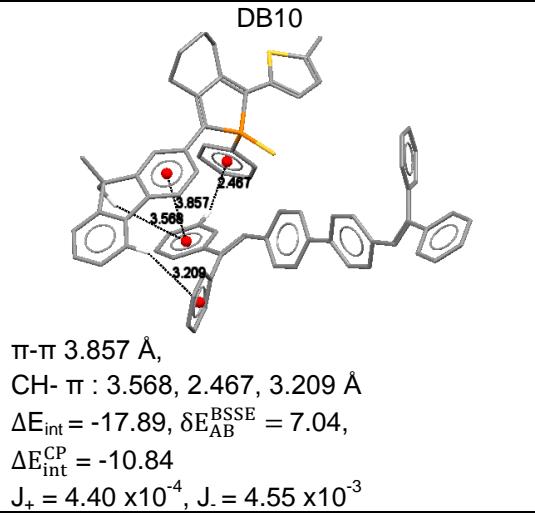
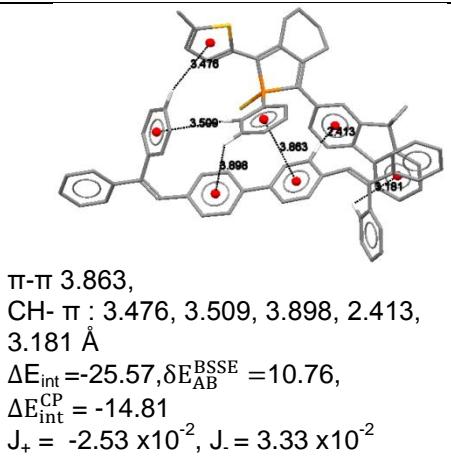
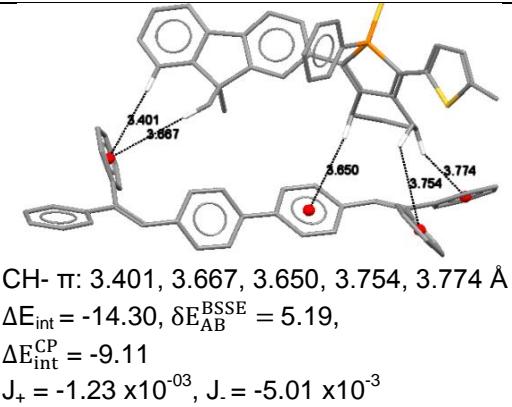
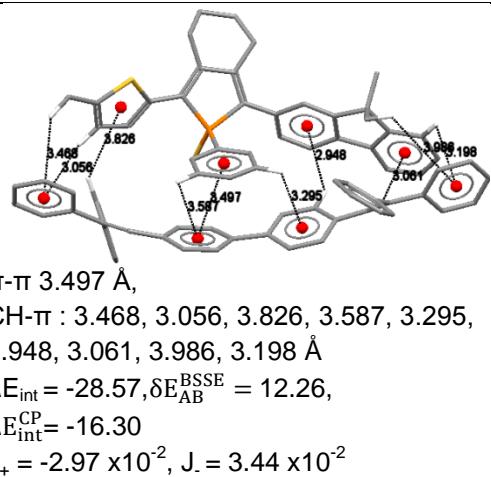
^a ref no. 11

Table S3. The calculated Interaction energies ($\Delta E_{\text{int}}^{\text{cp}}$, in kcal/mol), Effective charge transfer integrals ($(J_{\text{eff}})_{ij}$ in eV) for hole and electron transfer of heterodimers DPVBi-A(**DA**) and DPVBi-B(**DB**).^{a,b}

DA		
DA1  <p>CH-π: 3.594, 2.426, 2.509, 3.743, 3.067, 3.014, 3.842, 2.874 Å $\Delta E_{\text{int}} = -28.90$, $\delta E_{\text{AB}}^{\text{BSSE}} = 11.59$, $\Delta E_{\text{int}}^{\text{CP}} = -17.31$ $J_+ = 4.11 \times 10^{-3}$, $J_- = -4.89 \times 10^{-3}$</p>	DA2  <p>$\pi-\pi$: 3.725 Å CH-π: 3.455, 3.262, 2.747 Å $\Delta E_{\text{int}} = -21.58$, $\delta E_{\text{AB}}^{\text{BSSE}} = 9.73$, $\Delta E_{\text{int}}^{\text{CP}} = -11.85$ $J_+ = 7.14 \times 10^{-3}$, $J_- = 7.48 \times 10^{-3}$</p>	DA3  <p>CH-π: 3.870, 3.853, 2.946, 3.733, 3.138, 3.515, 3.869, 2.744 $\Delta E_{\text{int}} = -19.68$, $\delta E_{\text{AB}}^{\text{BSSE}} = 7.82$, $\Delta E_{\text{int}}^{\text{CP}} = -11.86$ $J_+ = -1.01 \times 10^{-2}$, $J_- = 1.96 \times 10^{-2}$</p>
DA4  <p>$\pi-\pi$: 3.662 Å CH-π: 3.641, 3.376, 3.703 Å CH-PS : 3.800 Å, $\Delta E_{\text{int}} = -24.39$, $\delta E_{\text{AB}}^{\text{BSSE}} = 9.64$, $\Delta E_{\text{int}}^{\text{CP}} = -14.75$ $J_+ = 4.16 \times 10^{-2}$, $J_- = -1.43 \times 10^{-3}$</p>	DA5  <p>CH-π: 3.356, 3.457, 3.745 Å CH-PS: 2.972 Å, $\Delta E_{\text{int}} = -8.84$, $\delta E_{\text{AB}}^{\text{BSSE}} = 3.34$, $\Delta E_{\text{int}}^{\text{CP}} = -5.49$ $J_+ = -1.20 \times 10^{-4}$, $J_- = 2.23 \times 10^{-3}$</p>	DA6  <p>CH-π: 2.962, 3.293, 3.489, 3.455, 3.057, 3.541 Å $\Delta E_{\text{int}} = -23.81$, $\delta E_{\text{AB}}^{\text{BSSE}} = 8.62$, $\Delta E_{\text{int}}^{\text{CP}} = -15.19$ $J_+ = 3.80 \times 10^{-4}$, $J_- = -7.28 \times 10^{-3}$</p>
DA7  <p>$\pi-\pi$ 3.947 Å, CH-π: 3.787, 3.383, 3.840, 3.031, 3.583, 3.963, 2.798, 3.353, 3.011 Å $\Delta E_{\text{int}} = -23.48$, $\delta E_{\text{AB}}^{\text{BSSE}} = 9.89$, $\Delta E_{\text{int}}^{\text{CP}} = -13.59$</p>	DA8  <p>CH-π: 3.166, 3.694, 3.223, 3.079, 3.375, 3.528, 2.799, 2.556, 3.353, 3.792 Å $\Delta E_{\text{int}} = -28.93$, $\delta E_{\text{AB}}^{\text{BSSE}} = 11.86$, $\Delta E_{\text{int}}^{\text{CP}} = -17.07$ $J_+ = -7.08 \times 10^{-2}$, $J_- = -2.24 \times 10^{-2}$</p>	DA9  <p>CH-π: 2.496, 3.766, 3.660, 3.680, 3.558, 3.845, 3.994, 2.517, 3.305, 3.355, 3.481 Å $\Delta E_{\text{int}} = -23.32$, $\delta E_{\text{AB}}^{\text{BSSE}} = 9.48$,</p>

$J_+ = -2.93 \times 10^{-2}$, $J_- = -5.17 \times 10^{-3}$		$\Delta E_{\text{int}}^{\text{CP}} = -13.85$ $J_+ = -1.17 \times 10^{-2}$, $J_- = 5.99 \times 10^{-3}$
<p>DA10</p> <p>$\Delta E_{\text{int}} = -27.62$, $\delta E_{AB}^{\text{BSSE}} = 11.14$, $\Delta E_{\text{int}}^{\text{CP}} = -16.48$ $J_+ = -2.89 \times 10^{-2}$, $J_- = 7.93 \times 10^{-3}$</p>	<p>DA11</p> <p>$\Delta E_{\text{int}} = -13.78$, $\delta E_{AB}^{\text{BSSE}} = 5.83$, $\Delta E_{\text{int}}^{\text{CP}} = -7.94$ $J_+ = -1.22 \times 10^{-2}$, $J_- = -5.19 \times 10^{-3}$</p>	<p>DA12</p> <p>$\Delta E_{\text{int}} = -17.79$, $\delta E_{AB}^{\text{BSSE}} = 7.52$, $\Delta E_{\text{int}}^{\text{CP}} = -10.27$ $J_+ = 1.04 \times 10^{-2}$, $J_- = 1.02 \times 10^{-2}$</p>
<p>DA13</p> <p>$\Delta E_{\text{int}} = -27.86$, $\delta E_{AB}^{\text{BSSE}} = 11.58$, $\Delta E_{\text{int}}^{\text{CP}} = -16.28$ $J_+ = 1.29 \times 10^{-3}$, $J_- = 2.72 \times 10^{-2}$</p>	<p>DA14</p> <p>$\Delta E_{\text{int}} = -17.79$, $\delta E_{AB}^{\text{BSSE}} = 7.52$, $\Delta E_{\text{int}}^{\text{CP}} = -10.27$ $J_+ = 1.04 \times 10^{-2}$, $J_- = 1.02 \times 10^{-2}$</p>	<p>DA15</p> <p>$\Delta E_{\text{int}} = -18.50$, $\delta E_{AB}^{\text{BSSE}} = 7.32$, $\Delta E_{\text{int}}^{\text{CP}} = -11.18$ $J_+ = -1.31 \times 10^{-2}$, $J_- = -1.05 \times 10^{-2}$</p>
<p>DA16</p> <p>$\Delta E_{\text{int}} = -23.67$, $\delta E_{AB}^{\text{BSSE}} = 8.84$, $\Delta E_{\text{int}}^{\text{CP}} = -14.83$ $J_+ = 5.80 \times 10^{-4}$, $J_- = -1.30 \times 10^{-2}$</p>	<p>DA17</p> <p>$\Delta E_{\text{int}} = -27.19$, $\delta E_{AB}^{\text{BSSE}} = 11.65$, $\Delta E_{\text{int}}^{\text{CP}} = -15.54$ $J_+ = 5.68 \times 10^{-2}$, $J_- = -1.71 \times 10^{-3}$</p>	<p>DA18</p> <p>$\Delta E_{\text{int}} = -14.00$, $\delta E_{AB}^{\text{BSSE}} = 5.02$, $\Delta E_{\text{int}}^{\text{CP}} = -8.97$ $J_+ = 2.09 \times 10^{-2}$, $J_- = -2.21 \times 10^{-2}$</p>
DA19	DA20	

 <p>$\pi\text{-}\pi$ 3.599 Å, $\text{CH-}\pi$: 3.981, 2.884, 2.517, 2.419, 3.336, 3.203, 2.979 Å $\Delta E_{\text{int}} = -30.09$, $\delta E_{\text{AB}}^{\text{BSSE}} = 11.49$, $\Delta E_{\text{int}}^{\text{CP}} = -18.60$ $J_+ = -1.26 \times 10^{-2}$, $J_- = -4.30 \times 10^{-3}$</p>	 <p>$\text{CH-}\pi$: 3.832, 3.580, 3.513, 3.132, 2.611, 3.593, 3.876, 3.057, 2.780 Å $\Delta E_{\text{int}} = -26.70$, $\delta E_{\text{AB}}^{\text{BSSE}} = 10.63$, $\Delta E_{\text{int}}^{\text{CP}} = -16.07$ $J_+ = 3.72 \times 10^{-3}$, $J_- = -5.55 \times 10^{-3}$</p>	
<p style="text-align: center;">DB</p>  <p>$\text{CH-}\pi$: 2.707, 2.544, 3.229 Å $\Delta E_{\text{int}} = -13.63$, $\delta E_{\text{AB}}^{\text{BSSE}} = 4.78$, $\Delta E_{\text{int}}^{\text{CP}} = -8.85$ $J_+ = -1.39 \times 10^{-2}$, $J_- = -8.35 \times 10^{-3}$</p>	 <p>$\pi\text{-}\pi$ 3.829 Å $\text{CH-}\pi$: 3.015, 2.442, 2.532, 3.829, 3.153, 2.502, 2.834 Å $\Delta E_{\text{int}} = -26.84$, $\delta E_{\text{AB}}^{\text{BSSE}} = 11.71$, $\Delta E_{\text{int}}^{\text{CP}} = -15.13$ $J_+ = -1.84 \times 10^{-2}$, $J_- = 2.94 \times 10^{-2}$</p>	 <p>$\text{CH-}\pi$: 3.342, 3.914, 3.906, 3.472, 3.172, 3.346, 3.342 Å. $\Delta E_{\text{int}} = -26.61$, $\delta E_{\text{AB}}^{\text{BSSE}} = 11.02$, $\Delta E_{\text{int}}^{\text{CP}} = -15.59$ $J_+ = -2.40 \times 10^{-2}$, $J_- = -7.03 \times 10^{-3}$</p>
 <p>$\pi\text{-}\pi$ 3.807 Å, $\text{CH-}\pi$: 3.362, 2.978, 3.501, 3.362 Å $\Delta E_{\text{int}} = -20.55$, $\delta E_{\text{AB}}^{\text{BSSE}} = 7.69$, $\Delta E_{\text{int}}^{\text{CP}} = -12.86$ $J_+ = 5.30 \times 10^{-2}$, $J_- = -1.60 \times 10^{-2}$</p>	 <p>CH-PS 2.882 Å, $\text{CH-}\pi$: 3.071, 2.683 Å $\Delta E_{\text{int}} = -15.08$, $\delta E_{\text{AB}}^{\text{BSSE}} = 5.24$, $\Delta E_{\text{int}}^{\text{CP}} = -9.84$ $J_+ = 8.52 \times 10^{-3}$, $J_- = 1.29 \times 10^{-2}$</p>	 <p>$\text{CH-}\pi$ 2.797 Å, $\text{CH-}\pi$: 3.660, 2.778, 3.171, 2.879, 2.933, 2.335, 2.890 Å $\Delta E_{\text{int}} = -24.71$, $\delta E_{\text{AB}}^{\text{BSSE}} = 8.77$, $\Delta E_{\text{int}}^{\text{CP}} = -15.94$ $J_+ = -4.85 \times 10^{-3}$, $J_- = 2.60 \times 10^{-2}$</p>



^a ΔE_{int}^{CP} in kcal/mol obtained at B2PLYPD/6-31G(d,p)//B97D/6-31g(d) level.

^b Rest of quantities obtained at B3LYP/TZ2P level of theory

Figure S4. Frontier molecular Orbitals (Energies in eV) of DPVBi, Phospholes **A** and **B** calculated at B3LYP/6-31+G(d,p) level of theory in dichloromethane solvent (isovalue=0.02).

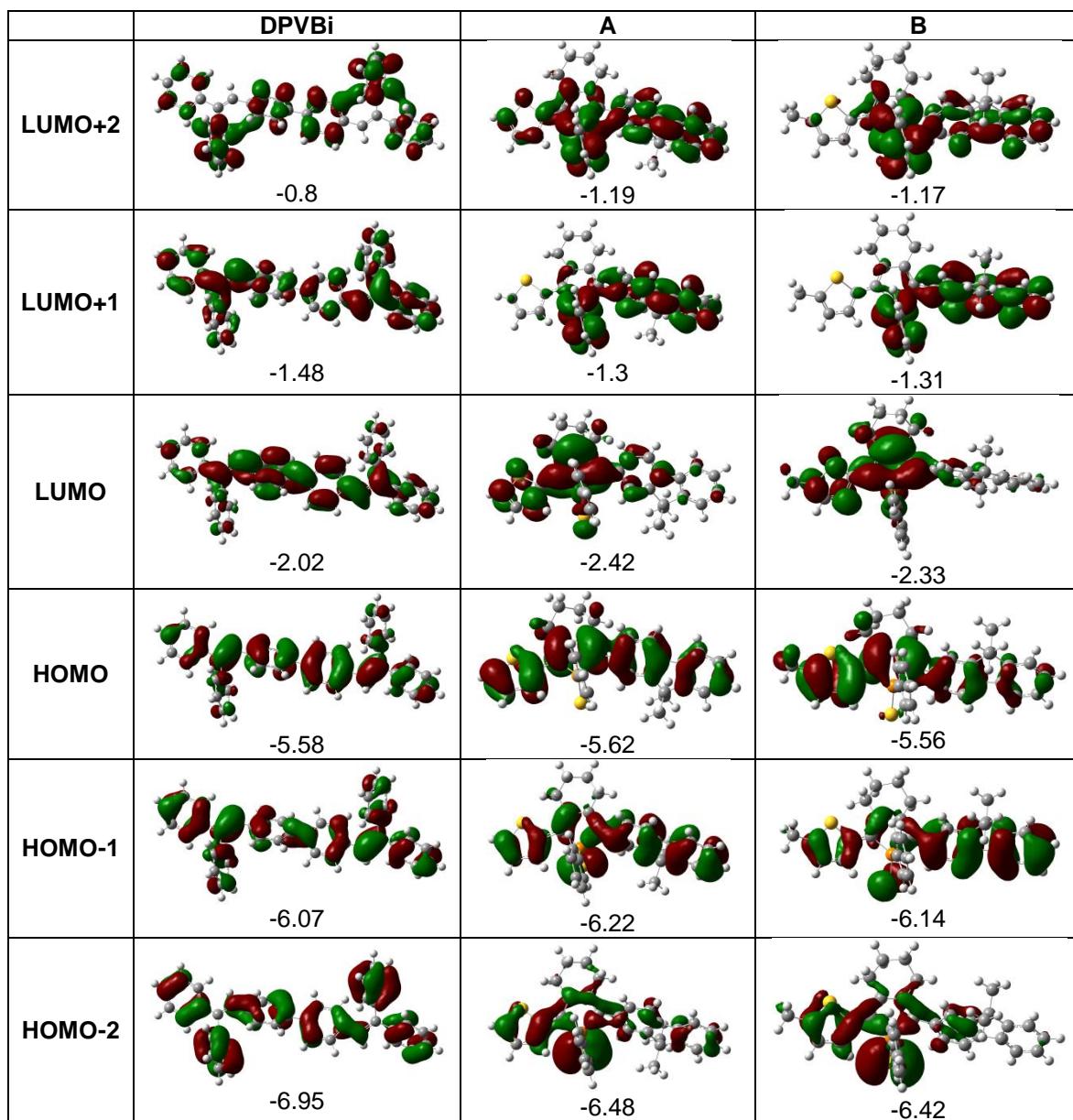


Figure S5.a. Natural Transition Orbitals (Energies in eV) of **DPVBi**, Phospholes **A** and **B** calculated at CAM-B3LYP/6-31+G(d,p) level of theory and dichloromethane solvent (isovalue=0.02) .

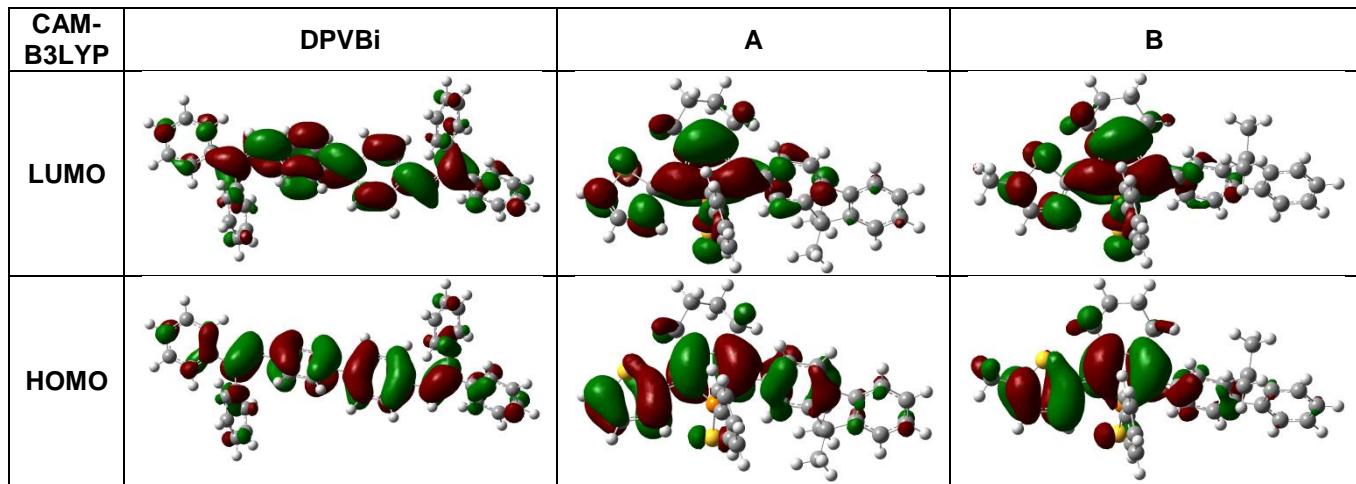


Figure S5.b. Natural Transition Orbitals (Energies in eV) of **DPVBi**, Phospholes **A** and **B** calculated at M06-2X/6-31+G(d,p) level of theory and dichloromethane solvent (isovalue=0.02).

