**SUPPORTING INFORMATION**

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

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**Table S1**. Selected bond lengths (A°), torsional angles (Ф, (°)) 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 Phospholes A and B | | | | | | | | | | |
| Bond | **DPVBi** | | | **Bond** | **A** | | | **B** | | |
|  | **GS** | **ES** | **Expa.** |  | **GS** | **ES** | **Expb.** | **GS** | **ES** | **Expb.** |
| 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-C1** | 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-C2** | 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-C5** | 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 | **C3-C2** | 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 | **C3-C4** | 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 | **C4-C5** | 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 | **C2-C7** | 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 | **C5-C6** | 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 |  |  |  |  |  |  |  |
| Ф1 | -33.6 | -3.0 | 0.8 | **Ф1** | 17.1 | -5.4 | 17.7 | -5.4 | -11.2 | 1.2 |
| Ф2 | 8.6 | 19.5 | 3.3 | **Ф2** | 53.6 | 20.4 | 52.4 | 64.1 | 27.9 | 62 |
| Ф3 | -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 | | | | | | | | | | |

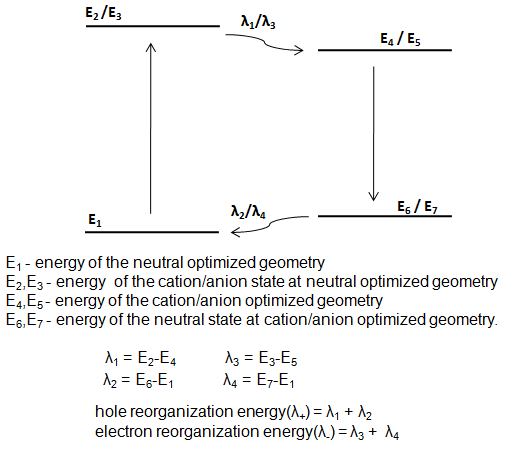
**Figure S1.** Frontier molecular Orbitals (Energies in eV) of homodimers **DPVBi**, **A** and **B** calculated at B3LYP/6-31+g(d,p) level of theory in gas phase (isovalue=0.02).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **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 |
| **AA4** | -5.59 | -5.23 | -2.38 | -1.97 |
| **AA5** | -5.41 | -5.34 | -2.16 | -2.14 |
| **BB1** | -5.49 | -5.44 | -2.2 | -2.07 |
| **BB2** | -5.32 | -5.26 | -2.01 | -1.96 |
| **BB3** | -5.31 | -5.11 | -1.97 | -1.94 |
| **BB4** | -5.26 | -5.18 | -1.97 | -1.95 |

**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 |
| **DA9** | -5.33 | -5.19 | -2.43 | -2.1 |
| **DA10** | -5.37 | -5.29 | -2.41 | -1.98 |
| **DA11** | -5.41 | -5.36 | -2.44 | -2.06 |
| **DA12** | -5.36 | -5.3 | -2.47 | -2.02 |
| **DA13** | -5.39 | -5.28 | -2.5 | -1.99 |
| **DA14** | -5.36 | -5.3 | -2.47 | -2.02 |
| **DA15** | -5.32 | -5.23 | -2.46 | -1.96 |
| **DA16** | -5.44 | -5.4 | -2.34 | -2.08 |
| **DA17** | -5.48 | -5.24 | -2.37 | -2.24 |
| **DA18** | -5.41 | -5.35 | -2.38 | -2.02 |
| **DA19** | -5.44 | -5.32 | -2.46 | -2.05 |
| **DA20** | -5.42 | -5.32 | -2.31 | -1.96 |
| **DB1** | -5.29 | -5.23 | -2.41 | -1.93 |
| **DB2** | -5.29 | -5.21 | -2.28 | -1.93 |
| **DB3** | -5.53 | -5.37 | -2.25 | -2.17 |
| **DB4** | -5.35 | -5.22 | -2.29 | -2.0 |
| **DB5** | -5.38 | -5.36 | -2.31 | -2.08 |
| **DB6** | -5.4 | -5.34 | -2.3 | -2.03 |
| **DB7** | -5.39 | -5.19 | -2.24 | -2.0 |
| **DB8** | -5.53 | -5.21 | -2.23 | -2.21 |
| **DB9** | -5.41 | -5.19 | -2.38 | -1.85 |
| **DB10** | -5.39 | -5.14 | -2.32 | -1.9 |
| **DB11** | -5.34 | -5.26 | -2.28 | -1.97 |
| **DB12** | -5.42 | -5.22 | -2.41 | -2.02 |

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



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **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 |
| Ф1 | 143.9 | -158.2 | -161.7 | 180.0 |
| Ф2 | -174.0 | -168.6 | -168.7 | -179.4 |
| Ф3 | 173.8 | 168.5 | 168.6 | 179.4 |
| a See ref no. 66 | | | | |

**Table S2**.**a**. Selected bond lengths (A°) and torsional angles (°) 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)

**Table S2**.**b**. Selected bond lengths (Å) and torsional angles (°) 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)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Phospholes **A** and **B** | | | | | | | | |
| **Bond** | **A** | | | | **B** | | | |
|  | **GS** | **Optimized cation** | **Optimized anion** | **Expa.** | **GS** | **Optimized cation** | **Optimized anion** | **Expa.** |
| **P=S** | 1.978 | 1.969 | 2.015 | 1.953 | 1.980 | 1.969 | 2.018 | 1.953 |
| **P-C1** | 1.842 | 1.829 | 1.858 | 1.818 | 1.840 | 1.828 | 1.856 | 1.816 |
| **P-C2** | 1.844 | 1.850 | 1.819 | 1.814 | 1.846 | 1.852 | 1.818 | 1.820 |
| **P-C5** | 1.830 | 1.848 | 1.811 | 1.799 | 1.829 | 1.85 | 1.811 | 1.800 |
| **C3-C2** | 1.369 | 1.403 | 1.414 | 1.358 | 1.368 | 1.402 | 1.411 | 1.361 |
| **C3-C4** | 1.488 | 1.443 | 1.429 | 1.479 | 1.490 | 1.446 | 1.431 | 1.491 |
| **C4-C5** | 1.362 | 1.403 | 1.415 | 1.355 | 1.359 | 1.398 | 1.413 | 1.350 |
| **C2-C7** | 1.446 | 1.417 | 1.432 | 1.450 | 1.447 | 1.413 | 1.433 | 1.452 |
| **C5-C6** | 1.475 | 1.437 | 1.449 | 1.479 | 1.478 | 1.443 | 1.453 | 1.481 |
| **Ф1** | -166.0 | -176.5 | -180.0 | -162.6 | 163.4 | 172.4 | 159.8 | -177.1 |
| **Ф2** | -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 (, in kcal/mol), Effective charge transfer integrals ((Jeff)ij in eV) for hole and electron transfer of heterodimers DPVBi-A(**DA**)andDPVBi-B(**DB**).a,b

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **DA** | | | | | |
| DA1    CH- π: 3.594, 2.426, 2.509, 3.743, 3.067, 3.014, 3.842, 2.874 Å  Eint = -28.90,11.59,  = -17.31  J+ = 4.11 x10-3, J- = -4.89 x10-3 | DA2    π-π: 3.725 Å  CH- π: 3.455, 3.262, 2.747 Å  Eint = -21.58, 9.73,  = -11.85  J+ = 7.14 x10-3, J- = 7.48 x10-3 | | DA3    CH- π: 3.870, 3.853, 2.946, 3.733, 3.138, 3.515, 3.869, 2.744  Eint = -19.68, 7.82,  =-11.86  J+ = -1.01 x10-2, J- = 1.96 x10-2 | | |
| DA4    π -π: 3.662 Å  CH- π: 3.641, 3.376, 3.703 Å  CH-PS : 3.800 Å,  Eint = -24.39, 9.64,  = -14.75  J+ = 4.16 x10-2, J- = -1.43 x10-3 | DA5    CH-π: 3.356, 3.457, 3.745 Å  CH-PS: 2.972 Å,  Eint = -8.84, 3.34,  = -5.49  J+ = -1.20 x 10-4 , J- = 2.23 x10-3 | | DA6    CH-π: 2.962, 3.293, 3.489, 3.455, 3.057, 3.541 Å  Eint =-23.81, 8.62,  = -15.19  J+ = 3.80 x10-4, J- = -7.28 x10-3 | | |
| DA7    π-π 3.947 Å,  CH-π: 3.787, 3.383, 3.840, 3.031, 3.583, 3.963, 2.798, 3.353, 3.011 Å  Eint = -23.48, 9.89,  = -13.59  J+ = -2.93 x10-2, J- = -5.17 x10-3 | DA8    CH-π: 3.166, 3.694, 3.223, 3.079, 3.375, 3.528, 2.799, 2.556, 3.353, 3.792 Å  Eint = -28.93,11.86,  = -17.07  J+ = -7.08 x10-2, J- = -2.24 x10-2 | | DA9    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  Eint = -23.32,9.48,  = -13.85  J+ = -1.17 x10-2, J- = 5.99 x10-3 | | |
| DA10    CH-π: 3.935, 3.782, 3.421, 3.579, 3.915, 3.649, 2.381, 2.844, 2.611, 3.127 Å  Eint =-27.62,11.14,  -16.48  J+ = -2.89 x10-2, J- = 7.93 x10-3 | DA11    CH –π: 3.585, 3.383, 3.675, 3.006, 2.541, 2.919  Eint = -13.78,5.83,  -7.94  J+ = -1.22 x10-2, J- = -5.19 x10-3 | | DA12    CH –π: 2.766, 3.806, 3.289, 3.207  π –π 3.617 Å,  Eint = -17.79, 7.52,  -10.27  J+ = 1.04 x10-2, J- = 1.02 x10-2 | | |
| DA13    CH –π: 2.544, 3.741, 3.229, 3.288  π –π 3.585 Å,  Eint = -27.86,11.58,  =-16.28  J+ =1.29 x10-3, J- = 2.72 x10-2 | DA14    CH –π: 2.766, 3.735, 3.289, 3.207 Å  π –π 3.616 Å,  Eint = -17.79,7.52,  = -10.27  J+ = 1.04 x10-2, J- = 1.02 x10-2 | | DA15    CH –π: 3.654, 3.664, 3.833, 3.427  π –π 3.778 Å,  Eint = -18.50,7.32,  =-11.18  J+ = -1.31 x10-2, J- = -1.05 x10-2 | | |
| DA16    CH –π: 3.673, 3.466, 3.147, 3.285, 3.639, 3.176, 3.786, 3.443, 3.978 Å  CH-P-ring: 2.977 Å  Eint = -23.67, 8.84,  =-14.83  J+ = 5.80 x10-4, J- = -1.30 x10-2 | DA17    CH –π: 3.336, 3.163, 3.378, 3.488, 2.721, 3.279, 3.661 Å  CH-P-ring: 3.155 Å  π –π 3.689 Å  Eint = -27.19,11.65,  =-15.54  J+ = 5.68 x10-2, J- = -1.71 x10-3 | | DA18  CH –π: 2.802, 2.542, 3.392, 3.718 Å.  Eint = -14.00,5.02, =-8.97  J+ = 2.09 x10-2, J- = -2.21 x10-2 | | |
| DA19    π-π 3.599 Å,  CH- π: 3.981, 2.884, 2.517, 2.419, 3.336, 3.203, 2.979 Å  Eint =-30.09,11.49,  =-18.60  J+ = -1.26 x10-2, J- = -4.30 x10-3 | DA20    CH- π : 3.832, 3.580, 3.513, 3.132, 2.611, 3.593, 3.876, 3.057, 2.780 Å  Eint = -26.70,10.63,  = -16.07  J+ = 3.72 x10-3, J- = -5.55 x10-3 | |  | | |
| **DB** | | | | |
| DB1    CH-π: 2.707, 2.544, 3.229 Å  Eint ­­= -13.63,4.78,  = -8.85  J+ = -1.39 x10-2, J- = -8.35 x10-3 | | DB2    π-π 3.829 Å  CH-π: 3.015, 2.442, 2.532, 3.829, 3.153, 2.502, 2.834 Å  Eint ­­= -26.84, 11.71,  = -15.13  J+ = -1.84 x10-2, J- = 2.94 x10-2 | | DB3    CH-π: 3.342, 3.914, 3.906, 3.472, 3.172, 3.346, 3.342 Å.  Eint ­­= -26.61,11.02,  = -15.59  J+ = -2.40 x10-2, J- = -7.03 x10-3 |
| DB4    π-π 3.807 Å,  CH-π: 3.362, 2.978, 3.501, 3.362 Å  Eint ­­= -20.55,7.69,  = -12.86  J+ = 5.30 x10-2, J- = -1.60 x10-2 | | DB5    CH-PS 2.882 Å,  CH-π : 3.071, 2.683 Å  Eint ­­= - 15.08,5.24,  = -9.84  J+ = 8.52 x10-3, J- = 1.29 x10-2 | | DB6    CH-π 2.797 Å,  CH-π : 3.660, 2.778, 3.171, 2.879, 2.933, 2.335, 2.890 Å  Eint ­­= - 24.71,8.77,  = -15.94  J+ = -4.85 x10-3, J- = 2.60 x10-2 |
| DB7    π-π 3.497 Å,  CH-π : 3.468, 3.056, 3.826, 3.587, 3.295, 2.948, 3.061, 3.986, 3.198 Å  Eint = -28.57,12.26,  = -16.30  J+ = -2.97 x10-2, J- = 3.44 x10-2 | | DB8    CH- π: 3.401, 3.667, 3.650, 3.754, 3.774 Å  Eint = -14.30,5.19,  = -9.11  J+ = -1.23 x10-03, J- = -5.01 x10-3 | | DB9    π-π 3.863,  CH- π : 3.476, 3.509, 3.898, 2.413, 3.181 Å  Eint =-25.57,10.76,  = -14.81  J+ = -2.53 x10-2, J- = 3.33 x10-2 |
| DB10    π-π 3.857 Å,  CH- π : 3.568, 2.467, 3.209 Å  Eint = -17.89,7.04,  = -10.84  J+ = 4.40 x10-4, J- = 4.55 x10-3 | | DB11    CH- π : 2.931, 2.557, 3.719 Å  Eint = -18.80,7.06,  = -11.74  J+ = -1.61 x10-2, J- = -2.43 x10-2 | | DB12    π - π: 3.603  CH- π : 2.510, 2.885, 3.531, 3.204,2.976 Å  Eint = -30.14,11.49  =-18.65  J+= 1.24 x10-2, J-= -4.53 x10-3 |
| a  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).

|  |  |  |  |
| --- | --- | --- | --- |
|  | **DPVBi** | **A** | **B** |
| **LUMO+2** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -0.8 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -1.19 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -1.17 |
| **LUMO+1** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -1.48 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -1.3 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -1.31 |
| **LUMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -2.02 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -2.42 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -2.33 |
| **HOMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -5.58 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -5.62 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -5.56 |
| **HOMO-1** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.07 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.22 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.14 |
| **HOMO-2** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.95 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.48 | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif  -6.42 |

**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) .

|  |  |  |  |
| --- | --- | --- | --- |
| **CAM-B3LYP** | **DPVBi** | **A** | **B** |
| **LUMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif |
| **HOMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif |

**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).

|  |  |  |  |
| --- | --- | --- | --- |
| **M06-2X** | **DPVBi** | **A** | **B** |
| **LUMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif |
| **HOMO** | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif | F:\woled-draft\draft-from-hissler\woled-comptc-revision\woled-orbitals\5a\a5-chair-b3lyp\a5-chair-b3lyp-homo.tif |