Electronic supplementary information to:

# Exploring the electrochemical properties of hole transporting materials from first-principles: an efficient strategy to improve the performance of perovskite solar cells

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## Table Captions

**Table S1** Calculated molecular orbital energy levels (HOMO and LUMO, eV) and band gap for molecule X60 with different functional in $CH_2Cl_2$.

**Table S2** Calculated molecular orbital energy levels (HOMO and LUMO) as well as the HOMO–LUMO energy gap of all the molecules at level of BMK/6-31G(d) in $CH_2Cl_2$.

**Table S3** Calculated wavelength of maximum absorption λmax (nm) and corresponding first excitation energy E (eV) of molecule X60 in $CH_2Cl_2$ with PBE0/6-31G(d) geometries.

**Table S4** The crystallographic data of all the HTMs.

**Table S1** Calculated molecular orbital energy levels (HOMO and LUMO, eV) and band gap for molecule X60 with different functional in $CH_2Cl_2$.

| Scheme | HOMO | LUMO | Band gap |
|---|---|---|---|
| Exp [a] | –5.16 | –2.20 | 2.96 |
| BMK/6-31G(d) | –5.15 | –0.28 | 4.87 |
| PBE0/6-31G(d) | –4.78 | –0.93 | 3.85 |
| B3LYP/6-31G(d) | –4.55 | –0.99 | 3.56 |
| M06/6-31G(d) | –4.94 | –1.05 | 3.89 |
| M06-2X/6-31G(d) | –5.87 | –0.42 | 5.45 |

[a] Experimental value from Ref. 24.

**Table S2** Calculated molecular orbital energy levels (HOMO and LUMO) as well as the HOMO–LUMO energy gap of all the molecules at level of BMK/6-31G(d) in $CH_2Cl_2$.

| Compounds | $\varepsilon_{HOMO}$ (eV) | $\varepsilon_{LUMO}$ (eV) | $\Delta\ \varepsilon$ (eV) |
|---|---|---|---|
| X60 | –5.15(–5.16) [a] | –1.98 | 3.17 |
| X59 | –5.15(–5.15) [b] | –2.03 | 3.12 |
| ST2 | –5.14 | –1.97 | 3.17 |
| ST | –5.16 | –2.02 | 3.14 |
| HT2 | –5.12 | –1.95 | 3.17 |
| HT | –5.15 | –1.97 | 3.18 |

[a] Experimental value from Ref. 24. [b] Experimental value from Ref. 25.

**Table S3** Calculated wavelength of maximum absorption $\lambda_{\max}$ (nm) and corresponding first excitation energy $E$ (eV) of molecule X60 in $CH_2Cl_2$ with PBE0/6-31G(d) geometries.

| Scheme | $\lambda_{\max}$ (nm) | $E$ (eV) |
|---|---|---|
| Exp [a] | 388 | – |
| PBE0/6-31G(d) | 390 | 3.17 |
| BMK/6-31G(d) | 358 | 3.45 |
| B3LYP/6-31G(d) | 403 | 3.06 |
| CAM-B3LYP/6-31G(d) | 344 | 3.59 |
| M06/6-31G(d) | 391 | 3.16 |
| M062X/6-31G(d) | 348 | 3.55 |

[a] Experimental value from Ref. 24.

**Table S4** The crystallographic data of all the HTMs.

| Molecules | Crystal system | Space group | $Z$ | $a$(Å) | $b$(Å) | $c$(Å) | $\alpha$(°) | $\beta$(°) | $\gamma$(°) |
|---|---|---|---|---|---|---|---|---|---|
| X60 | Triclinic | $P\bar{1}$ | 2 | 10.520 | 16.297 | 20.958 | 68.652 | 80.004 | 71.759 |
| X59 | Monoclinic | $P2_1/n$ | 4 | 12.175 | 23.452 | 14.706 | 90.000 | 98.280 | 90.000 |
| ST2 | Triclinic | $P\bar{1}$ | 2 | 16.158 | 19.127 | 17.549 | 53.430 | 75.626 | 60.513 |
| ST | Triclinic | $P\bar{1}$ | 2 | 17.505 | 17.614 | 10.460 | 70.597 | 59.432 | 54.087 |
| HT2 | Triclinic | $P\bar{1}$ | 2 | 13.954 | 17.384 | 18.001 | 86.333 | 78.081 | 71.441 |
| HT | Triclinic | $P\bar{1}$ | 2 | 29.479 | 13.250 | 13.033 | 120.393 | 120.519 | 110.437 |

## Figure Captions

**Fig. S1** The optimized geometries of the investigated molecules in this work as obtained using the BMK/6-31G(d) method.

**Fig. S2** The calculated crystal structures with the lowest total energies of the investigated molecules, and the centroid to centroid distances together with the angles of projected electronic coupling pathways relative to reference axis.

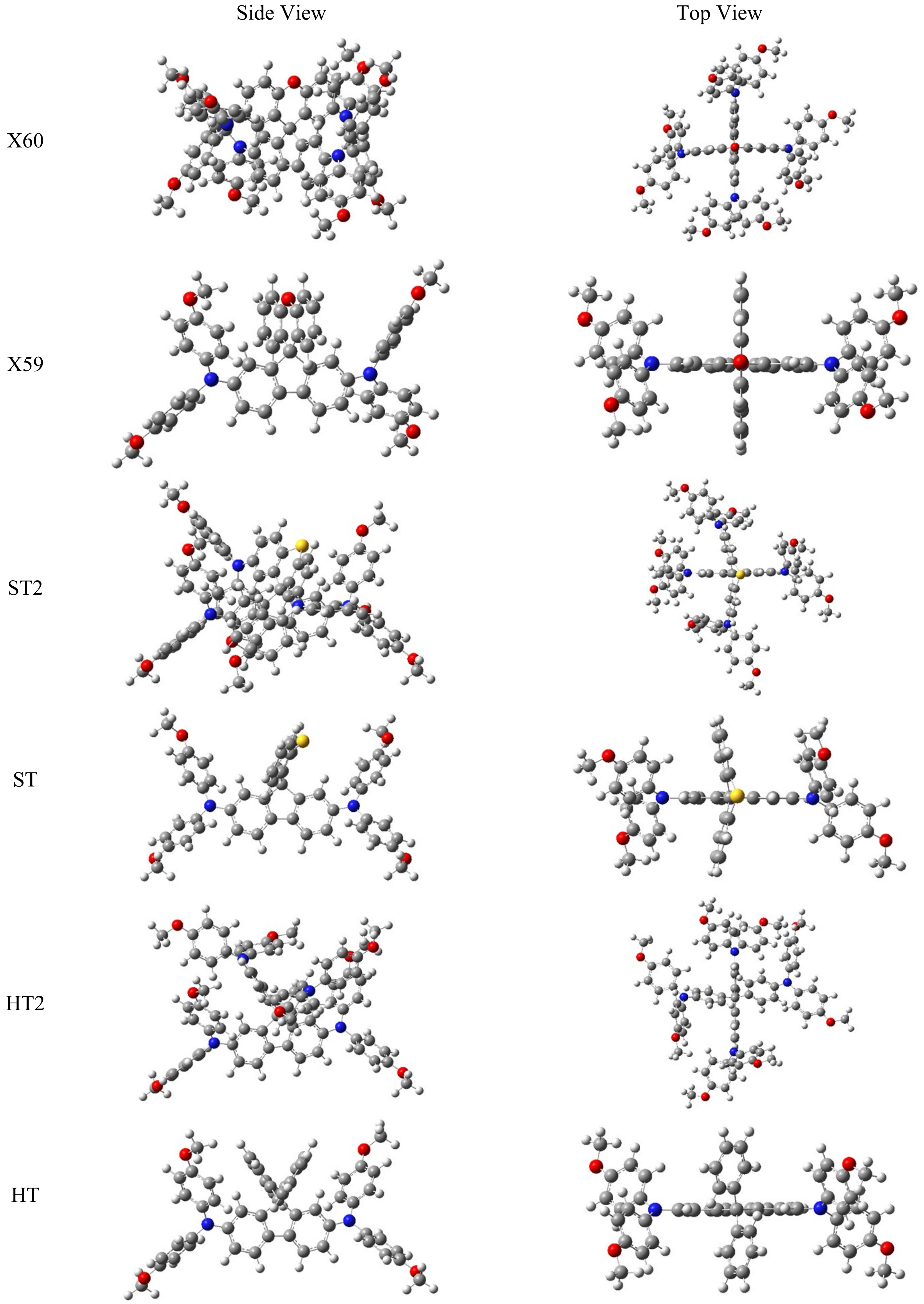
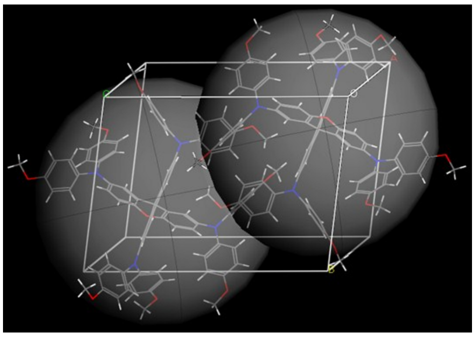
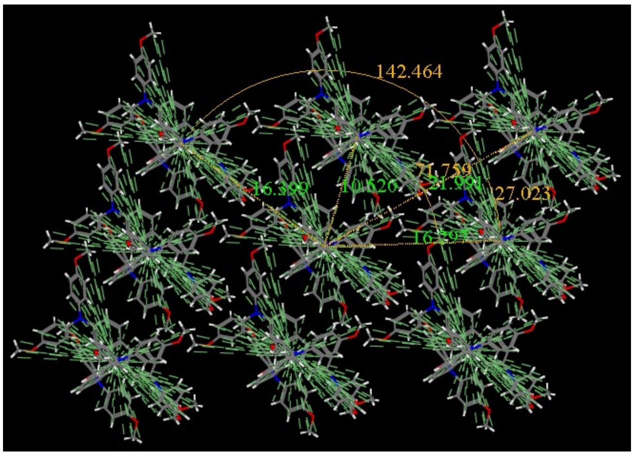


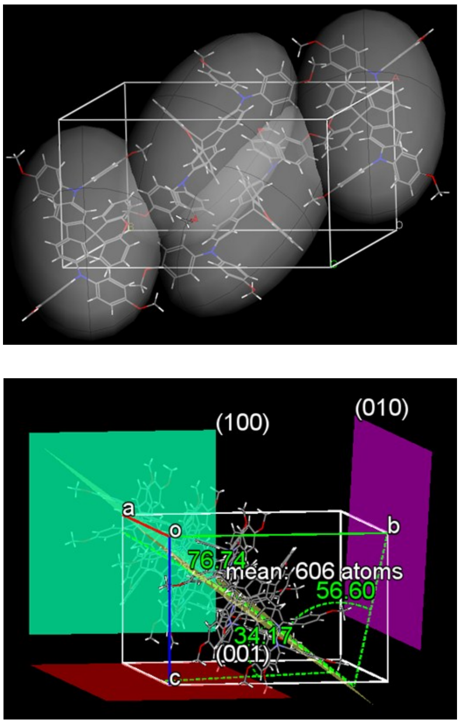
**Fig. S1** The optimized geometries of the investigated molecules in this work as obtained using the BMK/6-31G(d) method.



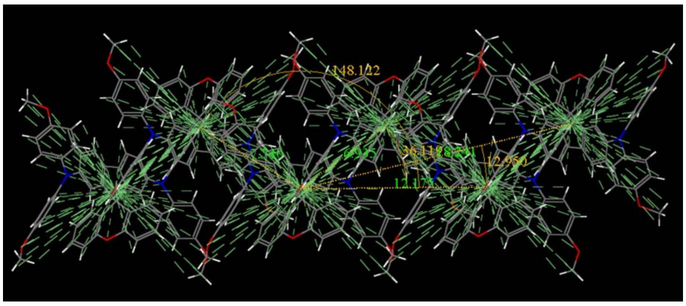
X60 ( $P\bar{1}$ space group)



AOB 面



X59 ($P2_1/n$ space group)



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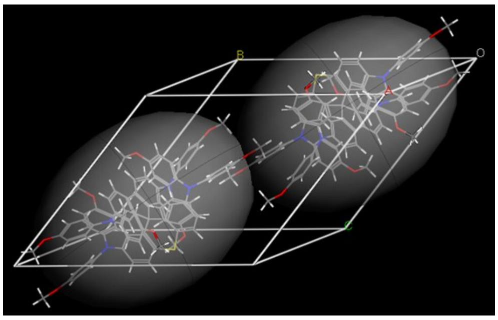
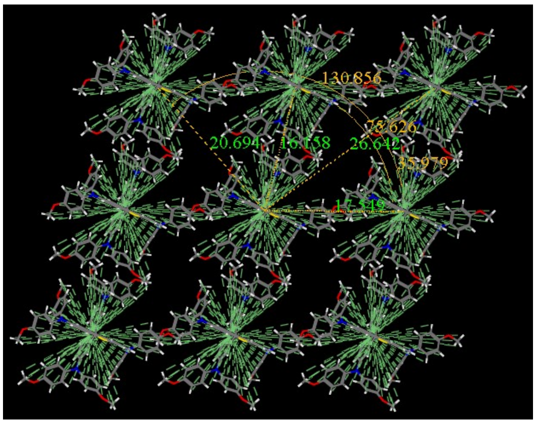
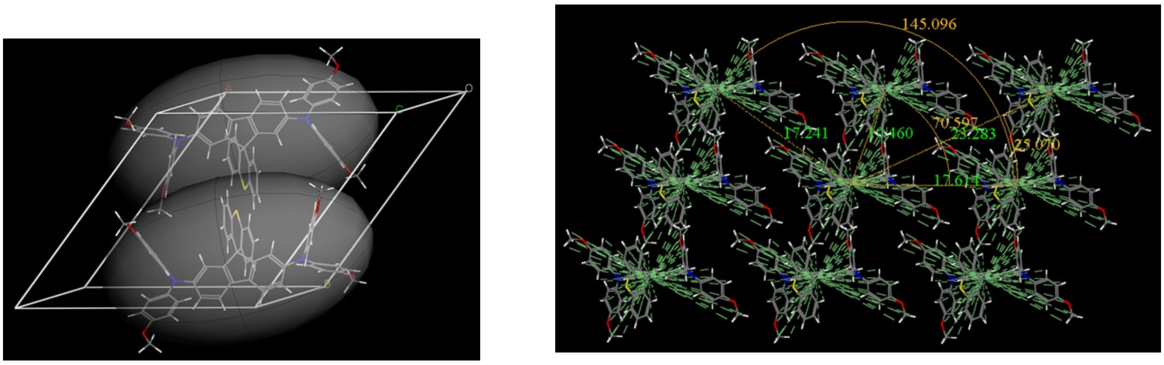


ST2 ( $P\bar{1}$ space group)

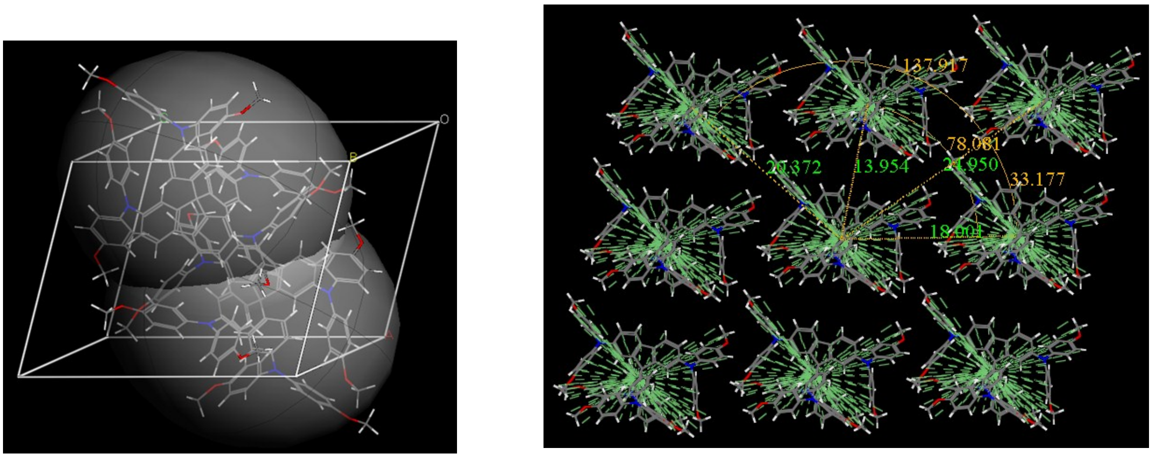


AOC 面



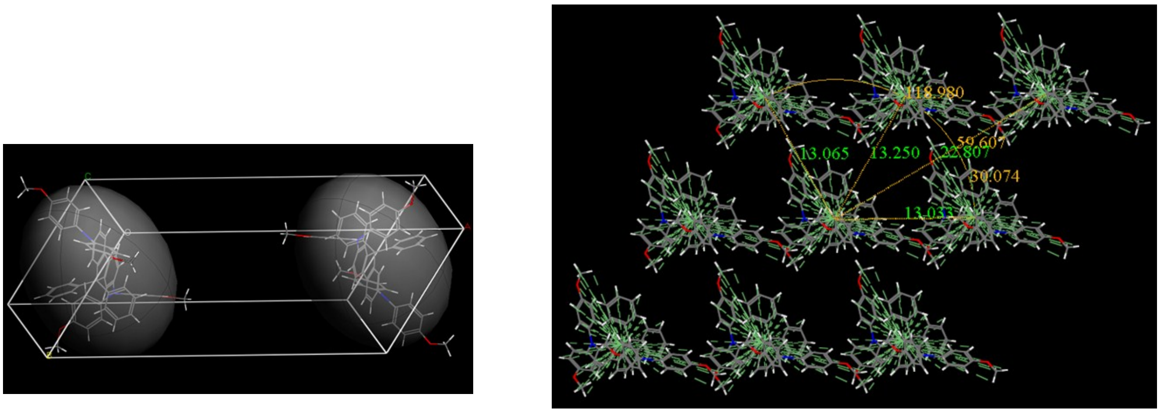
ST ( $P\bar{1}$ space group)

BOC 面



HT2 ( $P\bar{1}$ space group)

AOC 面



HT ( $P\bar{1}$ space group)

BOC 面

**Fig. S2** Calculated crystal structures with the lowest total energies of the investigated molecules, and the centroid to centroid distances together with the angles of projected electronic coupling pathways relative to reference axis.