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**Supporting Information**

# Ab initio study on the excited states of pyrene and its derivatives using multi-reference perturbation theory methods

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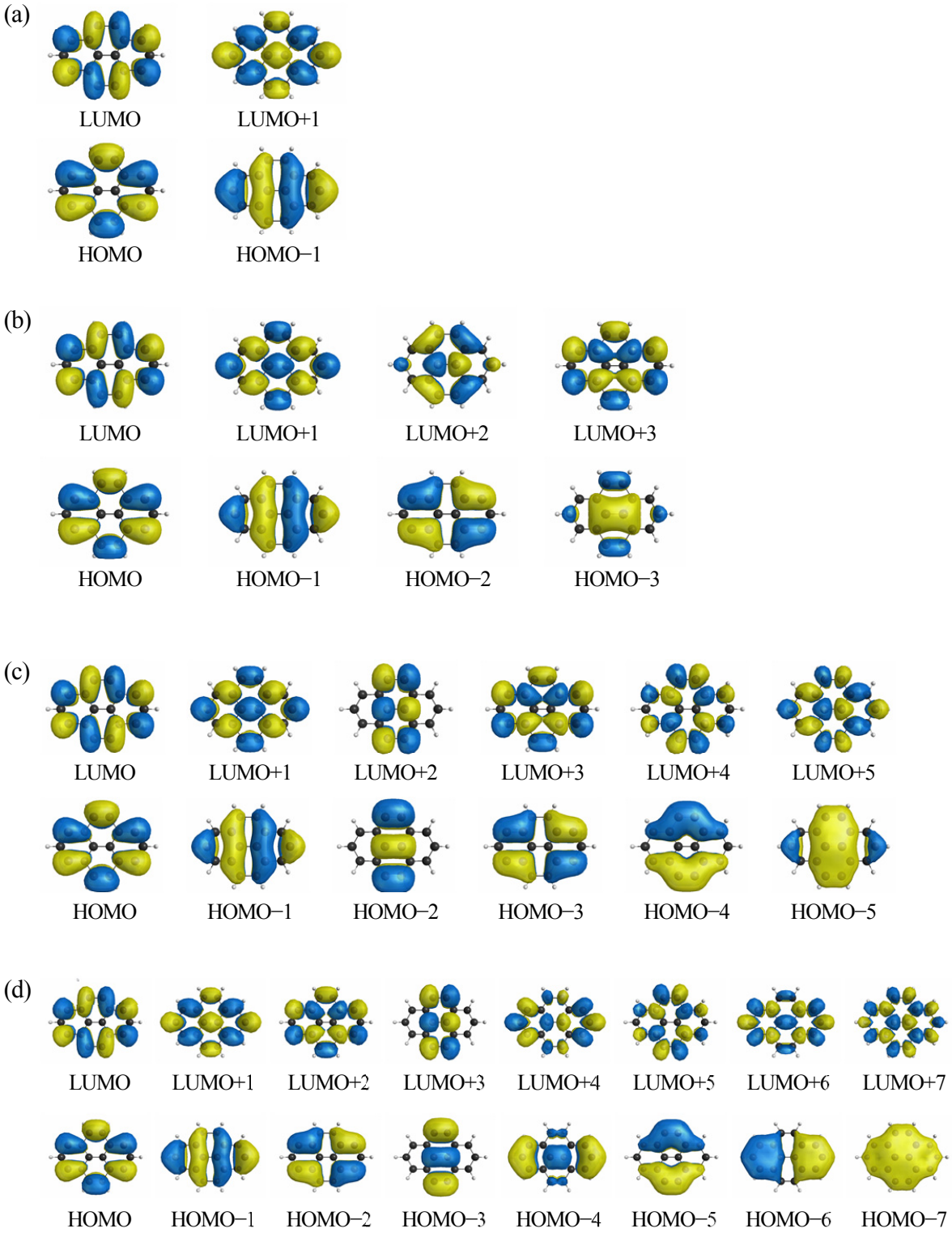


**Fig. S1** Natural orbitals of pyrene from MCSCF wave functions:
(a) CAS(4πe, 4πo), (b) CAS(8πe, 8πo), (c) CAS(12πe, 12πo) and (d) MRX(4).

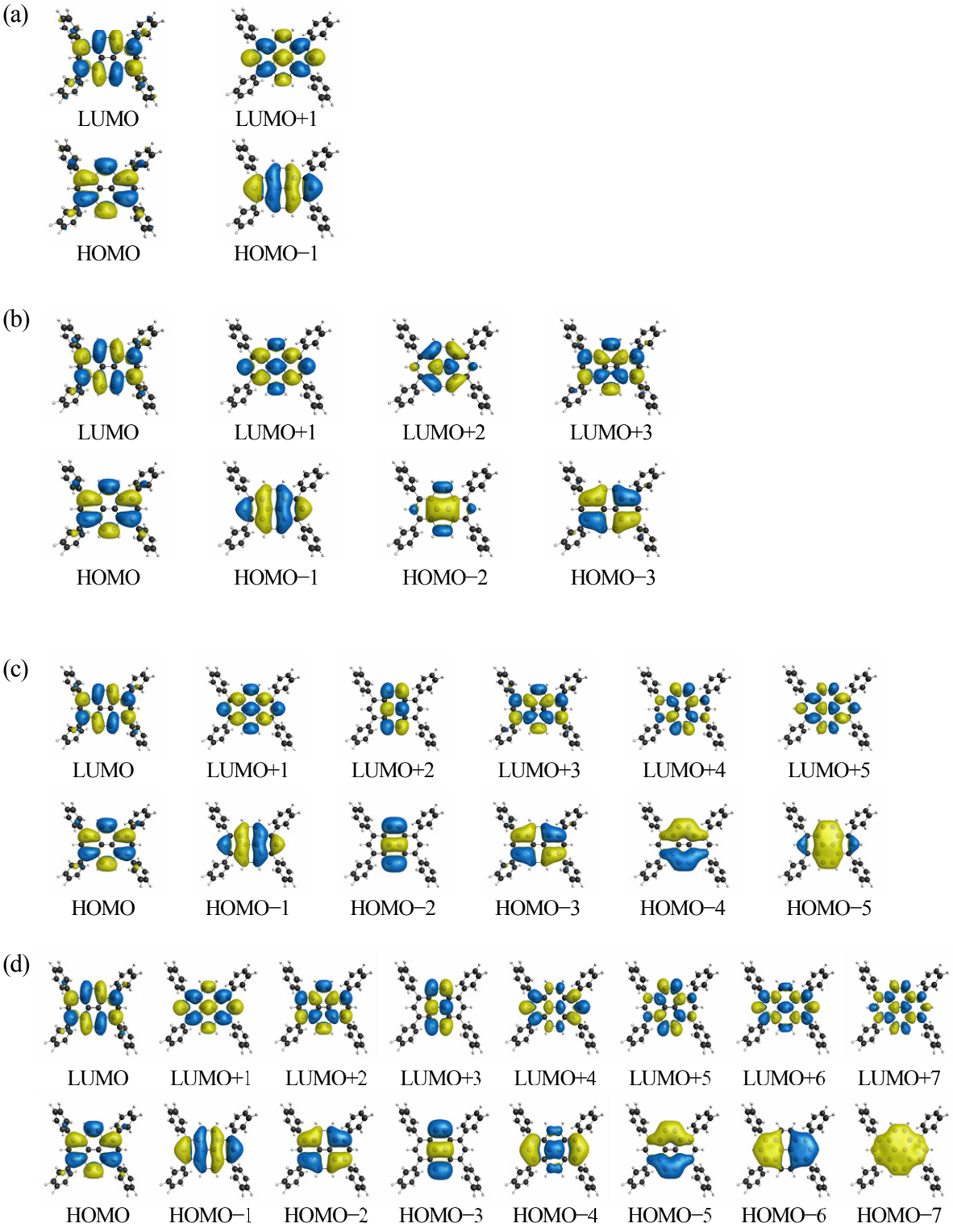


**Fig. S2** Natural orbitals of 1,3,6,8-tetraphenylpyrene (TPPy) from MCSCF wave functions: (a) CAS(4πe, 4πo), (b) CAS(8πe, 8πo), (c) CAS(12πe, 12πo) and (d) MRX(4).

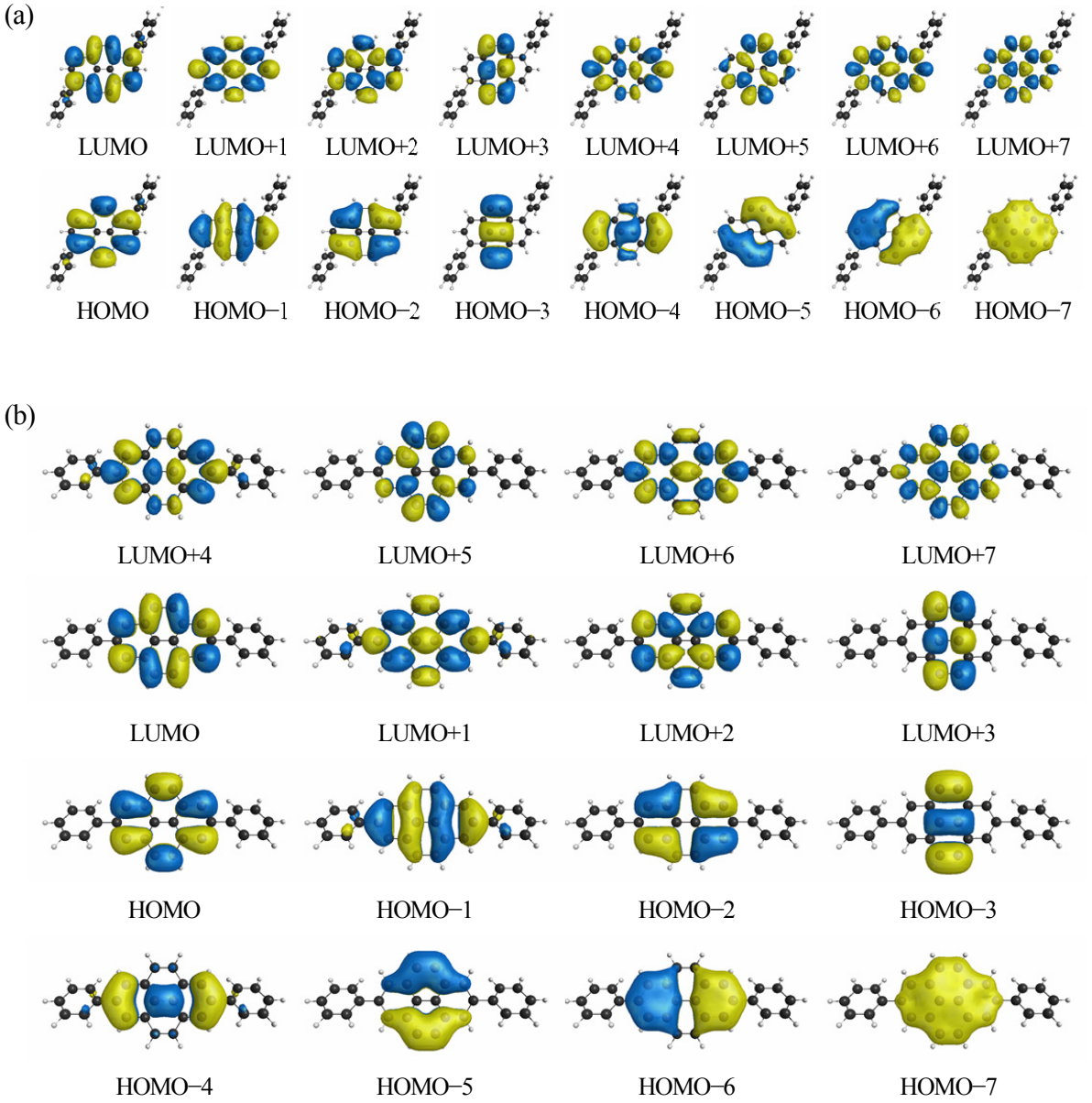


**Fig. S3** Natural orbitals of (a) 1,6-diphenylpyrene (1,6-DPPy) and (b) 2,7-diphenylpyrene (2,7-DPPy) from MCSCF wave functions with MRX(4) configuration space.

**Table S1.** Calculated electronic total energies and excitation energies.

| molecule | method | reference space | electronic state total energy | | | excitation energy | |
|---|---|---|---|---|---|---|---|
| | | | ground state | $^1L_a$ | $^1L_b$ | $^1L_a$ | $^1L_b$ |
| pyrene | GMCSCF | MRX(2) | −611.963398 | −611.683908 | −611.732426 | 7.61 | 6.28 |
| | | MRX(3) | −611.969412 | −611.773601 | −611.827047 | 5.33 | 3.87 |
| | | MRX(4) | −611.998334 | −611.786239 | −611.854412 | 5.77 | 3.92 |
| | CASSCF | CAS(4πe, 4πo) | −611.826258 | −611.630826 | −611.633173 | 5.32 | 5.25 |
| | | CAS(8πe, 8πo) | −611.873724 | −611.673541 | −611.698314 | 5.45 | 4.77 |
| | | CAS(12πe, 12πo) | −611.938240 | −611.733420 | −611.773669 | 5.57 | 4.48 |
| | GMCQDPT | MRX(2) | −613.895808 | −613.757849 | −613.779477 | 3.75 | 3.17 |
| | | MRX(3) | −613.898739 | −613.758249 | −613.777274 | 3.82 | 3.31 |
| | | MRX(4) | −613.904548 | −613.763264 | −613.779616 | 3.84 | 3.40 |
| | MCQDPT | CAS(4πe, 4πo) | −613.888464 | −613.758129 | −613.784435 | 3.55 | 2.83 |
| | | CAS(8πe, 8πo) | −613.895007 | −613.757183 | −613.775339 | 3.75 | 3.26 |
| | | CAS(12πe, 12πo) | −613.912130 | −613.771275 | −613.764713 | 3.83 | 4.01 |
| | EOM-CCSD | | −613.927251 | −613.763560 | −613.786867 | 4.45 | 3.82 |
| TPPy | GMCSCF | MRX(2) | −1530.208096 | −1529.939689 | −1529.982544 | 7.30 | 6.14 |
| | | MRX(3) | −1530.214345 | −1530.028781 | −1530.075887 | 5.05 | 3.77 |
| | | MRX(4) | −1530.243303 | −1530.040528 | −1530.102935 | 5.52 | 3.82 |
| | CASSCF | CAS(4πe, 4πo) | −1530.072126 | −1529.887052 | −1529.892707 | 5.04 | 4.88 |
| | | CAS(8πe, 8πo) | −1530.119736 | −1529.934120 | −1529.950080 | 5.05 | 4.62 |
| | | CAS(12πe, 12πo) | −1530.183896 | −1529.992171 | −1530.023859 | 5.22 | 4.35 |
| | GMCQDPT | MRX(2) | −1535.272512 | −1535.158154 | −1535.163555 | 3.11 | 2.96 |
| | | MRX(3) | −1535.274668 | −1535.154509 | −1535.159934 | 3.27 | 3.12 |
| | | MRX(4) | −1535.280775 | −1535.167838 | −1535.161723 | 3.07 | 3.24 |
| | MCQDPT | CAS(4πe, 4πo) | −1535.277130 | −1535.169965 | −1535.181531 | 2.92 | 2.60 |
| | | CAS(8πe, 8πo) | −1535.306796 | −1535.191025 | −1535.195163 | 3.15 | 3.04 |
| | | CAS(12πe, 12πo) | −1535.368049 | −1535.232284 | −1535.236305 | 3.69 | 3.58 |
| | EOM-CCSD | | −1535.391457 | −1535.247783 | −1535.257238 | 3.91 | 3.65 |
| 1,6-DPPy | GMCSCF | MRX(4) | −1071.121009 | −1070.913546 | −1070.978846 | 5.65 | 3.87 |
| | GMCQDPT | MRX(4) | −1074.592114 | −1074.467613 | −1074.470366 | 3.39 | 3.31 |
| 2,7-DPPy | GMCSCF | MRX(4) | −1071.128369 | −1070.917149 | −1070.987240 | 5.75 | 3.84 |
| | GMCQDPT | MRX(4) | −1074.592383 | −1074.458462 | −1074.471182 | 3.64 | 3.30 |

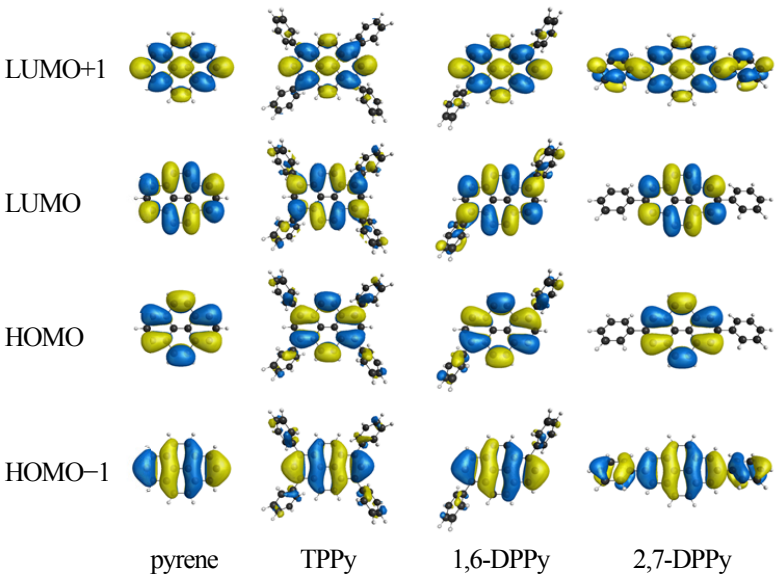


**Fig. S4** Molecular orbitals of pyrene, TPPy, 1,6-DPPy, and 2,7-DPPy obtained from the Hartee-Fock calculations.