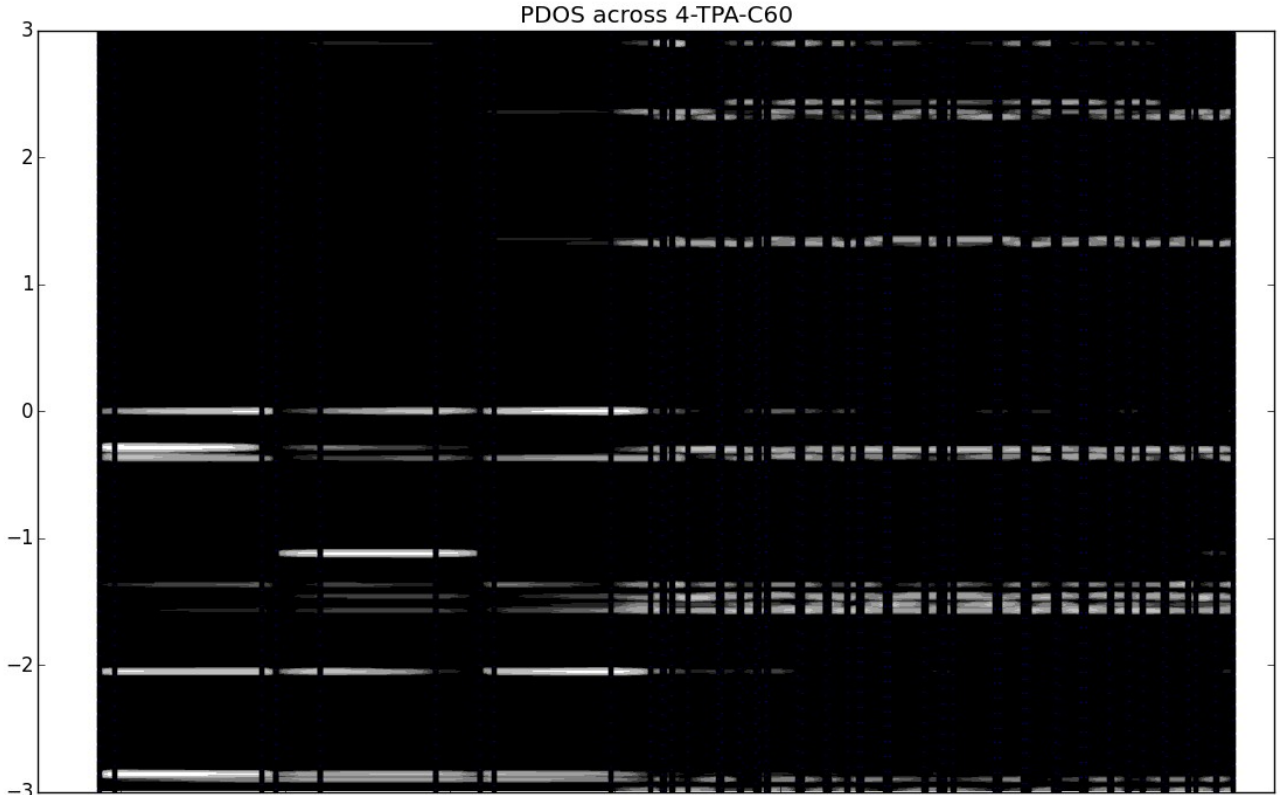
Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

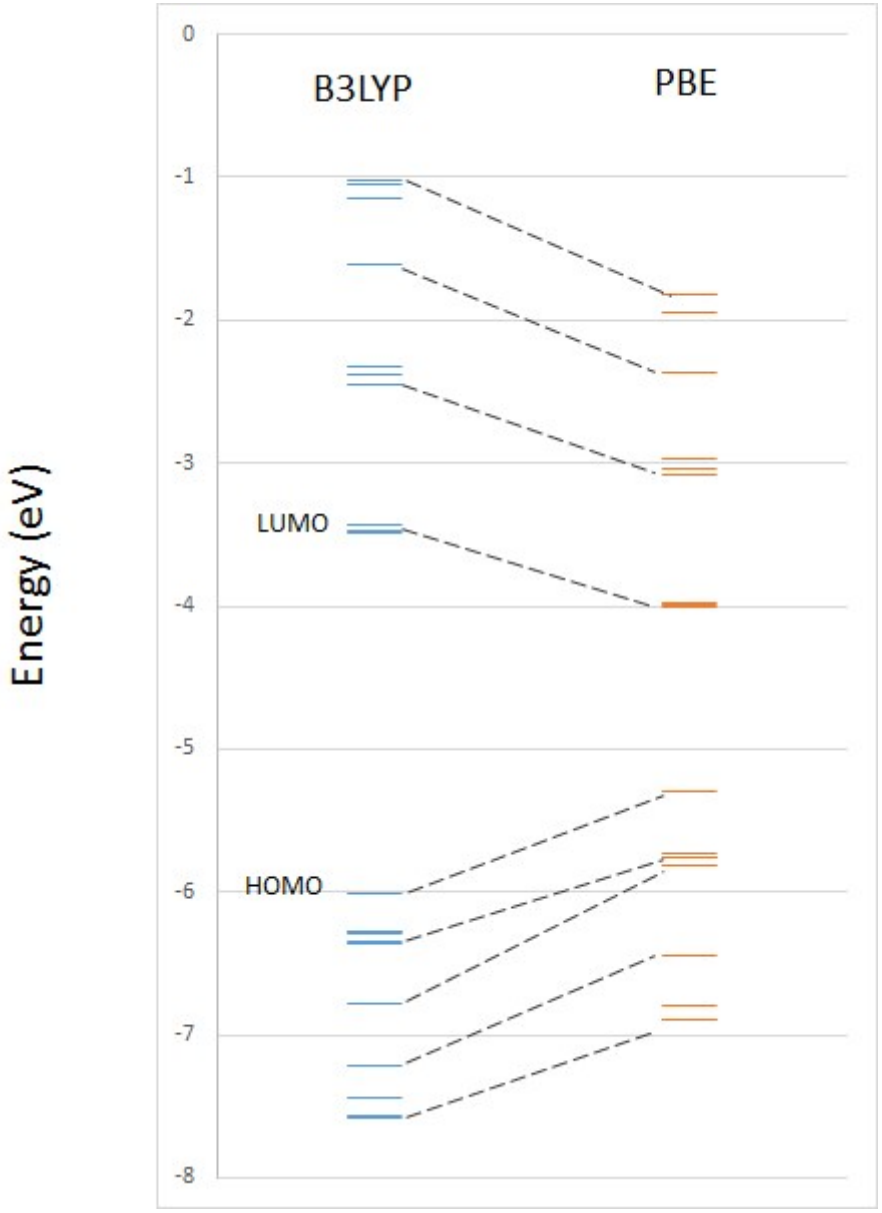
1) Projected Density of States across 4TPA-C_{60} in the gas phase

Plot of energy (y-axis: E-E_{HOMO} in eV) and spatial (x-axis: along longitudinal molecule axis) resolved density of states showing how the electronic states are distributed along the molecule. $E_{LUMO} - E_{HOMO}$ = 1.32 eV



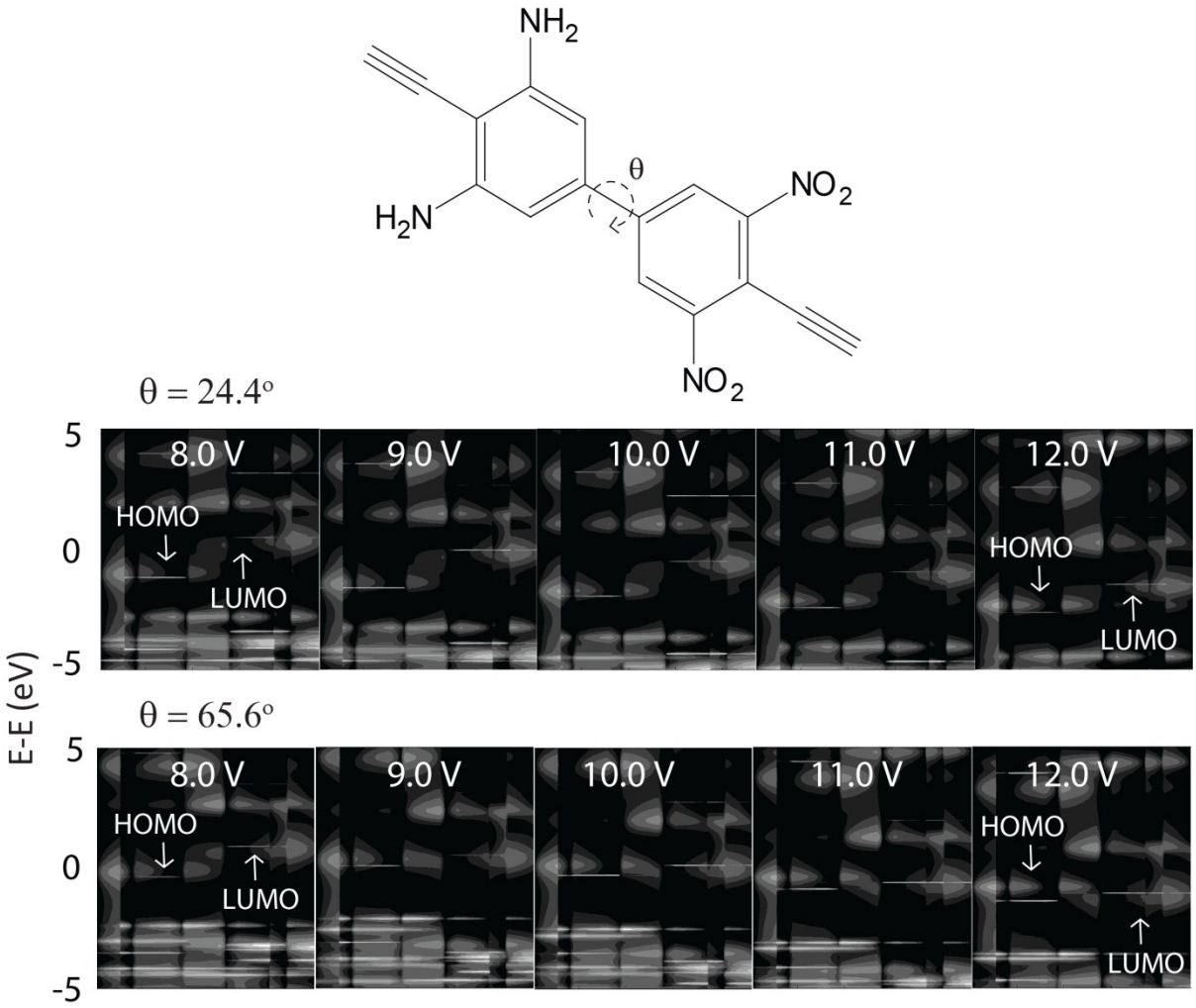
2) Energy level diagram of gas phase 4TPA-C_{60} using B3LYP and PBE functionals

PBE calculations are known to underestimate the band gap (HOMO-LUMO gap) in materials. In the case of 4TPA-C60, the band gap is underestimated by about 1.25 eV ($E_{gap,PBE}$ = 1.28 eV, $E_{gap,B3LYP}$ = 2.53 eV)



3. PDOS across a similar donor/acceptor biphenyl system

Bias dependent PDOS of a biphenyl system consisting of a donor (-NH_2 substituted) and acceptor (-NO_2 substituted) were calculated using a density functional based tight binding method (PLATO). The calculations show that the fourth rule was not unique to the 4TPA-C_{60} system. HOMO-LUMO pinning can be observed in the biphenyl system at theta = 24.4° between 8 and 12V, which prevents the HOMO and LUMO states from crossing. However, HOMO/LUMO level inversion can be observed when theta = 65.6° at 11V, due to a smaller coupling between the donor and acceptor fragments.



4. Reference calculations of 4TPA-C_{60} performed in PLATO

To ensure that the tight-binding simulations were reasonably accurate, reference calculations were performed on the 4TPA-C_{60} system. PDOS of 4TPA-C_{60} were calculated in PLATO, which showed a qualitatively similar picture as DFT calculations performed in the main paper.

The larger band gaps in the PLATO calculation is attributed to the smaller basis set size used in the tight binding calculations. Furthermore, the energies in DFT are more smeared out due to interactions with the gold leads, which were not taken into account in the tight-binding calculations.