

# Density Functional Theory Studies of the [2]Rotaxane Component of the Stoddart-Heath Molecular Switch

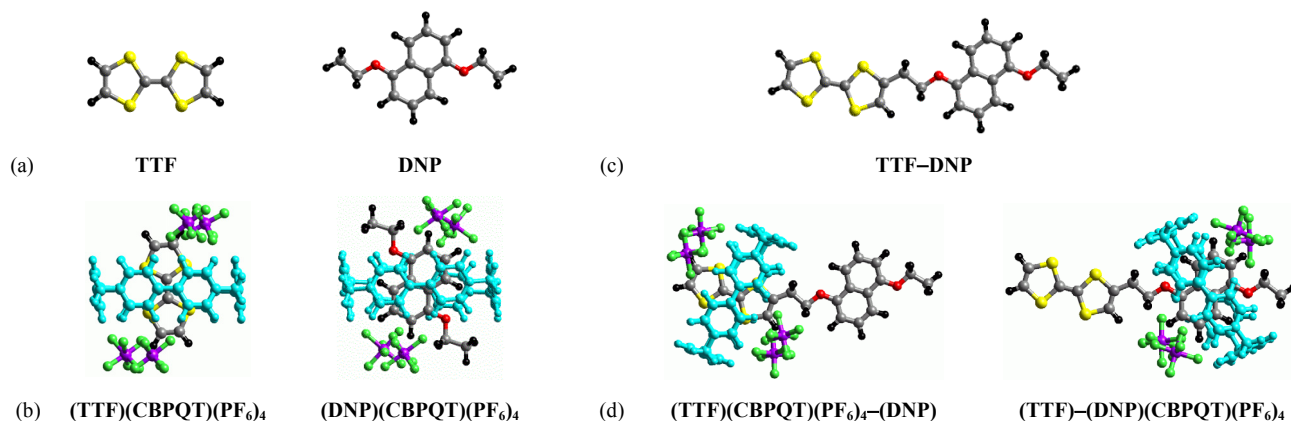
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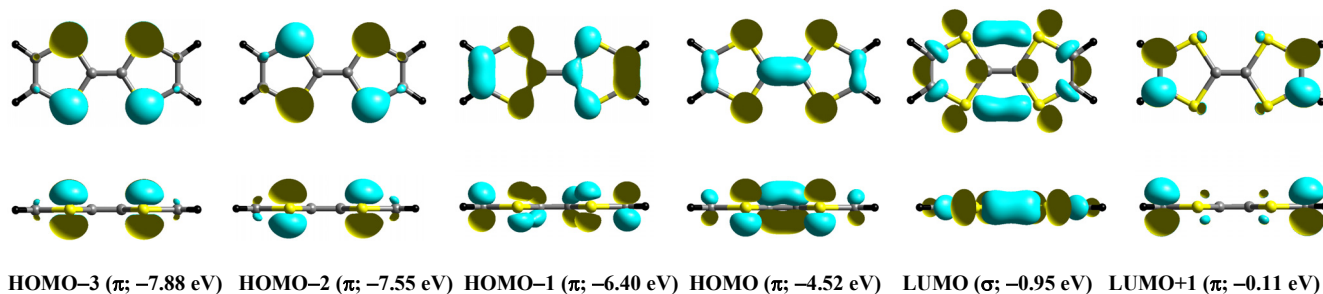
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## Supporting Information

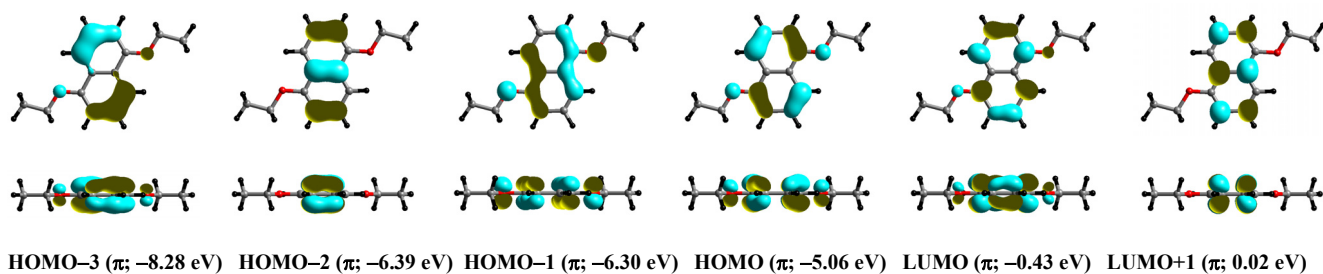
### A. Detailed Figures



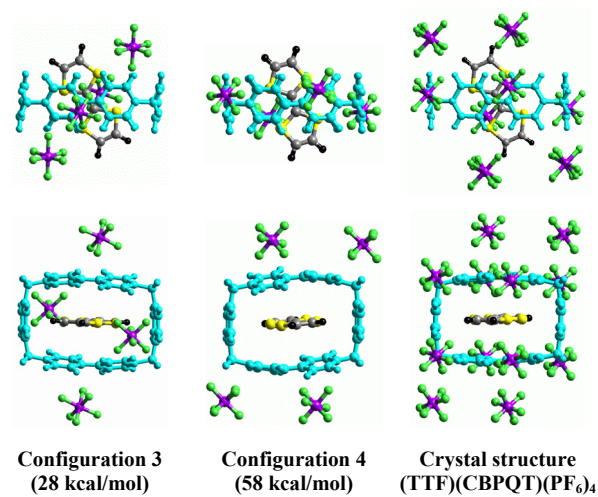
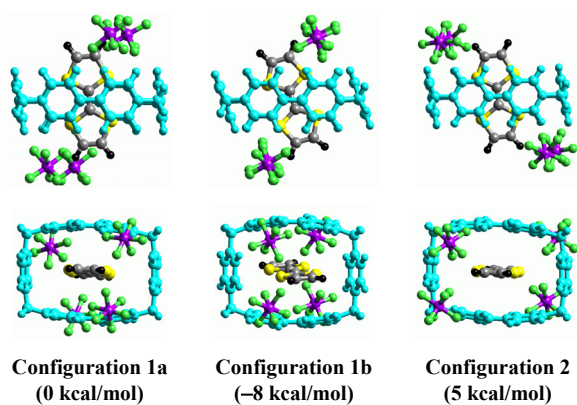
**Figure S1.** Simplified models of **1** employed in this study. Color code: yellow (S), red (O), gray (C), black (H), purple (P), light green (F), and light blue (CBPQT).



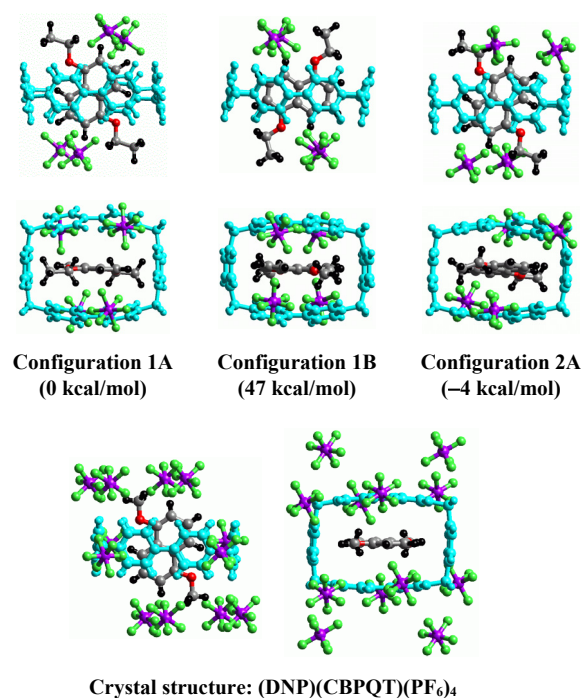
**Figure S2.** Frontier molecular orbitals of TTF (B3LYP/6-31G\*\*). Essentially the same shapes are found with PBE/6-31G\*\*. Color code: yellow (S), gray (C), and black (H).



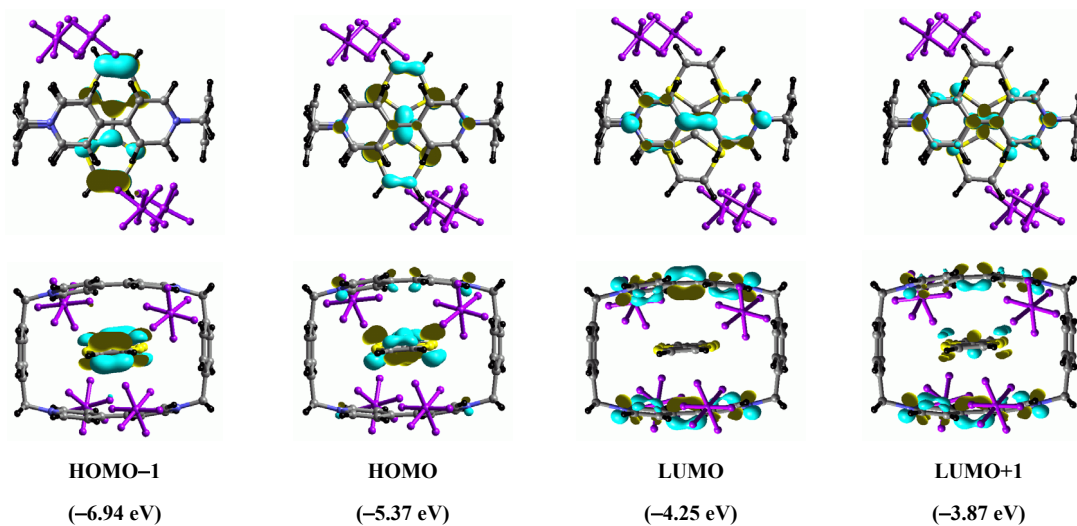
**Figure S3.** Frontier molecular orbitals of DNP (B3LYP/6-31G\*\*). Essentially the same shapes are found with PBE/6-31G\*\*. Color code: red (O), gray (C), and black (H).



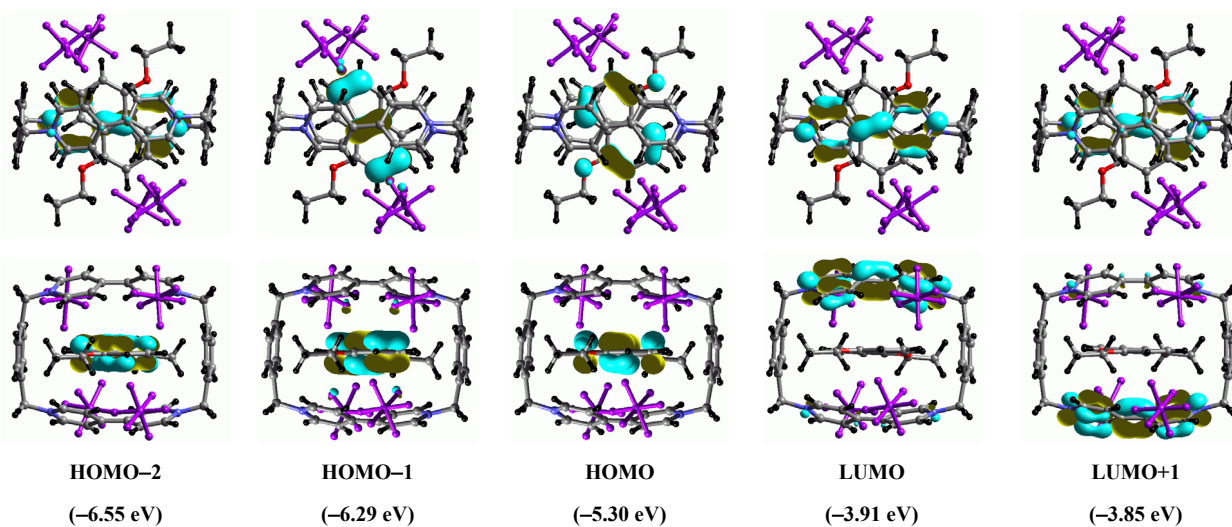
**Figure S4.** Side and top view of the optimized structures for (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> with five different arrangements of the four PF<sub>6</sub><sup>-</sup>'s around the CBPQT<sup>4+</sup> ring. We find **Configurations 1** and **2** to be the most favorable. Shown also is the arrangement of nearest-neighbor PF<sub>6</sub><sup>-</sup>'s around a CBPQT in the crystal structure of (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>.<sup>23</sup> Color code: yellow (S), gray (C), black (H), purple (P), light green (F), and light blue (CBPQT).



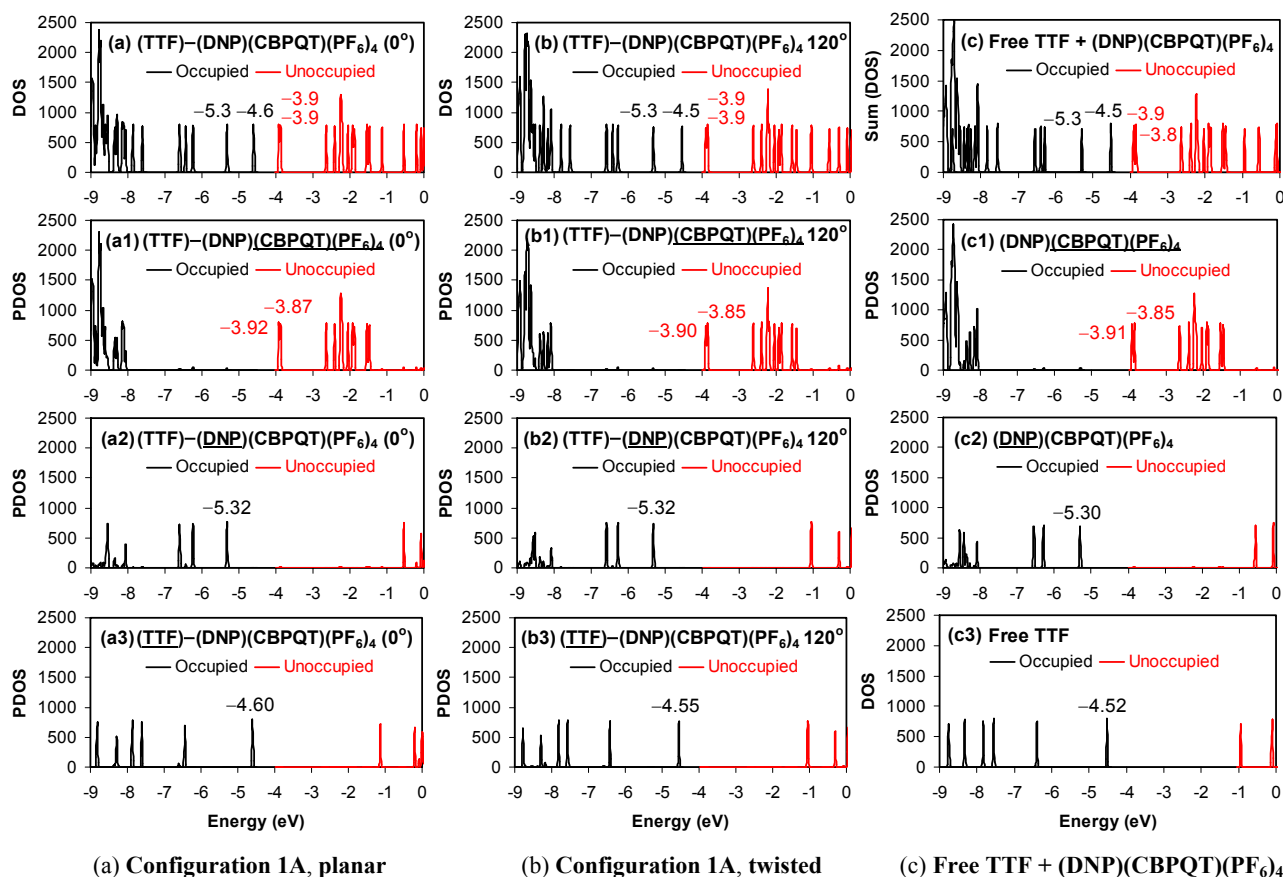
**Figure S5.** Side and top view of optimized structures of (DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> for two different orientations of DNP relative to the CBPQT<sup>4+</sup> ring (**Configuration 1A/1B**). The more stable is **Configuration 1A** which is also found in the x-ray crystal structure,<sup>24</sup> shown above. Another similarly stable configuration of PF<sub>6</sub><sup>-</sup>'s was also found (**Configuration 2A**). Color code: red (O), gray (C), black (H), purple (P), light green (F), and light blue (CBPQT).



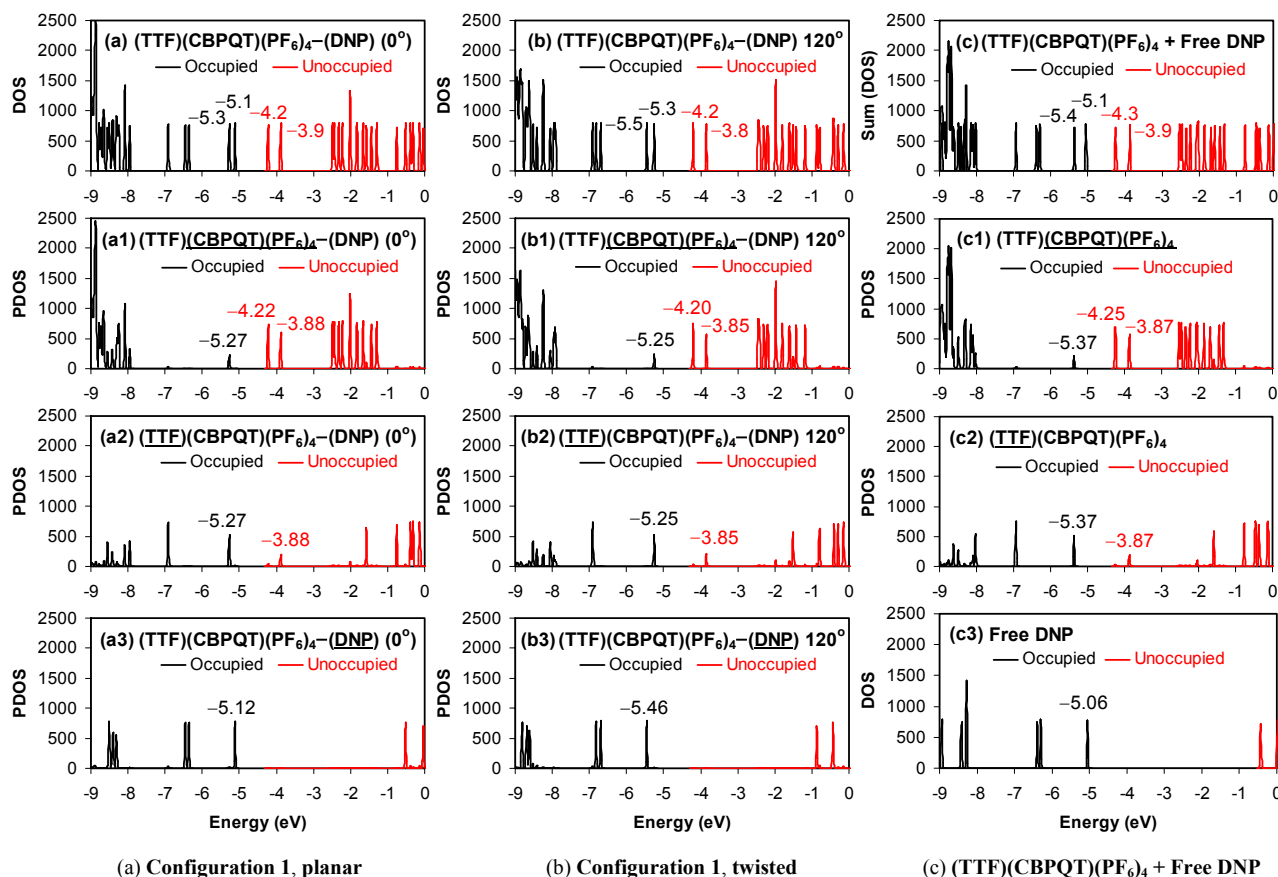
**Figure S6.** FMO's of (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>. Color code: yellow (S), blue (N), gray (C), black (H), and purple (PF<sub>6</sub><sup>-</sup>).



**Figure S7.** FMO's of (DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>. Color code: red (O), blue (N), gray (C), black (H), and purple (PF<sub>6</sub><sup>-</sup>).

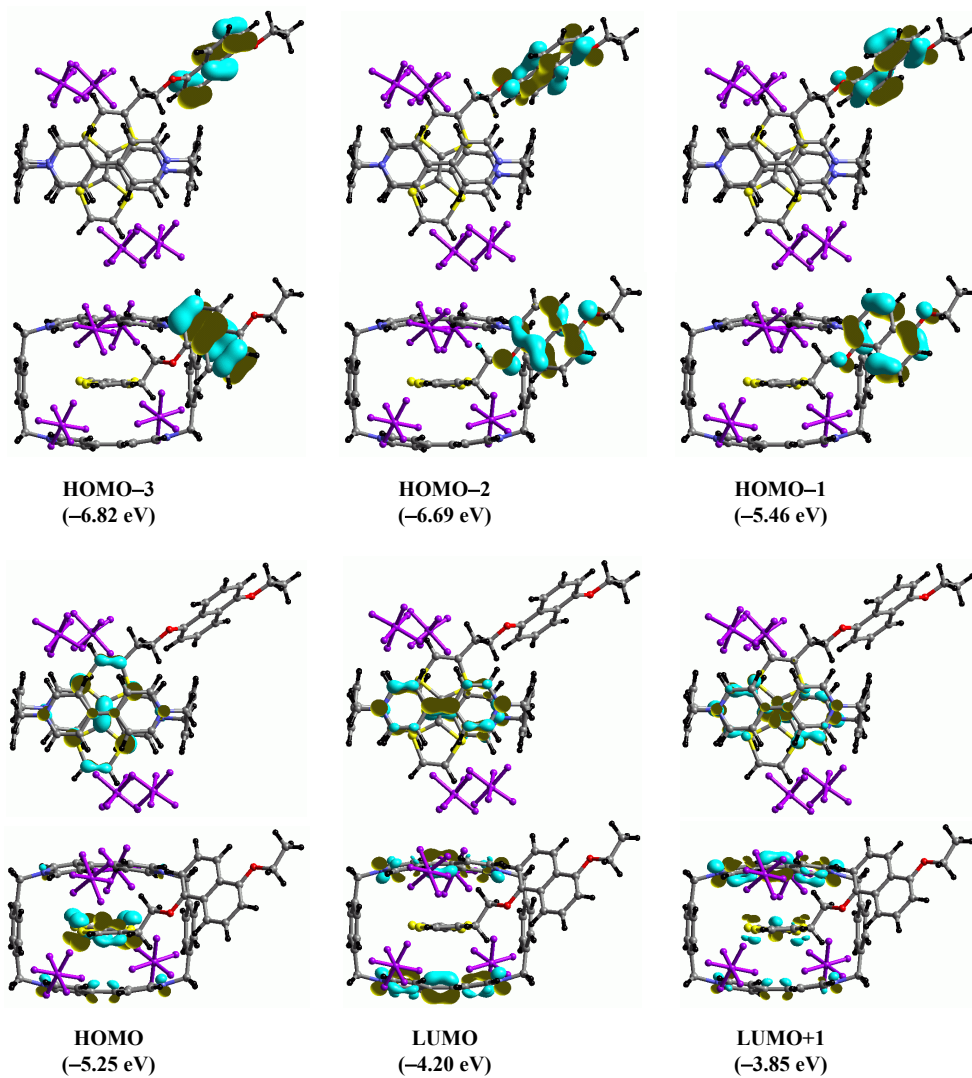


**Figure S8.** DOS's and PDOS's from DFT (B3LYP/6-31G\*\*) for (TTF)-(DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>. (a) **Configuration 1A, planar** and (b) **Configuration 1A, twisted**. The DOS's and PDOS's of the composite system are essentially the same as the sum of individual parts: free TTF and (DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> shown in (c).

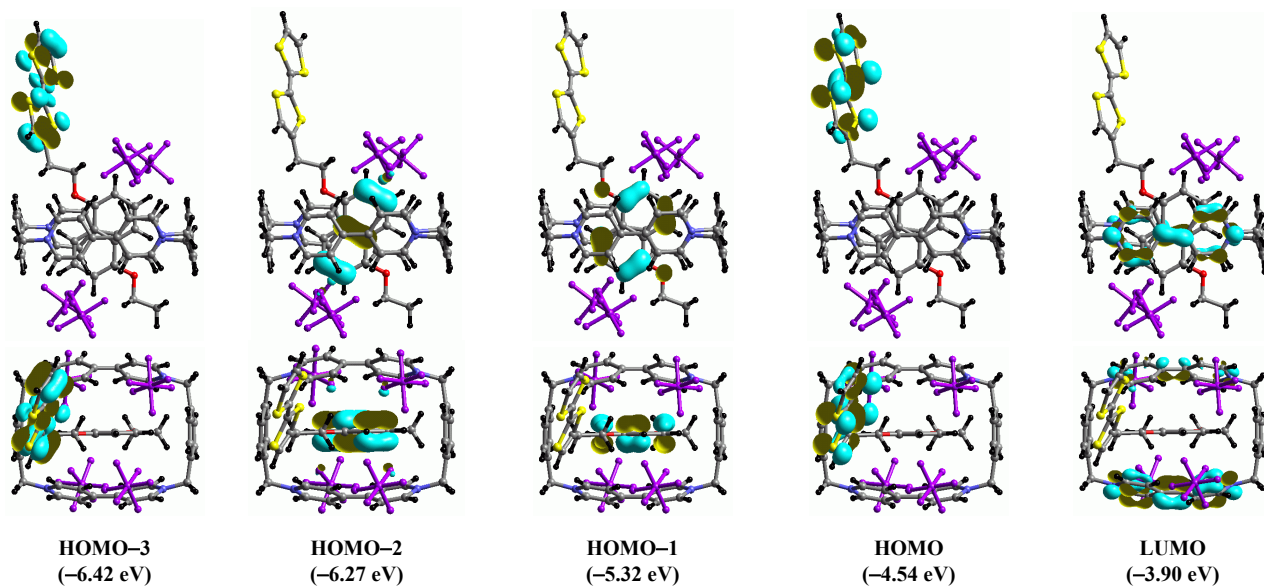


**Figure S9.** DOS's and PDOS's (B3LYP/6-31G\*\*) of (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>-(DNP). (a) **Configuration 1a, planar** and (b) **Configuration 1a, twisted**. The sum of DOS's and PDOS's of the individual parts, (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> and free DNP, are shown together in (c).



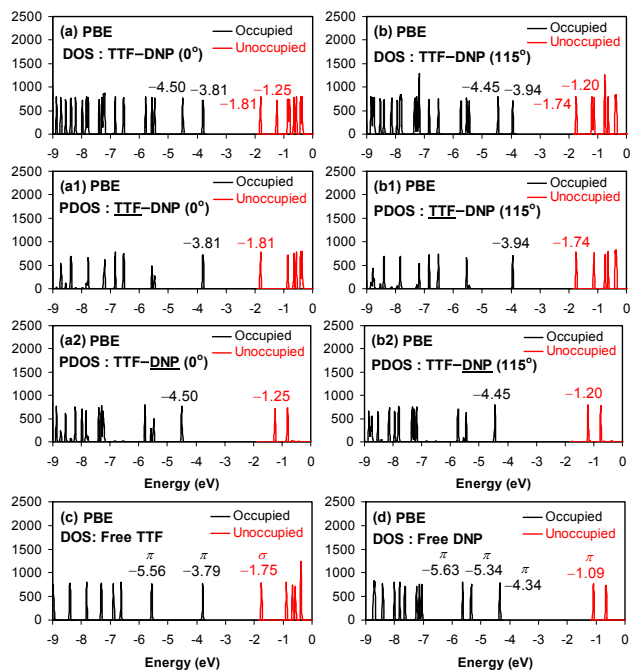


**Figure S10.** FMO's of (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>-(DNP) (Configuration 1a, twisted). Color code: yellow (S), red (O), blue (N), gray (C), black (H), purple (PF<sub>6</sub><sup>-</sup>).

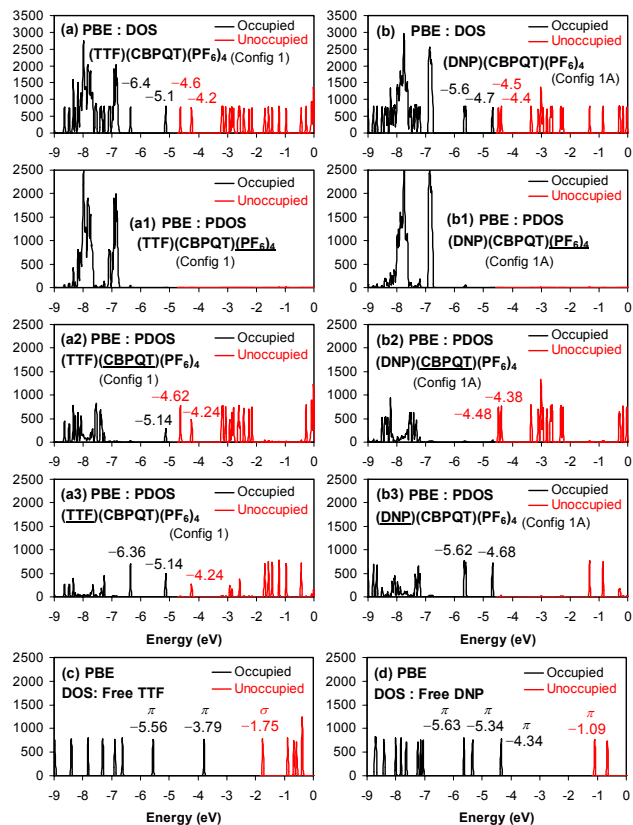


**Figure S11.** FMO's of (TTF)-(DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> (Configuration 1A, twisted). Color code: yellow (S), red (O), blue (N), gray (C), black (H), purple (PF<sub>6</sub><sup>-</sup>).

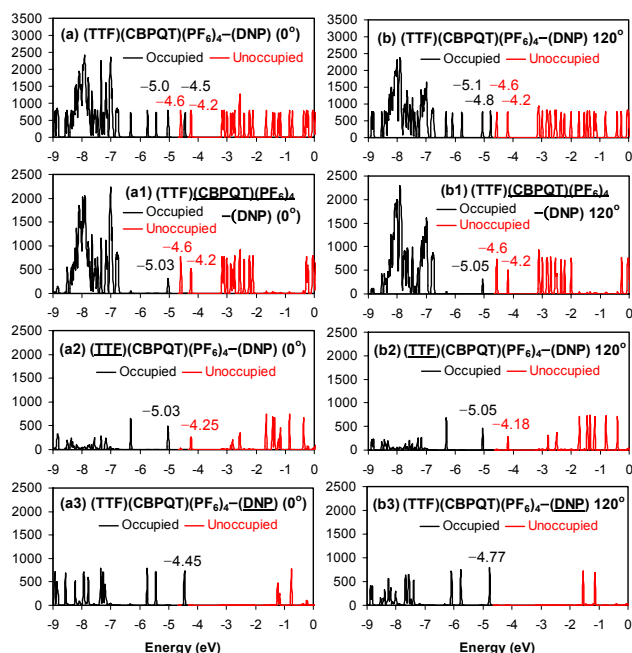
## B. PBE/6-31G\*\*



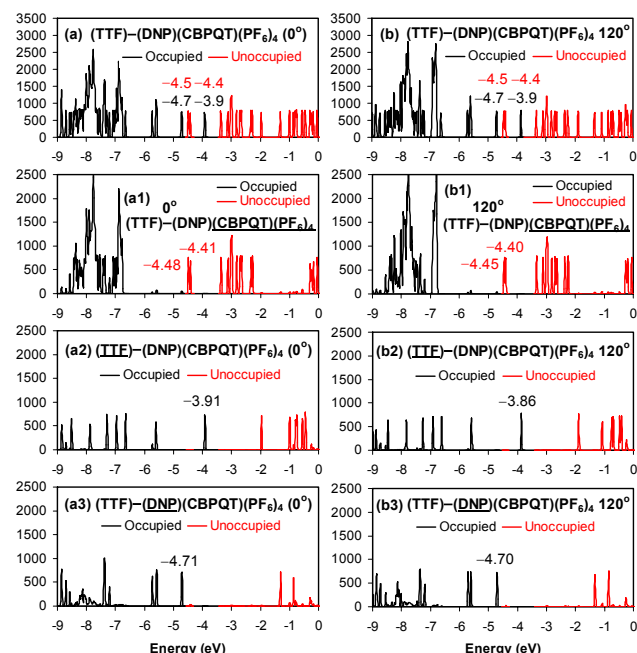
**Figure S12.** DOS's and PDOS's from PBE/6-31G\*\* calculations of TTF-DNP for two different conformations (a) **planar** and (b) **twisted**. As in the B3LYP/6-31G\*\* calculation, the states of each station, TTF and DNP, preserves its identity after the connection to each other, and the two conformations show essentially the same characteristics.



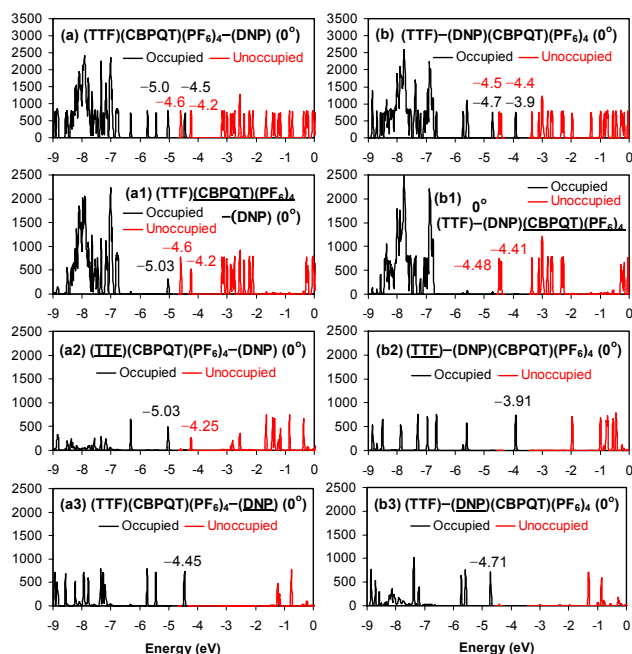
**Figure S13.** DOS's and PDOS's from PBE/6-31G\*\* calculations of (a) (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub> and (b) (DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>. This shows the effect of complex formation for (a,c) TTF and (b,d) DNP. As in the B3LYP calculations, complex formation lowers the energy levels of the frontier orbitals of both TTF and DNP, but in greater extent for TTF than for DNP.



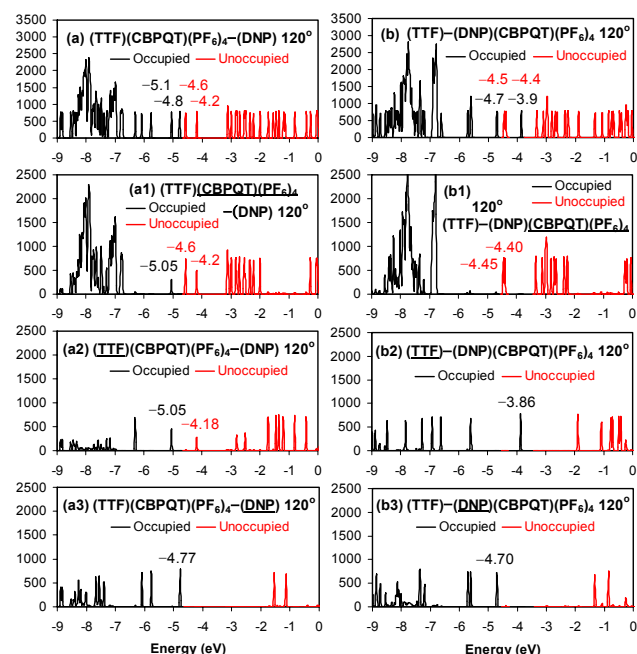
**Figure S14.** DOS's and PDOS's from PBE/6-31G\*\* calculations of (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>-(DNP). (a) planar and (b) twisted.



**Figure S15.** DOS's and PDOS's from PBE/6-31G\*\* calculations of (TTF)-(DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>. (a) planar and (b) twisted.



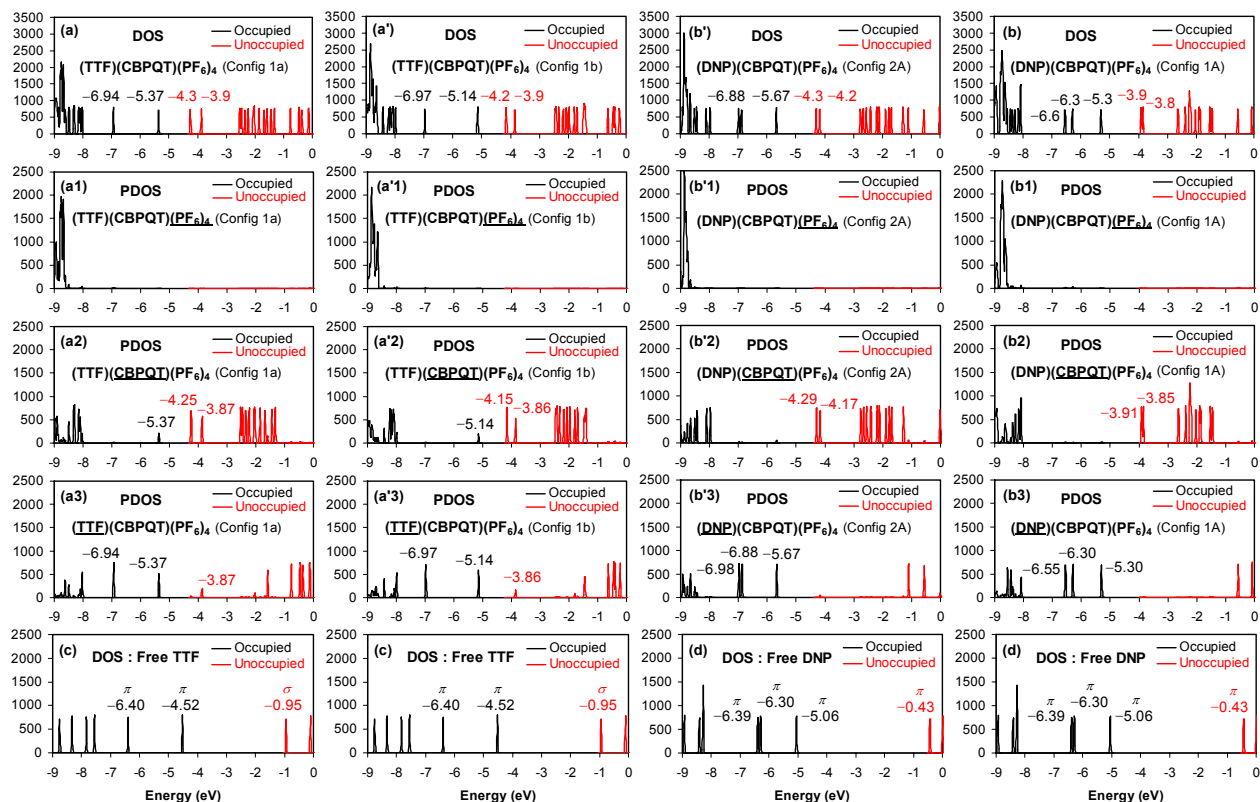
**Figure S16.** DOS's and PDOS's from PBE/6-31G\*\* calculations on the planar conformation of (a) (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>-(DNP) and (b) (TTF)-(DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>.



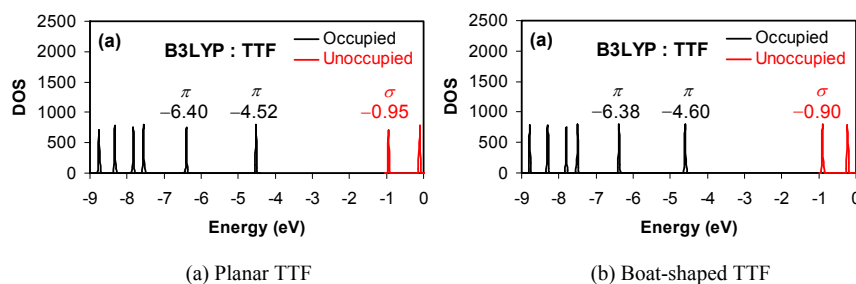
**Figure S17.** DOS's and PDOS's from PBE/6-31G\*\* calculations on the twisted conformation of (a) (TTF)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>-(DNP) and (b) (TTF)-(DNP)(CBPQT)(PF<sub>6</sub>)<sub>4</sub>.



## C. Alternative configurations



**Figure S18.** DOS and PDOS from B3LYP/6-31G\*\* calculations for two different configurations of  $(\text{TTF})(\text{CBPQT})(\text{PF}_6)_4$  and  $(\text{DNP})(\text{CBPQT})(\text{PF}_6)_4$ . (a)  $(\text{TTF})(\text{CBPQT})(\text{PF}_6)_4$  in **Configuration 1a**, (a')  $(\text{TTF})(\text{CBPQT})(\text{PF}_6)_4$  in **Configuration 1b**, (b')  $(\text{DNP})(\text{CBPQT})(\text{PF}_6)_4$  in **Configuration 2A**, and (b)  $(\text{DNP})(\text{CBPQT})(\text{PF}_6)_4$  in **Configuration 1A**. These figures include the PDOS of each fragment (TTF/DNP, CBPQT, and  $\text{PF}_6$ ) shown together. (c) DOS of free TTF. (d) DOS of free DNP.



**Figure S19.** DOS from B3LYP/6-31G\*\* calculations for two different minimum conformations of TTF. (a) Planar TTF and (b) boat-shaped TTF. The frontier orbital energy levels are very similar to each other, with the peak shifts less than 0.1 eV, which is much smaller than the shifts caused by forming a complex with  $(\text{CBPQT})(\text{PF}_6)_4$ .