Electronic Supplementary Information for

Rational Modifications of PCN-700 to Induce Electrical Conductivity: A Computational Study

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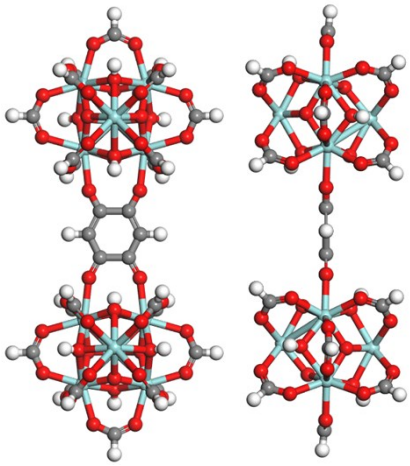
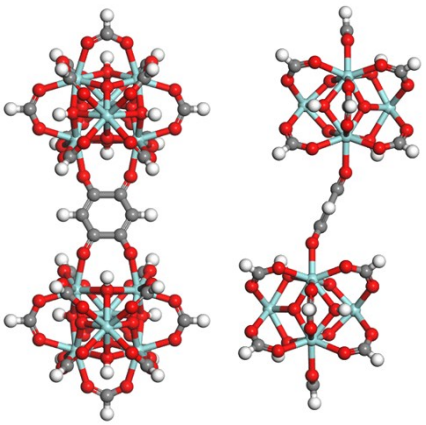
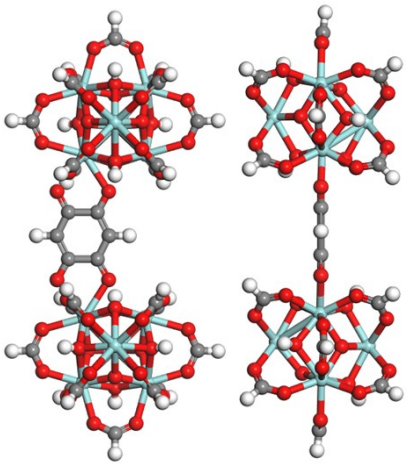
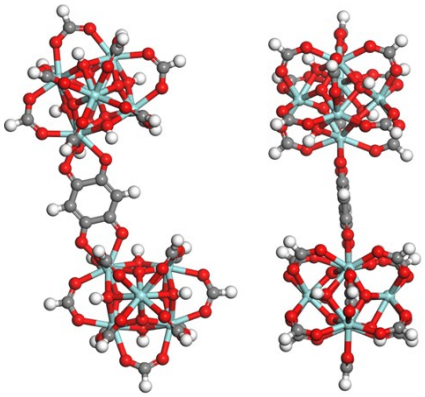
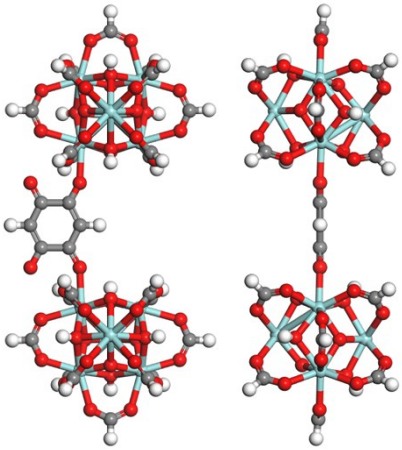
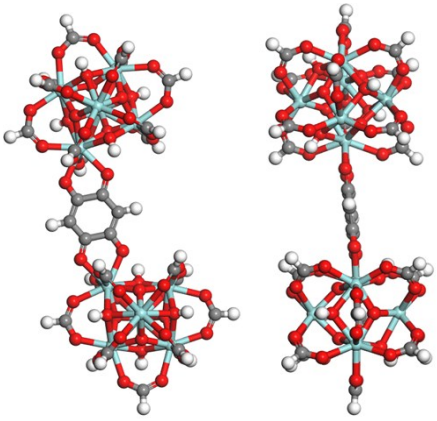
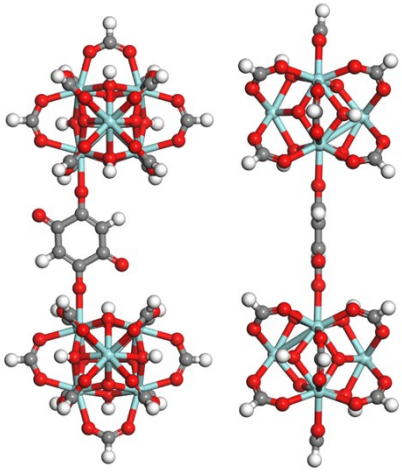
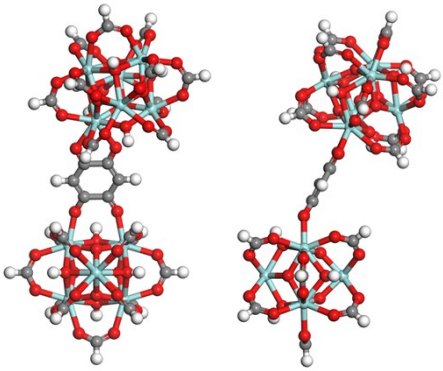
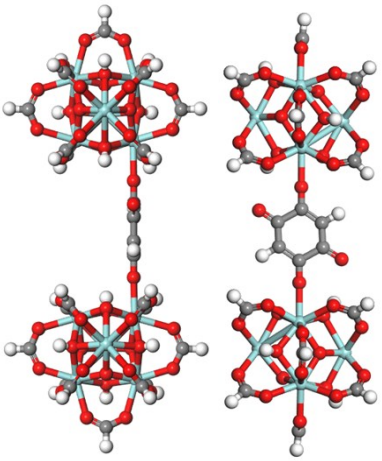
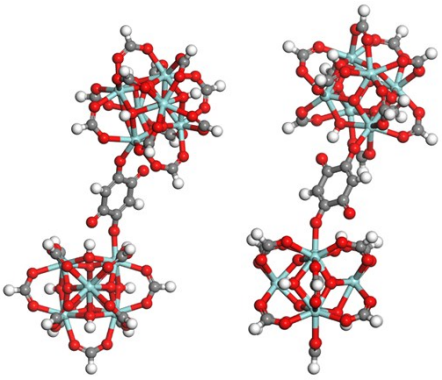
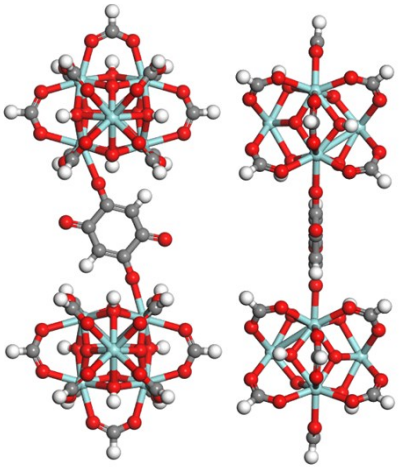
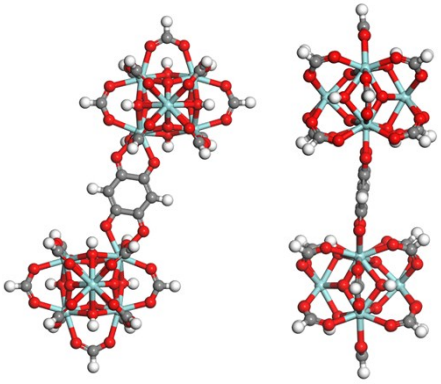
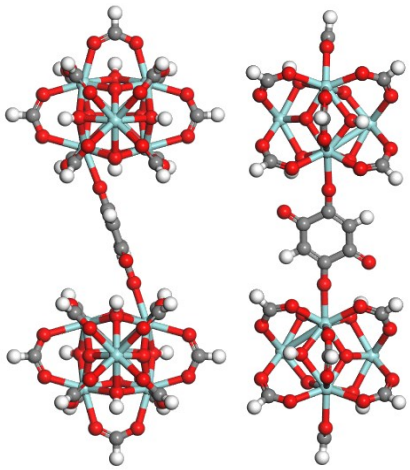
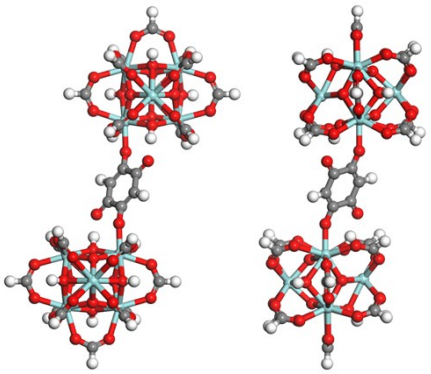
Table S1. Tested coordination configurations of DHBQ between two $Zr_6O_4(OH)_4$ clusters.

Configuration	Initial	DFT-Relaxed
1		
2		
3		

Configuration	Initial	DFT-Relaxed
4		
5		
6		

Configuration	Initial	DFT-Relaxed
7		

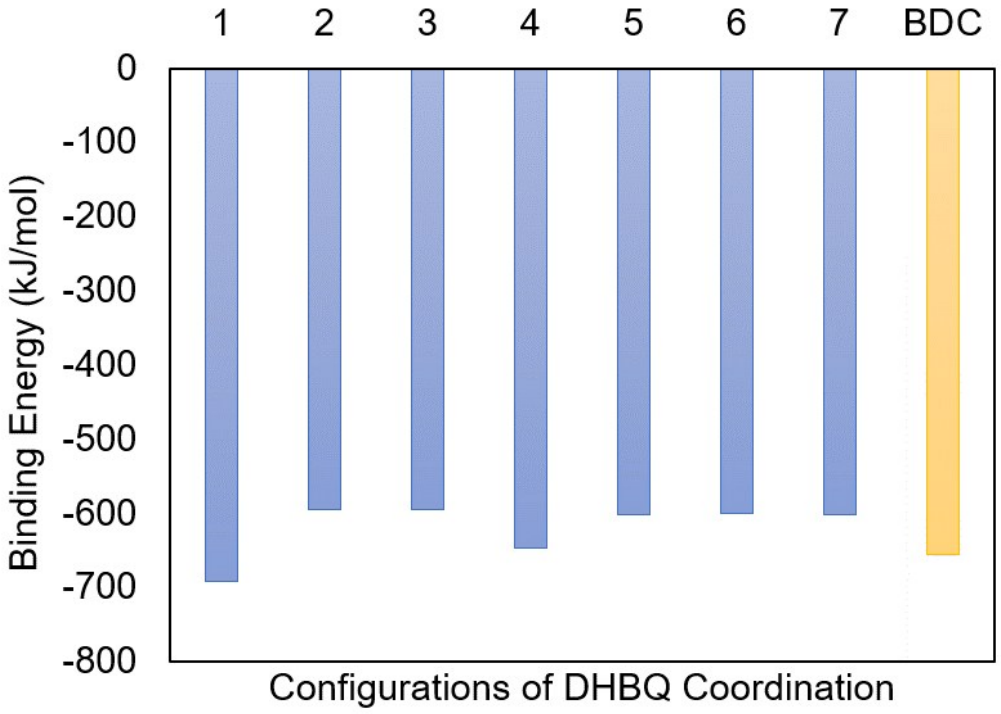


Figure S1. Binding energies from seven cases of DHBQ coordination between two $Zr_6O_4(OH)_4$ clusters. Results for BDC is also presented for comparison. Post-relaxation configuration of case 1, which is the most stable out of DHBQ coordination cases, is presented to the right.

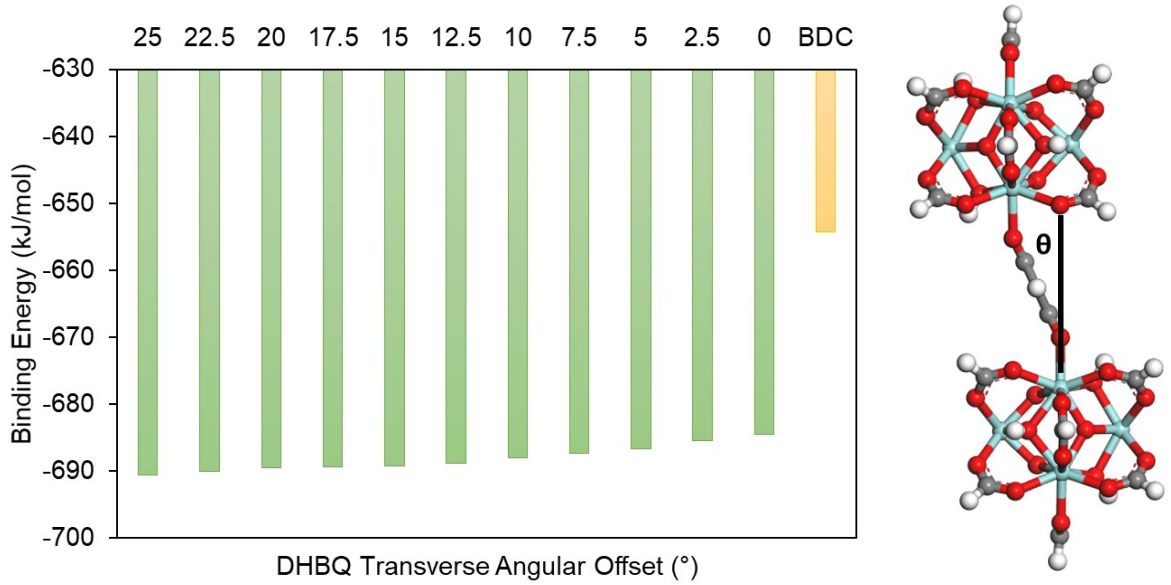


Figure S2. Binding energies of DHBQ coordinated between two $Zr_6O_4(OH)_4$ clusters with 1:1 metal-to-oxygen ratio, under different transverse angular offsets. Binding energy of BDC is also presented for comparison.

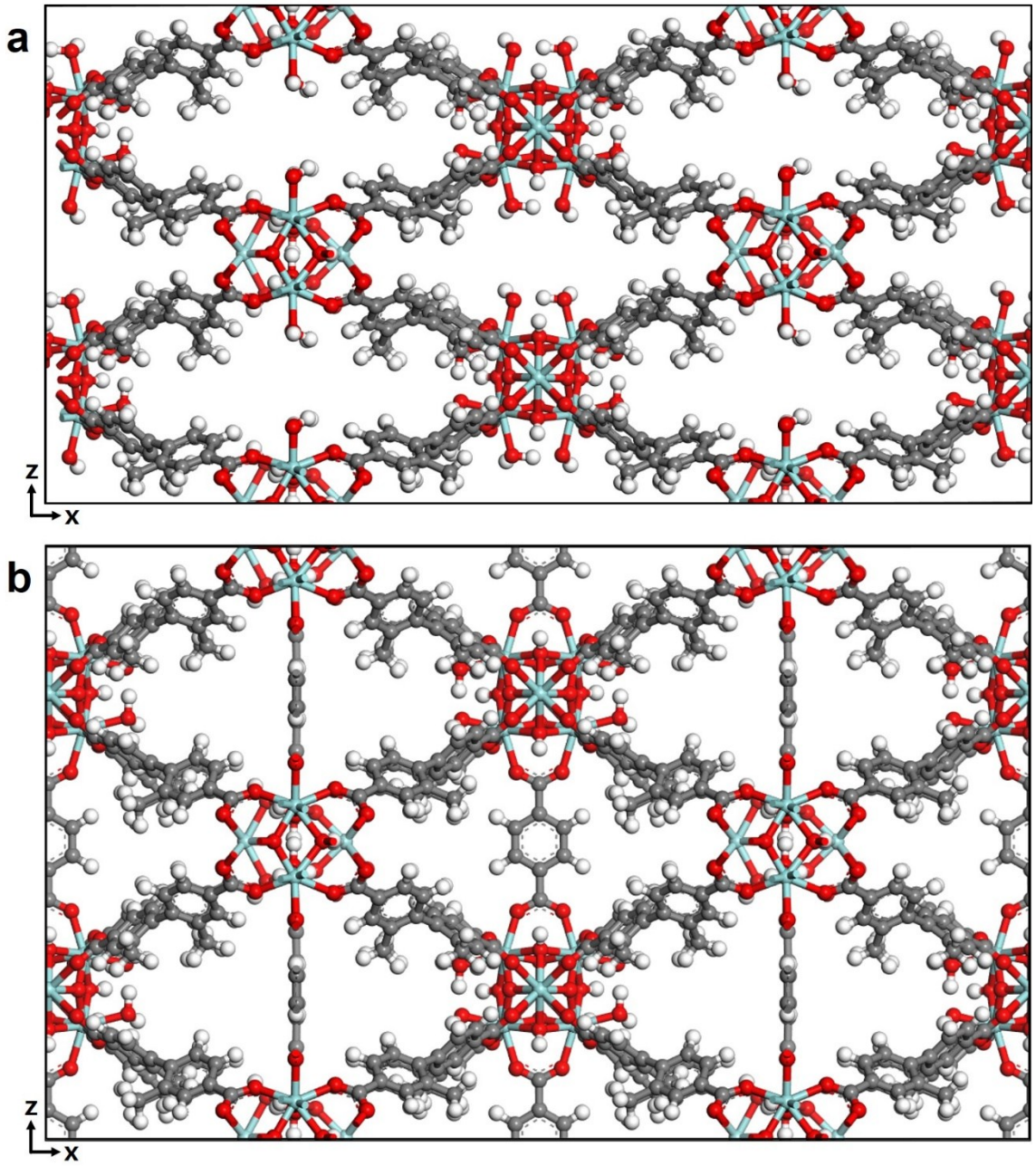


Figure S3. DFT optimized Structures of (a) PCN-700 and (b) PCN-700-BDC.

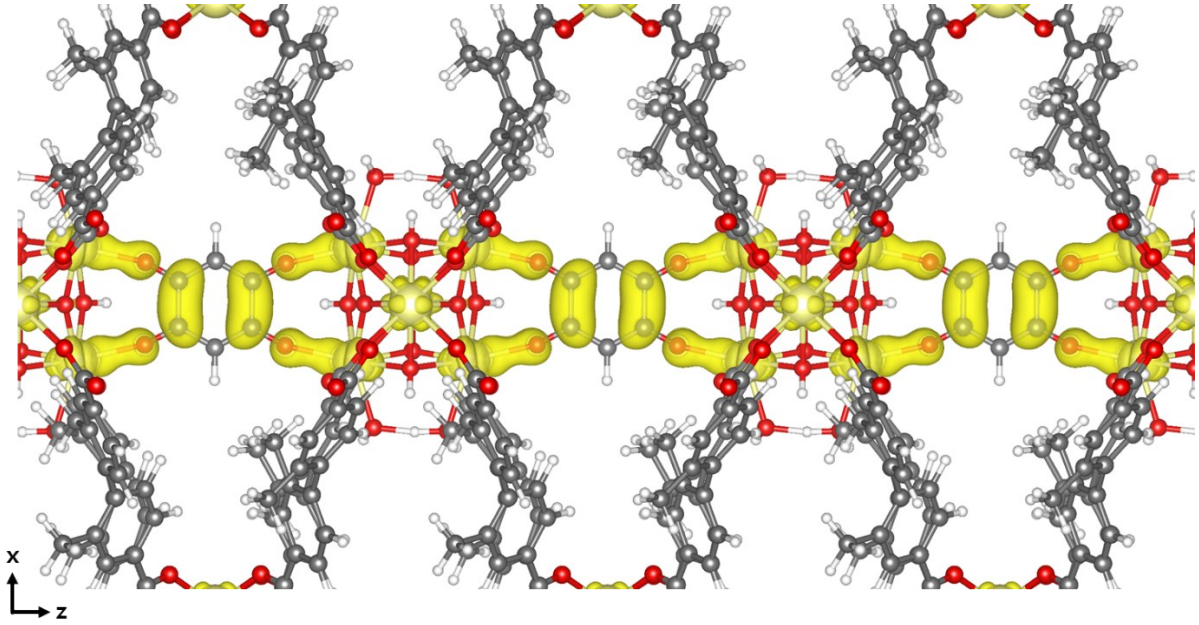


Figure S4. Electron density plot of LUCO in Ce-PCN-700-DHBQ. DHBQ linkers are only installed onto the z-axial vacant sites, and x/y-axial vacant sites are modulated with water and hydroxyl groups.

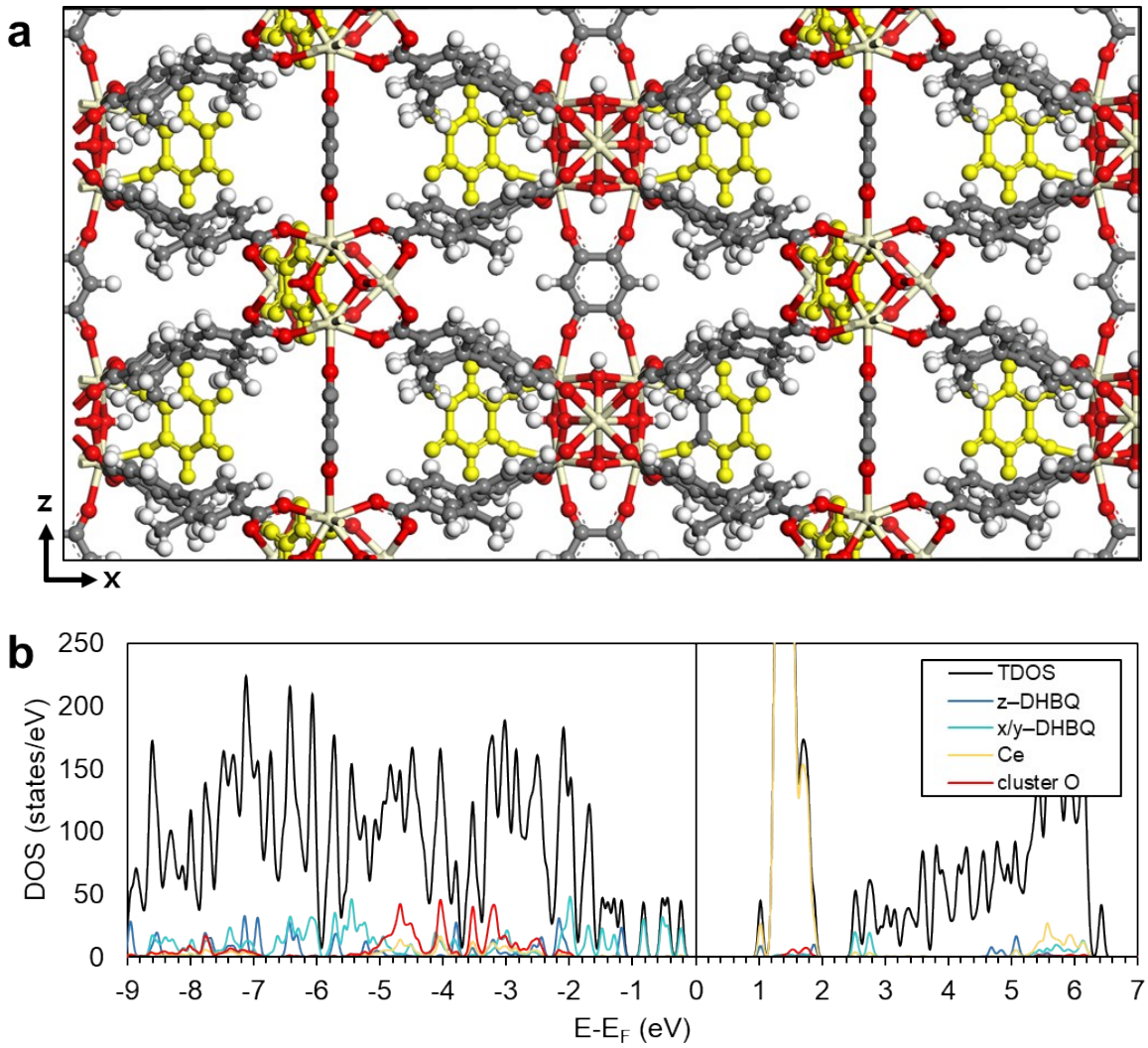
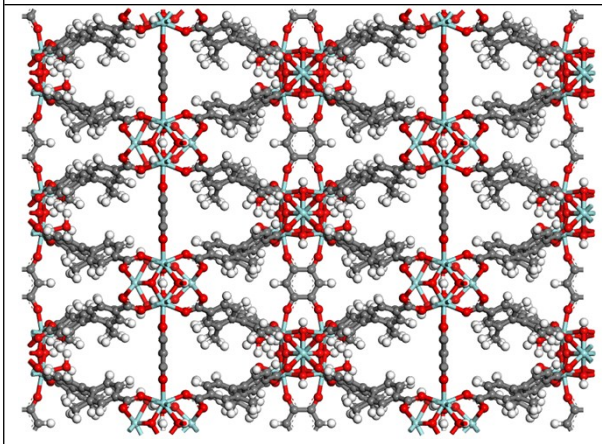
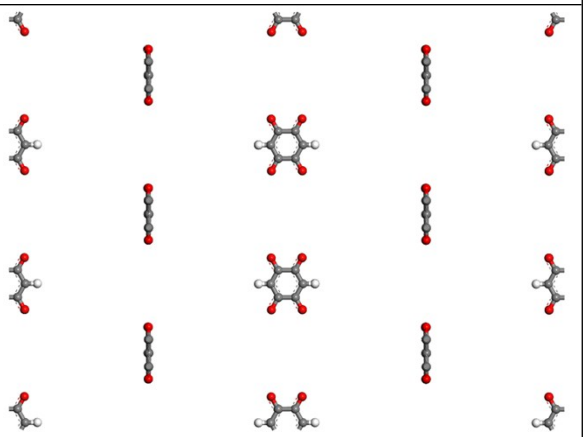
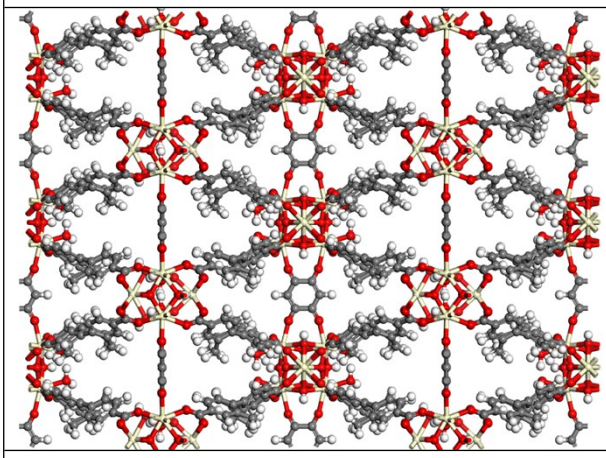
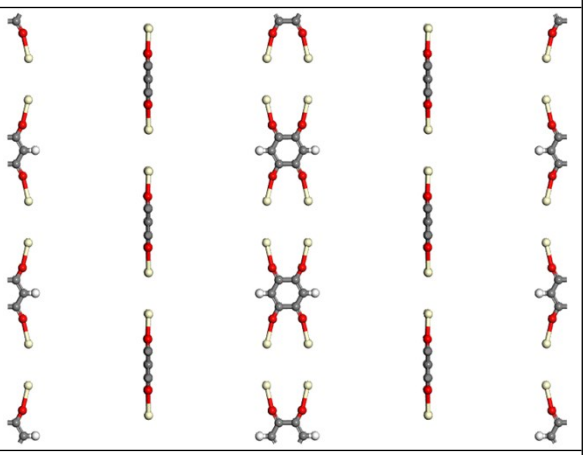


Figure S5. (a) Relaxed structure of linker saturated Ce-PCN-700-DHBQ with additionally coordinated DHBQ linkers in anionic state. x/y-axial DHBQ linkers are highlighted in yellow. (b) PDOS of linker saturated Ce-PCN-700-DHBQ with reduced x/y-axial DHBQ linkers.

Table S2. Each rationally modified MOF systems designed and considered in this work. MOF components that comprise the frontier orbitals are shown together. Continuous CT pathways in frontier orbitals is only achieved in linker saturated Ce-PCN-700-DHBQ.

Modified MOF systems	MOF components comprising the frontier orbitals
PCN-700-DHBQ	
	
Although π-delocalized orbitals of DHBQ are found to comprise the frontier orbitals, they are discontinuous. Metal clusters must be present in the frontier orbitals.	
Ce-PCN-700-DHBQ	
	
Metal substitution has newly incorporated cerium ions into the frontier. Nonetheless, frontier orbitals are still discontinuous at the metal clusters due to the oxygen atoms of metal-oxo units. Detouring paths are still needed.	

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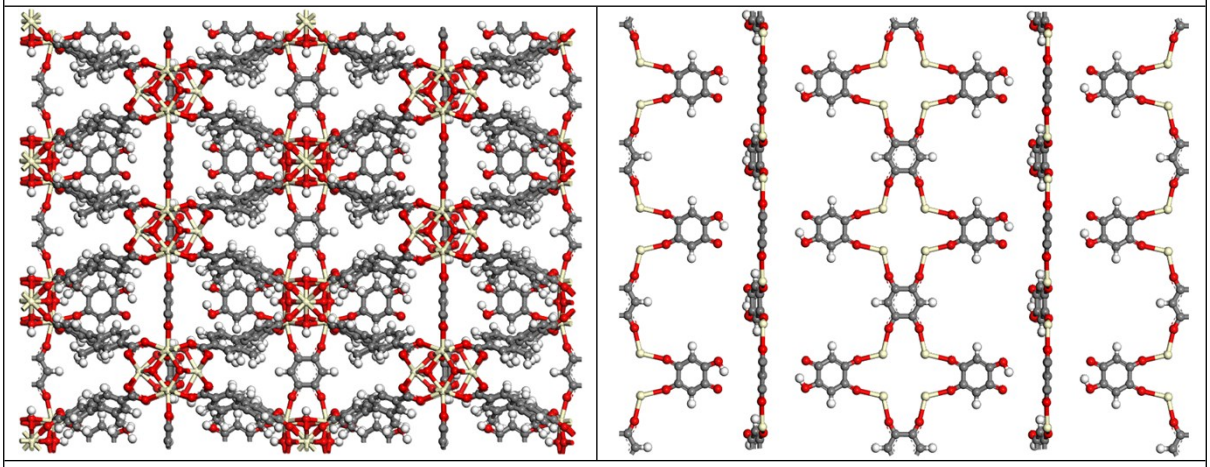
Linker saturated Ce-PCN-700-DHBQ



Continuous charge transport pathways are now created with the additional DHBQ linkers at the x/y-axial vacant sites serving as detour paths. **Conditions for long-range CT are now met.**