Superconductivity in sodium-doped triphenylene

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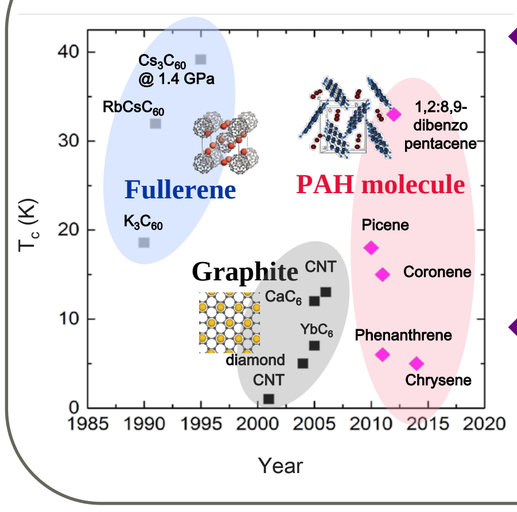
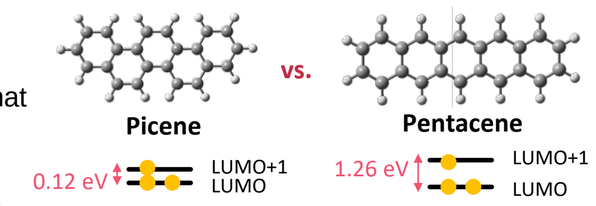
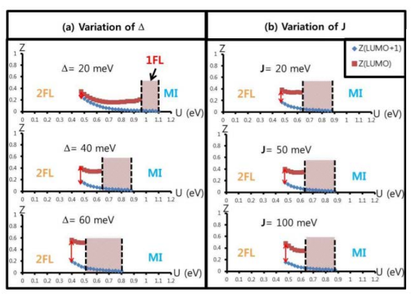
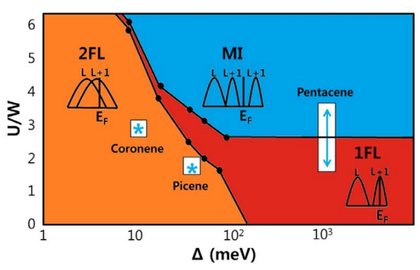
Introduction



- It was firstly reported in 2010 [1] that the picene crystal with doping of 3 equiv. of potassium atoms exhibit superconductivity. This category is called polycyclic aromatic hydrocarbon (PAH) superconductors, and its conjugated sp^2 carbons can delocalize doped electrons .
- It becomes one of core categories of organic SCs in addition to pure carbon-based SCs (fullerene and graphite intercalation compounds (GICs).)



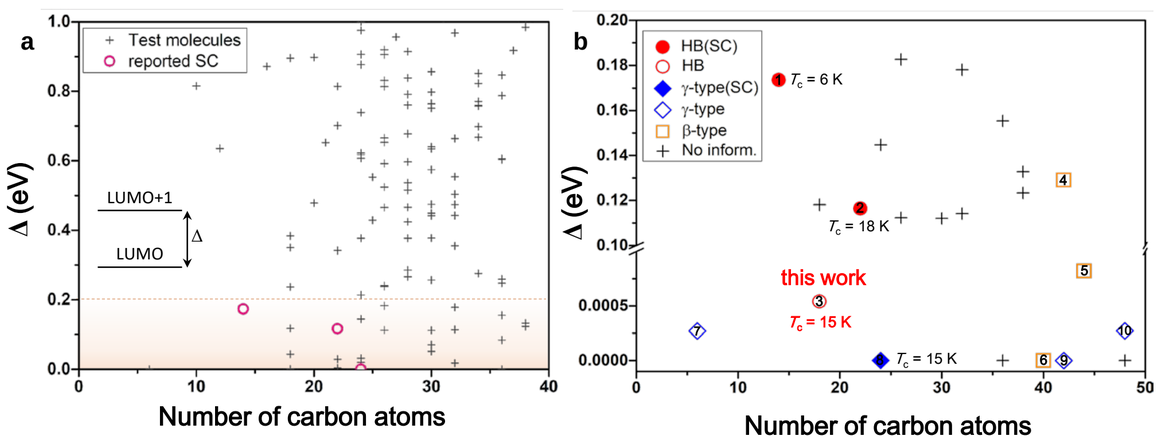


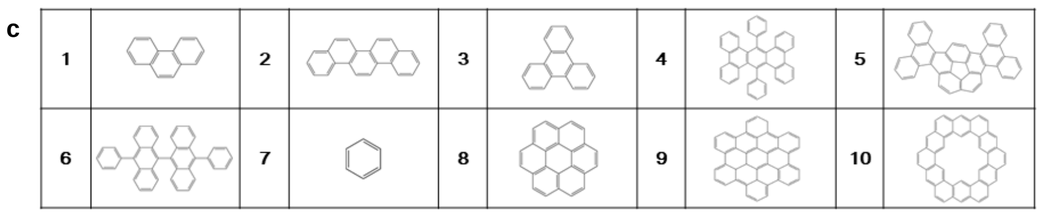


- Picene has almost degenerate LUMO and LUMO+1 states, and it is studied within DMFT that [2] smaller $\Delta = E_{LUMO+1}-E_{LUMO}$ make the system favors two-band Fermi-liquid state (2FL) and also increase the critical U of metal-insulator transition.
- Thus one can obtain the phase diagram of hydrocarbon^{3-} crystal below. PAH molecules with small Δ have high possibility of exhibiting superconductivity when doped with electrons.

- Calculation details
  - (VASP) GGA of PBE exchange-correlation potential with energy difference cutoff 1E-5 eV and 6x2x2 **k**-points mesh.
  - (Gaussian09) B3LYP exchange-correlation functional with 6-31G(d,p) basis.

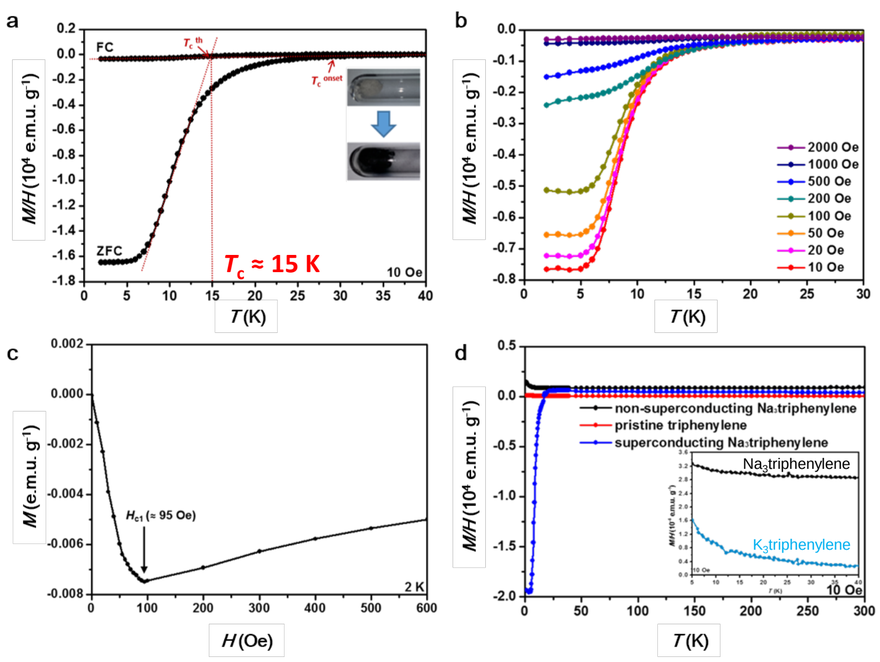
Material Search for PAH SCs



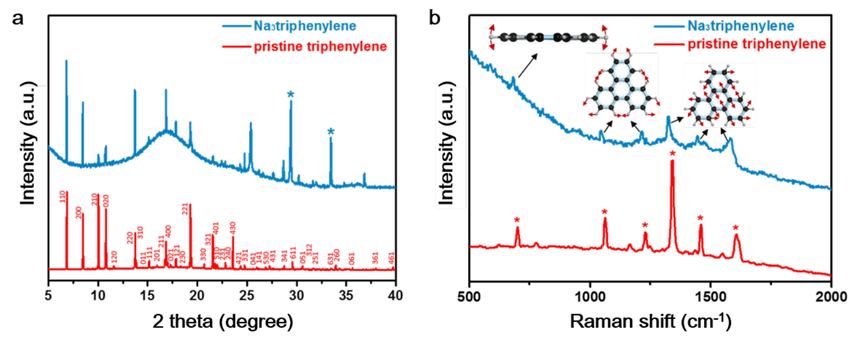


- Δ of 200 PAH molecules are calculated using Gaussian 09 package. In figure **a**, circles are reported superconducting molecules - phenanthrene, picene, and coronene - and all have small value of Δ under 0.2 eV. Besides, it is shown that there are no distinct correlation between the size of PAH molecule and that of Δ.
- The molecular stacking type of PAH molecules identified from experimental reports are depicted in figure **b**. Two of reported PAH SCs have herringbone type stacking, and one have γ-type stacking which is very similar to herringbone. The stacking type is one of the key factor to determine the transport properties of molecular crystals.
- Base on these two molecular-level parmeters, Δ and the stacking type, we found that triphenylene(3 in **c**) crystal has high possibility to exhibit superconductivity when doped with alkali metal atoms.

Sodium-doped triphenylene

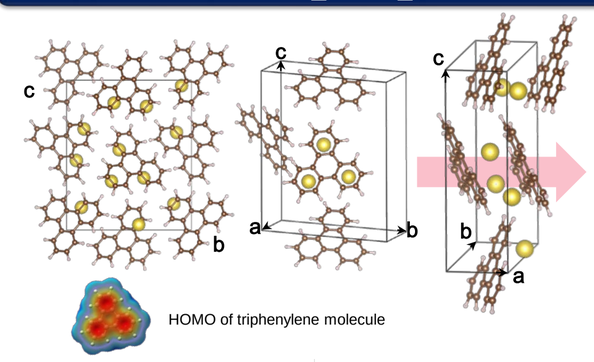


- Sodium-doped triphenylene shows clear Meissner effect with T_c = 15 K.
- It is type-II superconductor having H_{c1} = 95 Oe like potassium-doped picene. The value of H_{c1} is smaller than other PAH SCs - which have about 2-3 times larger H_{c1} - but H_{c2} is very large and was unable to measure.
- Pristine triphenylene is an insulator with the bandgap of about 3 eV. (inset) When doped with 3 equiv. of sodium atoms, it becomes a superconductor.
- Interestingly, non-superconducting Na_3triphenylene sample shows almost constant Pauli-like magnetic susceptibility, which means that it's a paramagnetic metal. On the other hand, K_3triphenylene shows Curie behavior already from 40 K. It suggests that potassium doping results in the Mott insulating state with local spin moments.
- This difference implies that the size of alkali metal atom would play an important role to produce the superconductivity in PAH SCs. Smaller sodium atoms will result in broader bandwith of conduction band so in metallic state.

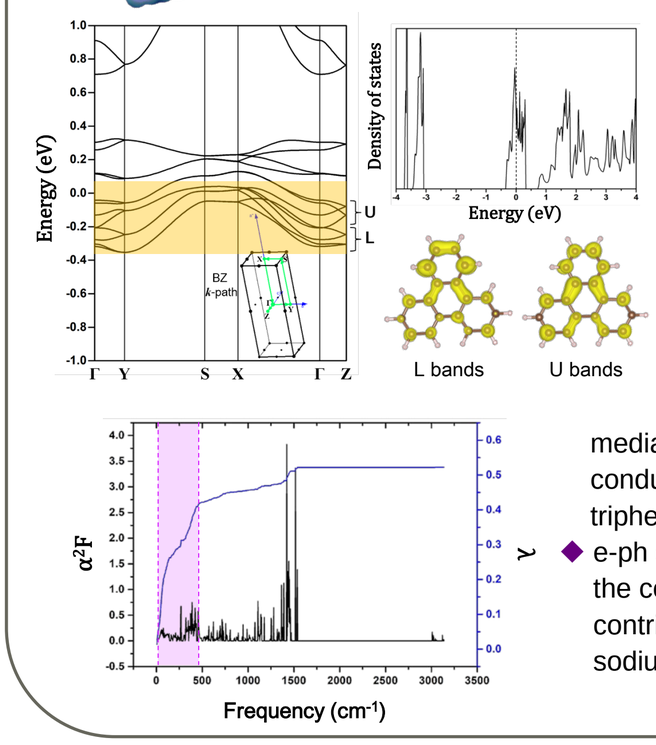


- In superconducting Na_3triphenylene, the main XRD peaks are remained. (a=13.1901, b=16.7708, c=5.2760 Å, and β = 90 °)
- Asterisks in a is marking NaH-related peaks, which may be caused by the decomposition of triphenylene molecules during the annealing.
- Raman spectra of Na_3triphenylene shows that main vibrational peaks of triphenylene molecules and redshift of the peaks, which indicates the charge-transfer from sodium atoms to triphenylene molecule. The broadening of peaks seems to be induced from the formation of amorphous carbon during annealing process, which is considered to be another reason of low shielding fraction.

Electronic properties of Na_3triphenylene



- Crystal structure of Na_3triphenylene was optimized using Quantum Espresso and VASP packages.
- It seems that the herringbone stacking has been still retained after the doping of 3 equiv. of sodium atoms, and they have been positioned between triphenylene molecules with in a sheet of herringbone (*ab*-plane).



- Electronic structure was calculated using VASP. There are 12 bands at the Fermi level, and 8 bands at bottom are mainly from LUMO and LUMO+1 states. They are well hybridized in, so charge density plot of U and L bands both have the characteristics of LUMO and LUMO+1.
- The dispersion is large along *a*-axis, and this can be easily inferred from the crystal structure. The interaction between two triphenylene molecules are seem to be mediated via sodium atoms, so the shape of overall conduction bands are quite different from pristine triphenylene.
- e-ph coupling constant was estimated to ~0.5, and the corresponding T_c was 1.94 K. The low-frequency contribution was dominant, i.e. the contribution of sodium atoms.

Conclusion

- We report a PAH superconductor, sodium-doped triphenylene (Na_3triphenylene), which has T_c of 15 K.
- Magnetic susceptibility of potassium- and sodium-doped triphenylene implies the important role of electronic correlation and bandwidth.
- This material was discovered via material search based on the material database and first-principles calculation. Molecular level parmeters, $\Delta = E_{LUMO+1} - E_{LUMO}$ and stacking types, are investigated to find a molecule with high possibility of superconductivity.
- This computational approach can significantly reduce the cost and time to find a target material.
- It will be worth to try the metal doping for other candidate molecules to see superconductivity.

[1] Ryoji Mitsuhashi. *et al. Nature* **464**, 76-79 (2010)
[2] Minjae Kim, *et al. New J. Phys.* **15**, 113030 (2013)

Computational Materials Design Lab.