Theoretical and experimental study of aromatic hydrocarbon superconductors

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Outline

- Research background
- Research plans
- Theoretical results
- Conclusions

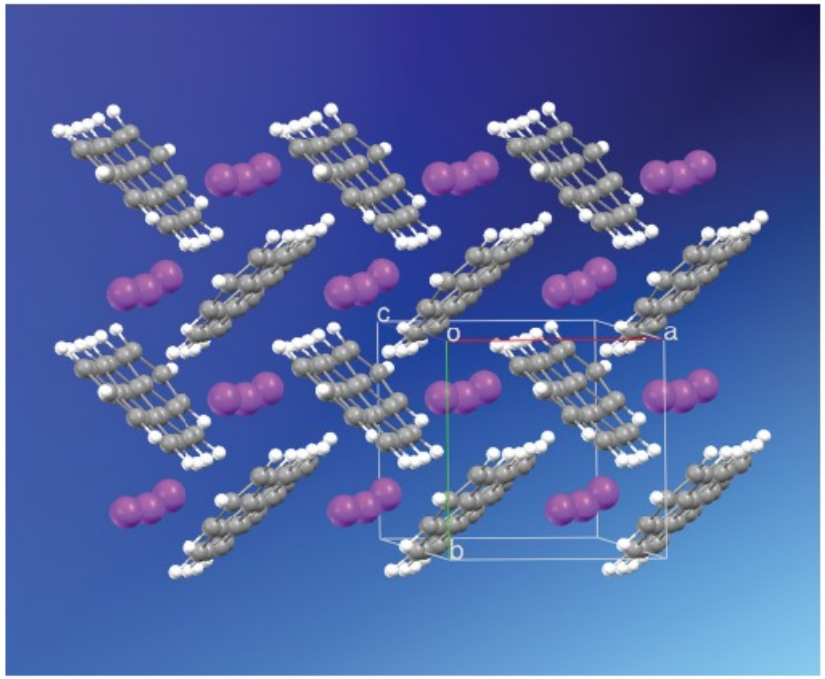
Picene ($C_{22}H_{14}$) (experiment)

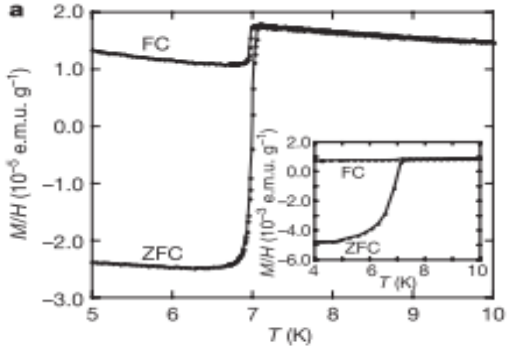
nature Vol 464|4 March 2010|doi:10.1038/nature08859

LETTERS

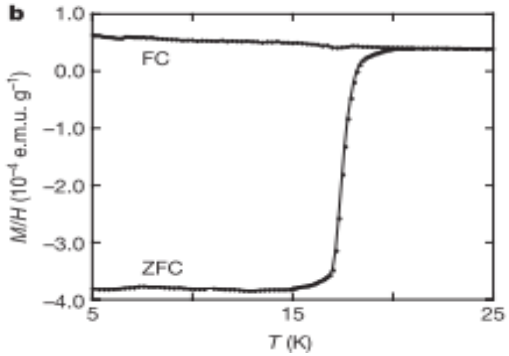
Superconductivity in alkali-metal-doped picene

Ryoji Mitsuhashi[1], Yuta Suzuki[2], Yusuke Yamanari[2], Hiroki Mitamura[1], Takashi Kambe[2], Naoshi Ikeda[2], Hideki Okamoto[3,4], Akihiko Fujiwara[5], Minoru Yamaji[6], Naoko Kawasaki[1], Yutaka Maniwa[7] & Yoshihiro Kubozono[1]





Tc = 7K



Tc = 18 K

PHYSICAL REVIEW B **87**, 060505(R) (2013)

Observation of zero resistivity in K-doped picene

Kazuya Teranishi,[1] Xuexia He,[1] Yusuke Sakai,[1] Masanari Izumi,[1] Hidenori Goto,[1,2] Ritsuko Eguchi,[1] Yasuhiro Takabayashi,[1] Takashi Kambe,[3] and Yoshihiro Kubozono[1,2,*]

[1]*Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan*

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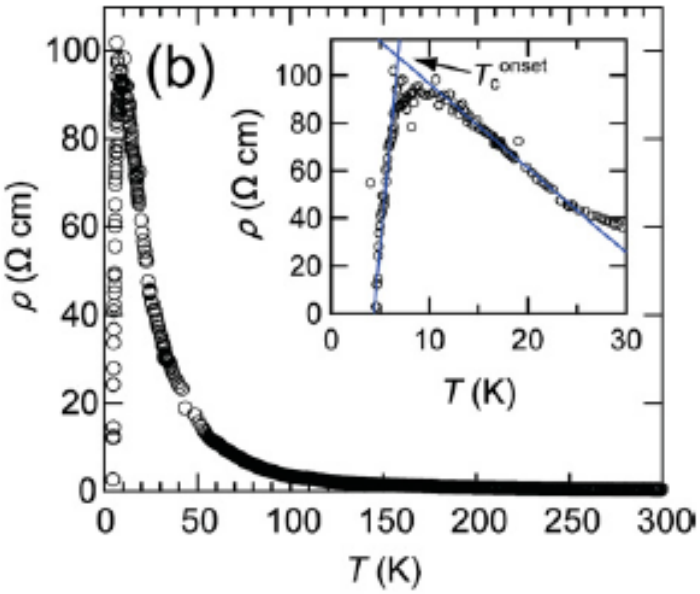
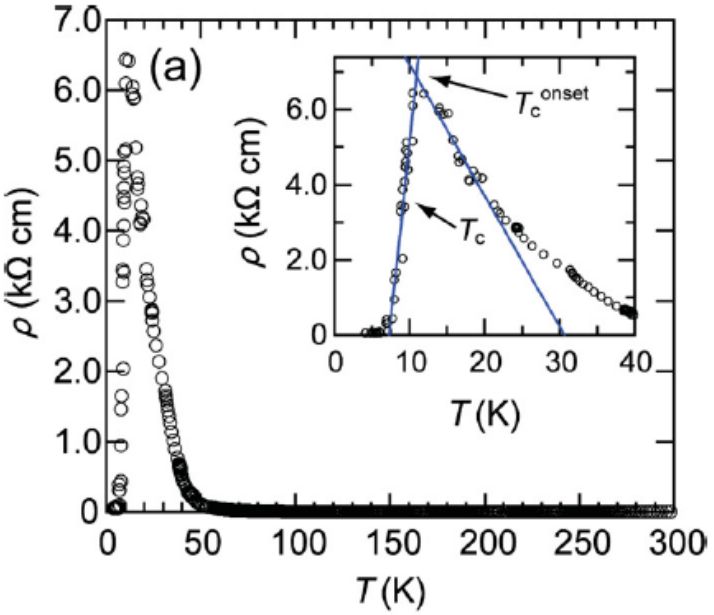
[3]*Department of Physics, Okayama University, Okayama 700-8530, Japan*



$K_{3.1}$picene



$K_{3.5}$picene

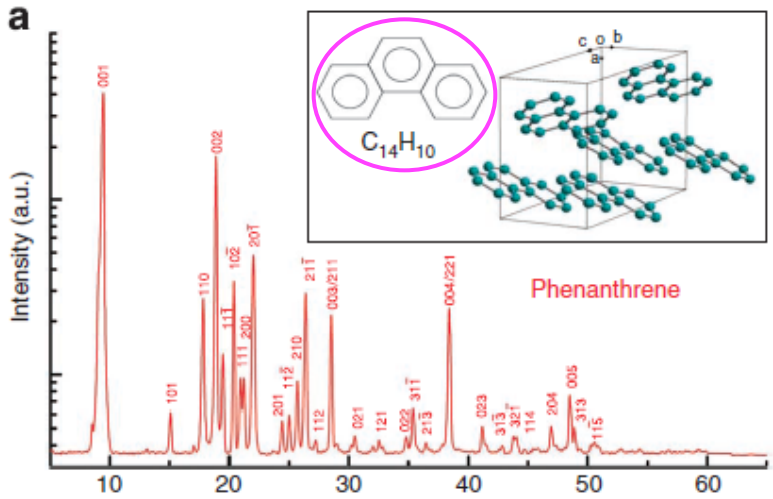
Phenanthrene ($C_{14}H_{10}$) (experiment)

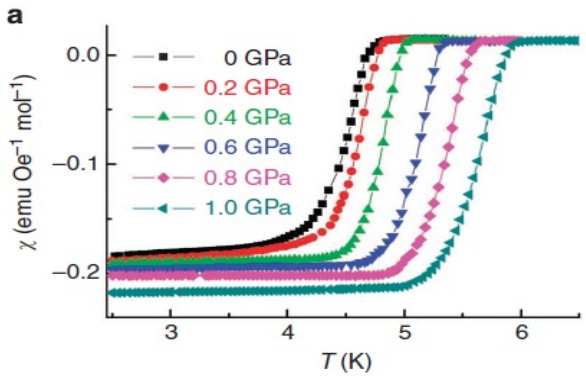
Received 13 Jul 2011 | Accepted 21 Sep 2011 | Published 18 Oct 2011

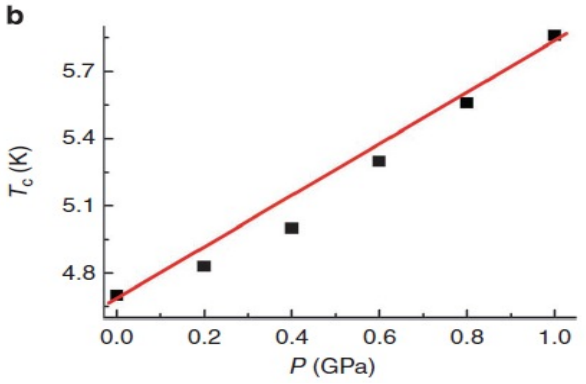
DOI: 10.1038/ncomms1513

Superconductivity at 5 K in alkali-metal-doped phenanthrene

X.F. Wang[1], R.H. Liu[1], Z. Gui[2], Y.L. Xie[1], Y.J. Yan[1], J.J. Ying[1], X.G. Luo[1] & X.H. Chen[1]







Tc ~ 5 K

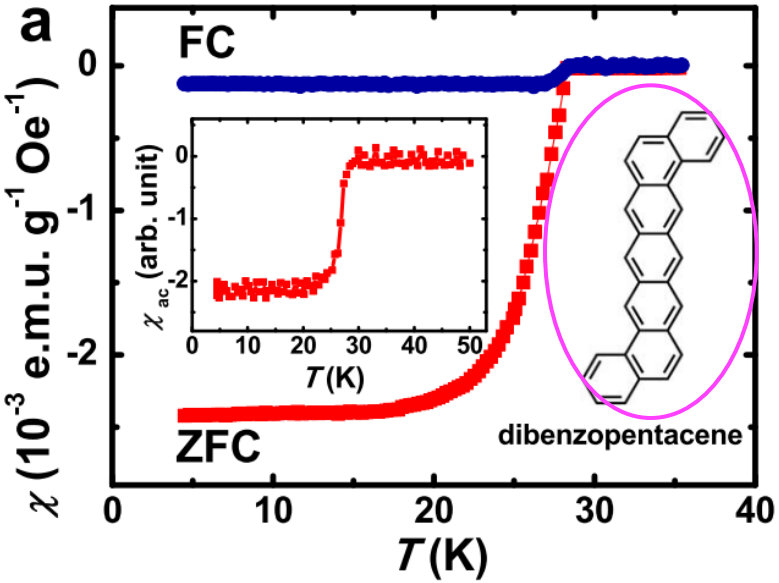
At 1 GPa, 20% increase of Tc

Dibenzopentacene($C_{30}H_{18}$)(experiment)

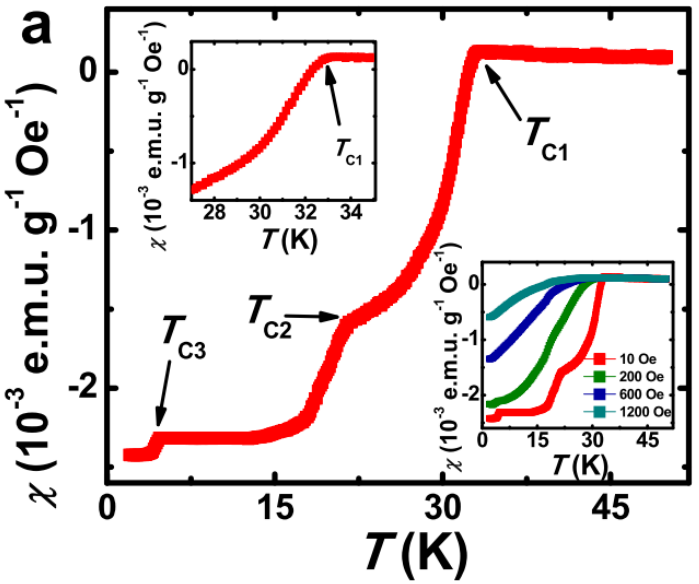
SCIENTIFIC REPORTS | 2 : 389 | DOI: 10.1038/srep00389

Superconductivity above 30 K in alkali-metal-doped hydrocarbon

Mianqi Xue[1,2], Tingbing Cao[2], Duming Wang[3], Yue Wu[1], Huaixin Yang[1], Xiaoli Dong[1], Junbao He[3], Fengwang Li[2] & G. F. Chen[1,3]



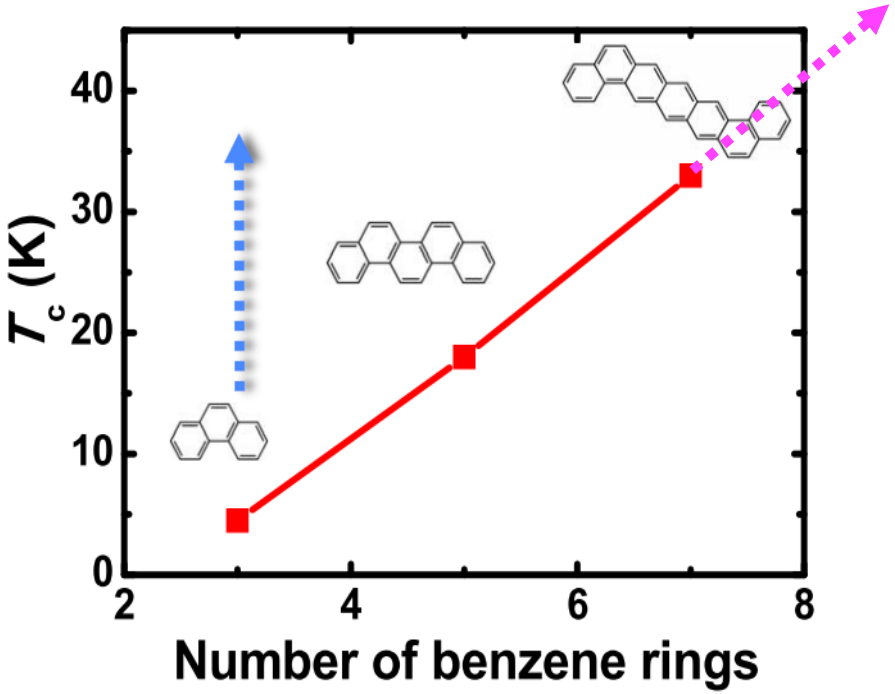
Tc ~ 28-33 K



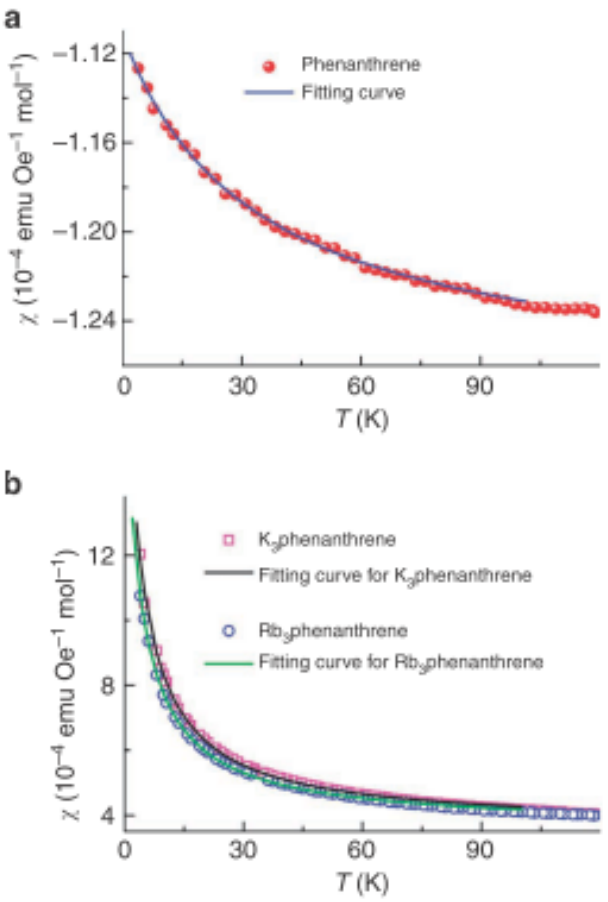
Tc1 ~ 33K, Tc2 ~ 22K, Tc3 ~ 4K

Important properties (experiment)

ambition



T_c increases with increasing the Number of benzene rings!



Curie-Weiss magnetic behavior

→ **local spin (~0.2μ_B)**

$C_{22}H_{14}$ (theory)

PHYSICAL REVIEW B **83**, 134508 (2011)

Electronic correlation effects in superconducting picene from *ab initio* calculations

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(Received 16 November 2010; revised manuscript received 21 February 2011; published 7 April 2011)

PHYSICAL REVIEW B **83**, 214510 (2011)

Density functional calculations of electronic structure and magnetic properties of the hydrocarbon K_3picene superconductor near the metal-insulator transition

Minjae Kim and B. I. Min*
Department of Physics, PCTP, Pohang University of Science and Technology, Pohang 790-784, Korea

Geunsik Lee, Hee Jae Kwon, Y. M. Rhee, and Ji Hoon Shim†
Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea
(Received 8 April 2011; revised manuscript received 27 April 2011; published 9 June 2011)

Effective Coulomb interaction between electrons U_{eff} is larger than the bandwidth W near the Fermi energy.

↓

Picene is a strongly correlated electron system.

$C_{22}H_{14}$ (theory)

PRL 107, 137006 (2011) PHYSICAL REVIEW LETTERS week ending 23 SEPTEMBER 2011

Intercalant and Intermolecular Phonon Assisted Superconductivity in K-Doped Picene

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[2]*SPIN-CNR–Dipartimento di Fisica, Università degli Studi di L'Aquila, 67100 L'Aquila, Italy and Max-Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*
(Received 8 June 2011; published 21 September 2011)

$\lambda = 0.73$, $\omega_{log} = 18.0$ meV (208 K)
Intercalant and intermolecular phonon modes contribute substantially (40%) to λ as also shown by the isotope exponents of potassium (0.19) and carbon (0.31).

Unlike C60, where intramolecular phohons dominate λ.

Open questions:

1. What are the crystal and electronic structures for the superconducting phase?
2. What is the physical origin for local spin?
3. Does electron correlation contribute to superconductivity?
4. Do there exist new aromatic superconductors?

Motivation for our study

Research plans:

Methods based on Density functional theory (LDA, GGA, HSE,…)

- Properties of molecular crystals
- Models of molecular crystals

Methods based on Many body theory (QMC, ED, DMFT…)

- Properties of models
- Electronic correlation effects beyond DFT

Experimental study (ongoing…)

Theoretical results

- **Magnetic and pairing properties of single molecule and molecular crystal**

  (Scientific Reports 2, 922, 2012, JAP 113, 17E131, 2013)

- **Identify the crystal structures for metal-doped picene**

  (arXiv: 1407.0747)

- **Identify the crystal structures for La/Ba-doped phenanthrene**

  (JCP 139, 204709, 2013, under review in JCP)

- **Prediction of superconductivity in K,Ba-codoped phenanthrene (unpublished)**
- **Prediction of superconductivity in K-doped benzene (unpublished)**

OPEN

Magnetic instability and pair binding in aromatic hydrocarbon superconductors

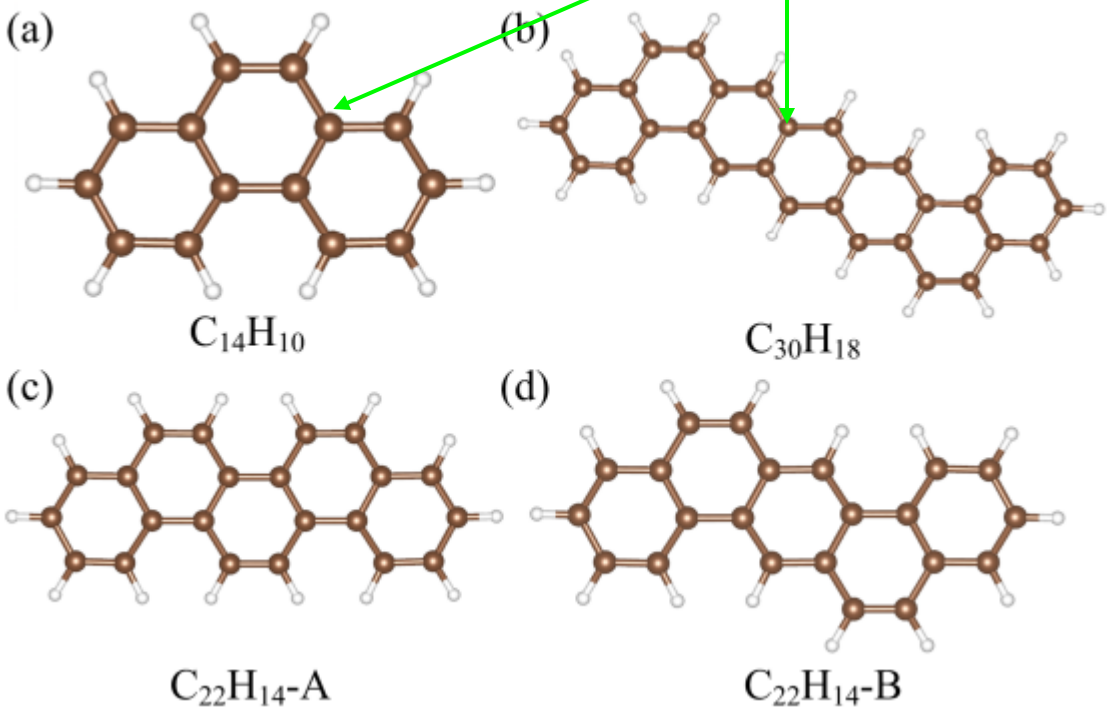
SUBJECT AREAS:
PHYSICS

Zhongbing Huang[1,2], Chao Zhang[1] & Hai-Qing Lin[1]

Scientific Reports 2, 922 (2012).

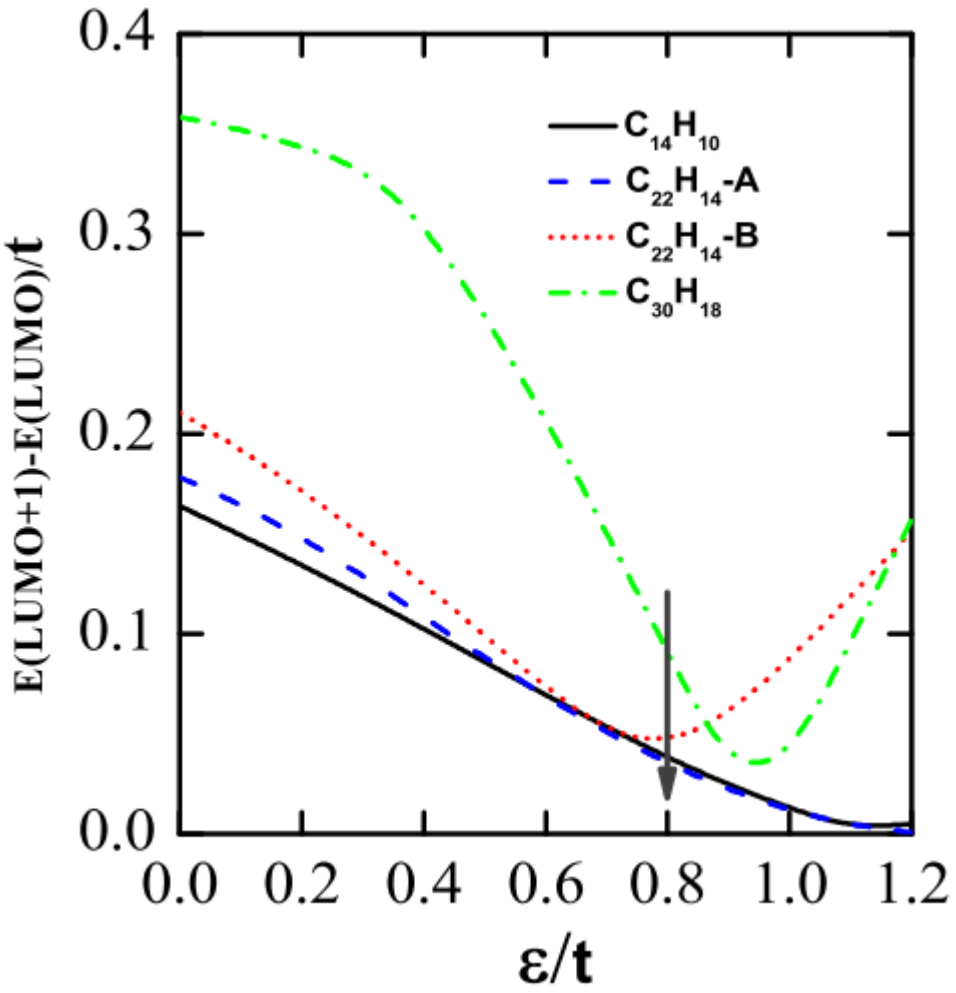
Starting point: One-orbital Hubbard model defined on a single molecule.

$$H = -t \sum_{\langle ij \rangle, \sigma} (c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma}) - \epsilon \sum_{i}{}' n_i + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$



t~2.7-3.0 eV

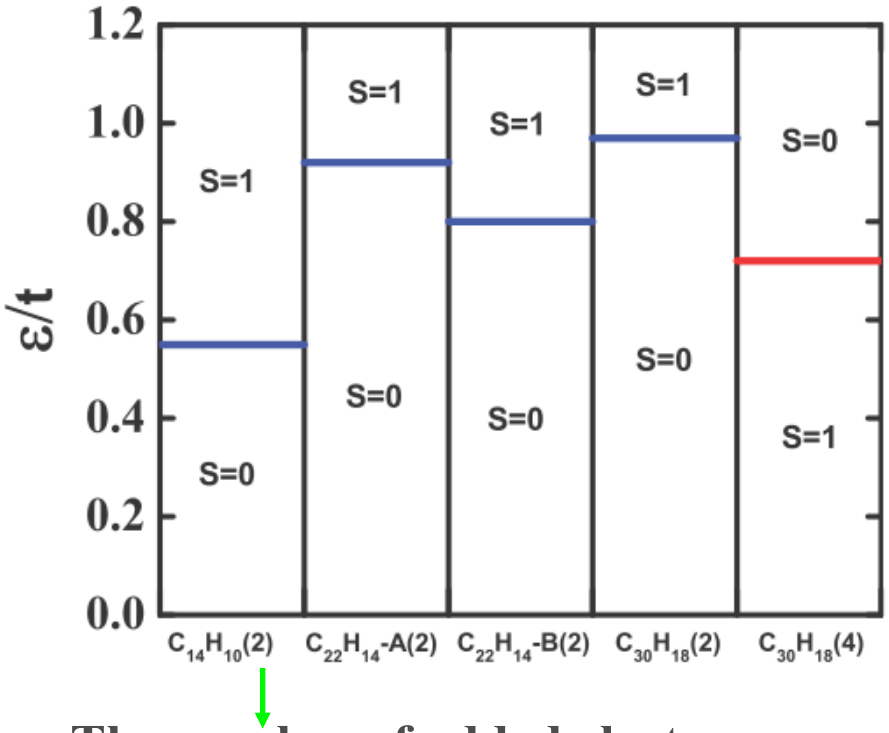
U/t~1-4

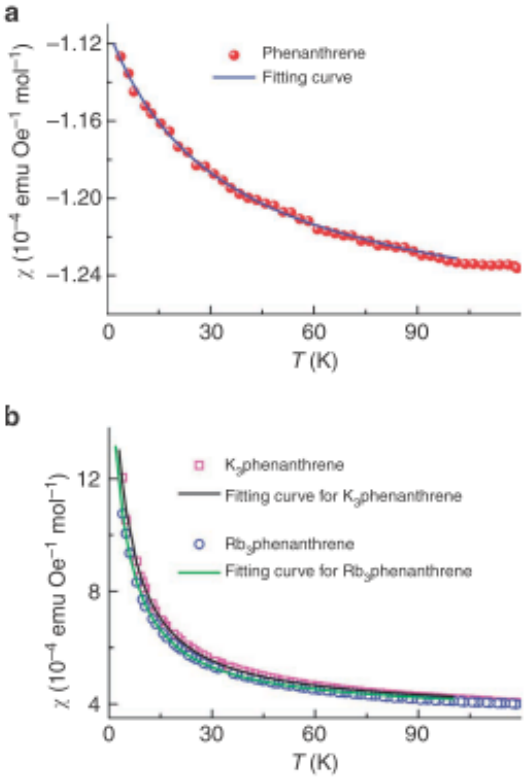


Density Functional Theory:
$C_{22}H_{14}$-A:
E(LUMO+1)-E(LUMO) < 0.1 eV

$\epsilon > 0.8t$

Spin phase diagram





The number of added electrons.

For the charged molecules with two added electrons, the spin polarized state (S=1) has lower energy than the paramagnetic state (S=0).

↓

local spin

nature Vol 464 | 4 March 2010 | doi:10.1038/nature08859

LETTERS

Superconductivity in alkali-metal-doped picene

Table 1 | List of $A_x$picene (A: alkali-metal) samples prepared in this study

A	x	Annealing temperature (K)	Annealing time (days)	Physical properties	Shielding fraction
K	1.0	440	6.5	Pauli-like	NA
K	1.8	440	7.0	Pauli-like	NA
K	**2.6**	**440**	**8.0**	**SC (T_c = 6.5 K)**	**≪ 0.1%**
K†	**2.9**	**440**	**9.0**	**SC (T_c = 7.0 K)**	**0.1%**
K	**3.0**	**440**	**8.0**	**SC (T_c = 6.5 K)**	**≪ 0.1%**
K	**3.0**	**440**	**9.0**	**SC (T_c = 17 K)**	**0.1%**
K	**3.1**	**440**	**4.0**	**SC (T_c = 7.4 K)**	**<0.1%**
K	**3.3**	**440**	**21.0**	**SC (T_c = 8 K)**	**≪ 0.1%**
***K‡**	**3.3**	**440**	**21.0**	**SC (T_c = 6.9 K)**	**15%**
K	**3.3**	**440**	**8.5**	**SC (T_c = 7.1 K)**	**≪ 0.1%**
K	**3.3**	**440**	**11.0**	**SC (T_c = 18 K)**	**0.55%**
***K§**	**3.3**	**440**	**11.0**	**SC (T_c = 18 K)**	**1.2%**
K	4.0	440	8.0	Curie-like	NA
K	5.1	440	12.5	Curie-like	NA
Na	3.4	570	5.0	Pauli-like	NA
Rb	2.8	440	16.5	Pauli-like	NA
Rb‖	**3.1**	**570**	**6.7**	**SC (T_c = 6.9 K)**	**10%**
Cs	3.0	440	9.0	Metal–insulator transition	NA

Normal state: Curie-like

Effect of nearest-neighbor Coulomb interaction V on the ground state.

TABLE I: V dependence of the energy difference $\Delta E = E(S=1) - E(S=0)$ for the charged molecules with two added electrons at $U = 2t$ and $\epsilon = 1.0t$. Statistical errors are in the last digit and shown in the parentheses.

V	$\Delta E(C_{14}H_{10})$	$\Delta E(C_{22}H_{14} - A)$	$\Delta E(C_{22}H_{14} - B)$
0.0	-0.0452(6)	-0.0074(8)	-0.1073(7)
0.1	-0.0305(6)	0.0009(8)	-0.1041(9)
0.2	-0.0016(8)	0.0121(9)	-0.1017(9)
0.3	-0.0044(8)	0.0257(9)	-0.0965(9)
0.4	0.0134(9)	0.043(1)	-0.090(1)
0.5	0.0289(9)	0.060(1)	-0.086(1)

The energy difference increases with increasing V, making S=0 state more stable than S=1 state for large V.

Pair binding energy

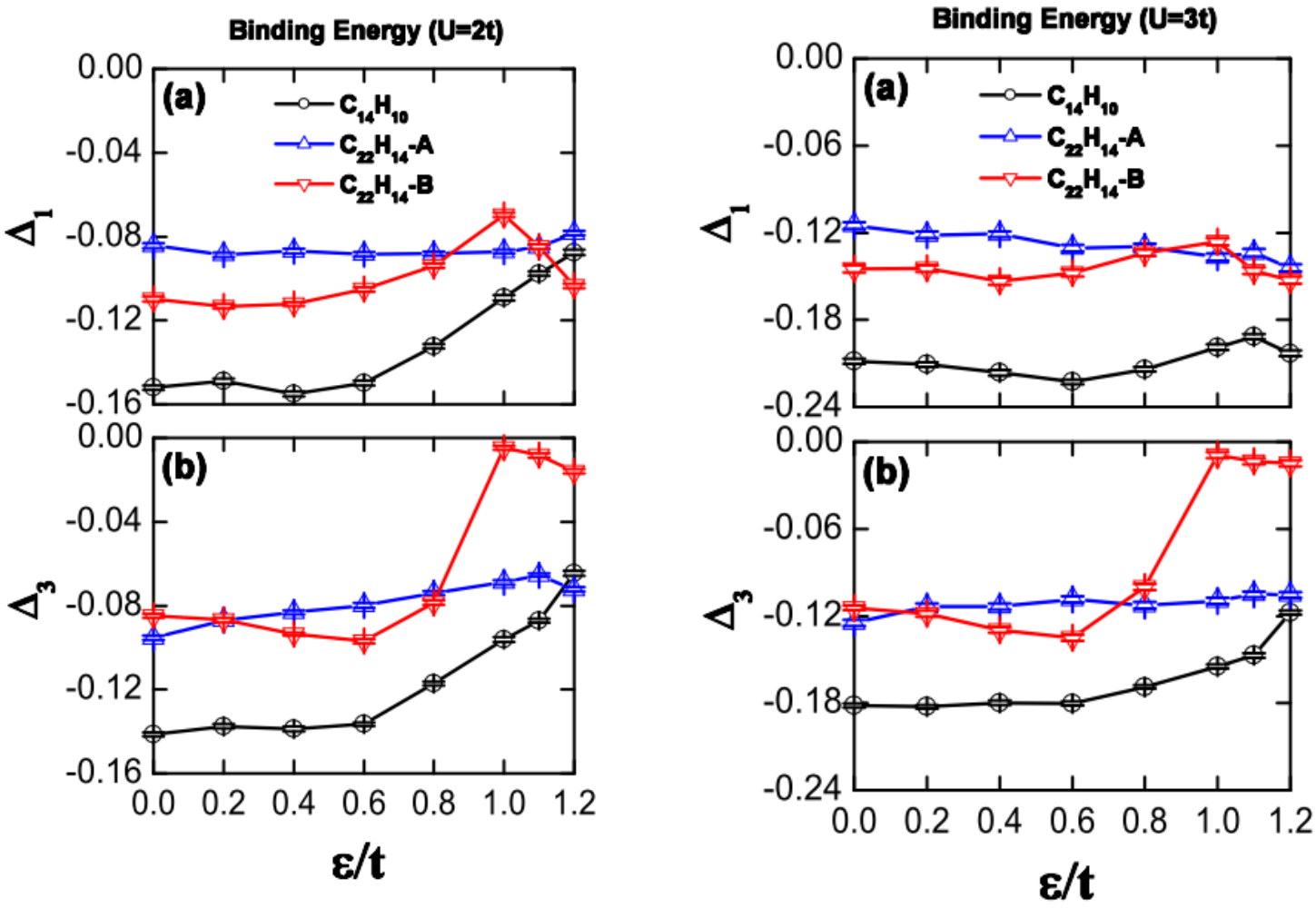
$$\Delta_i = 2E_i - E_{i-1} - E_{i+1} \qquad \text{i=1, 2, 3}$$

>0: attractive interaction for added electrons
<0: repulsive interaction for added electrons

Notes: (1) Applied for the low energy physics of renormalized electrons, not for the bare electrons.

(2) Applied for high-Tc superconductors and C60.

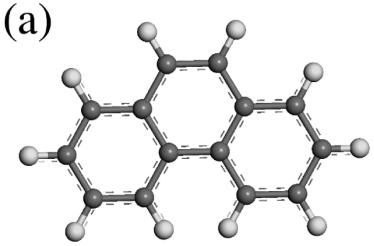
Pair binding energy for picene and phenanthrene



Pair binding energy is always negative => no contribution to formation of Cooper pairs.

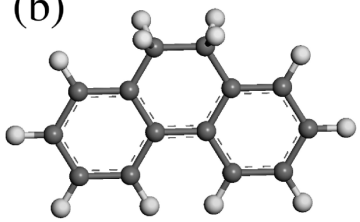
Other aromatic molecules

(a)



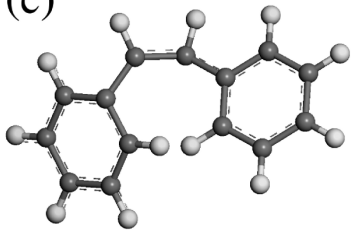
phenanthrene

(b)



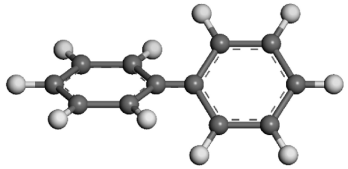
9,10-dihydrophenanthrene

(c)

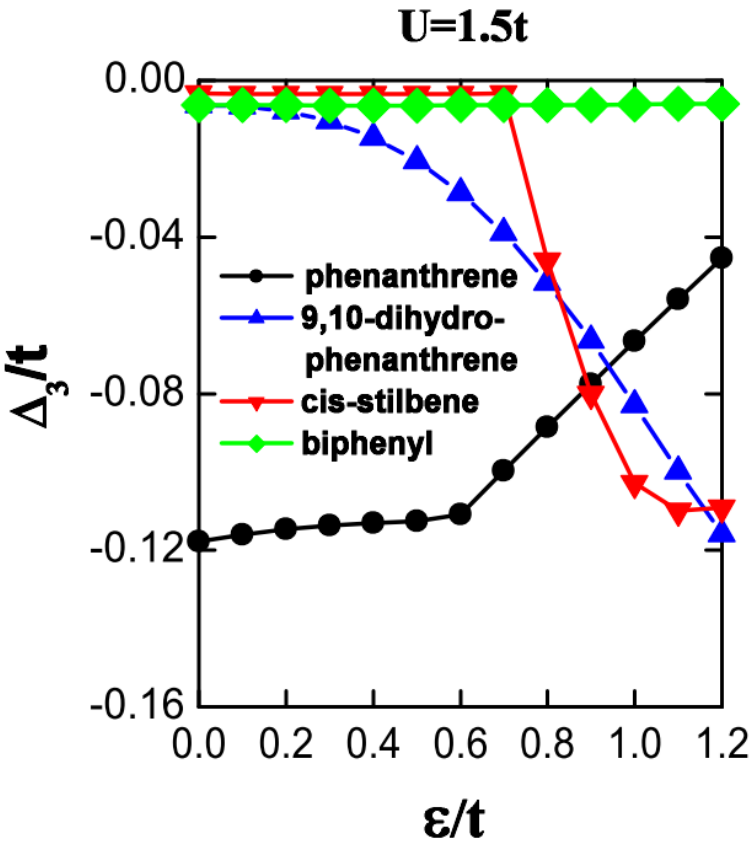


cis-stilbene

(d)



Biphenyl



- In the region ε<0.8t, the pair binding energy for 9,10-dihydro-phenanthrene, cis-stilbene, and biphenyl is much less negative than phenanthrene, suggesting that Coulomb pseudopotential μ* is rather weak in these molecular crystals. → Higher Tc!

Antiferromagnetism in potassium-doped polycyclic aromatic hydrocarbons

Calculated total energies at different magnetic states relative to their ground-states in unit of meV/f.u. and spin magnetic moment M in unit of μ_B/f.u..

System	NM	FM	AFM-1	AFM-2	M
$K_3C_{14}H_{10}$-A	6.2	6.2	∞	0	0.30
$K_3C_{22}H_{14}$-A	15.2	16.2	∞	0	0.42
$K_3C_{22}H_{14}$-B	12.2	11.3	∞	0	0.40
$K_3C_{30}H_{18}$-A	14.6	8.1	∞	0	0.55
$K_3C_{30}H_{18}$-B	19.2	4.4	∞	0	0.53

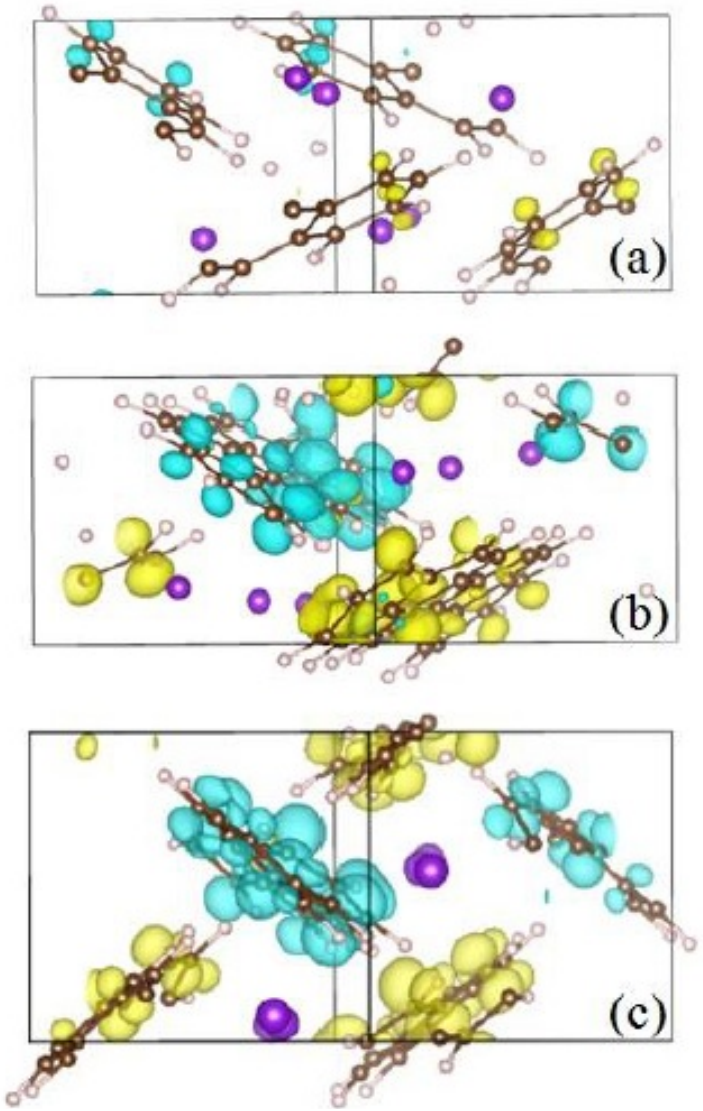
$K_3C_{14}H_{10}$-A: phenanthrene
$K_3C_{22}H_{14}$-A: picene
$K_3C_{22}H_{14}$-B: 1,2:5,6-dibenzanthrancene
$K_3C_{30}H_{18}$-A: 7-phenacene
$K_3C_{30}H_{18}$-B: 1,2:8,9-dibenzopentacene

1. The ground state lies in the AFM-2 state, with spins antiparalleling between two molecular layers
2. The magnetic moment increases with Increasing the benzene numbers

phenanthrene

picene

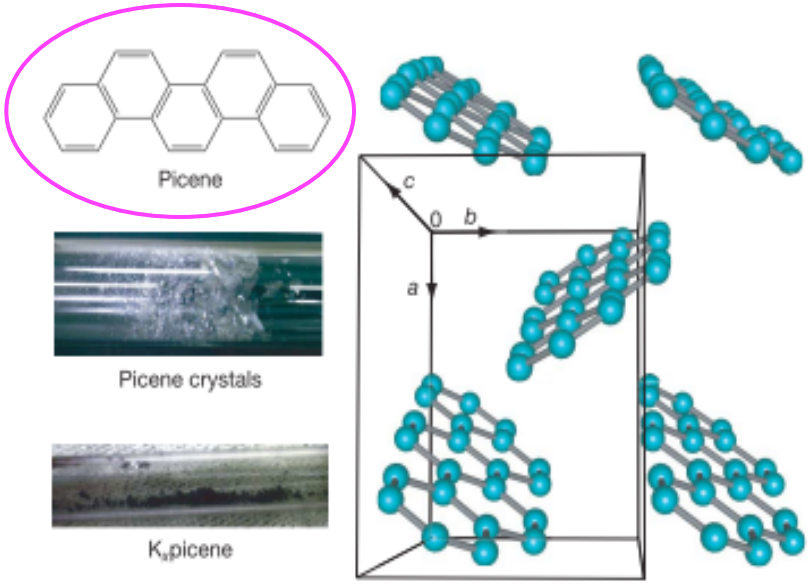
1,2:8,9-dibenzo pentacene

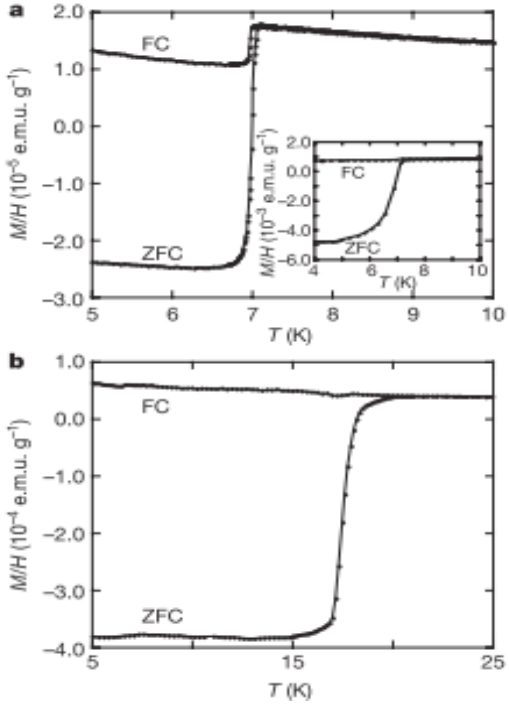


Polarized spin density is enhanced with increasing the benzene number

Identify the two superconducting phases in potassium-doped picene superconductors

(arXiv:1407.0747)





Tc = 7K

Tc = 18 K

Previous studies

Comparison of lattice parameters between experiment and theory

	a (Å)	b (Å)	c (Å)	β (°)	space group
—experiment—					
$K_{2.9}$picene [1]	8.707	5.912	12.97	92.77	$P2_1$
K_3picene [6]	8.571	6.270	14.001	91.68	$P2_1$
—calculation—					
K_3picene [11]	7.359	7.361	14.018	105.71	$P2_1$
K_3picene [10]	7.421	7.213	14.028	104.53	$P2_1$

→ **Tc ~ 7K**

→ **Tc ~ 18K**

(LDA)

Large discrepancies for a and b axises!

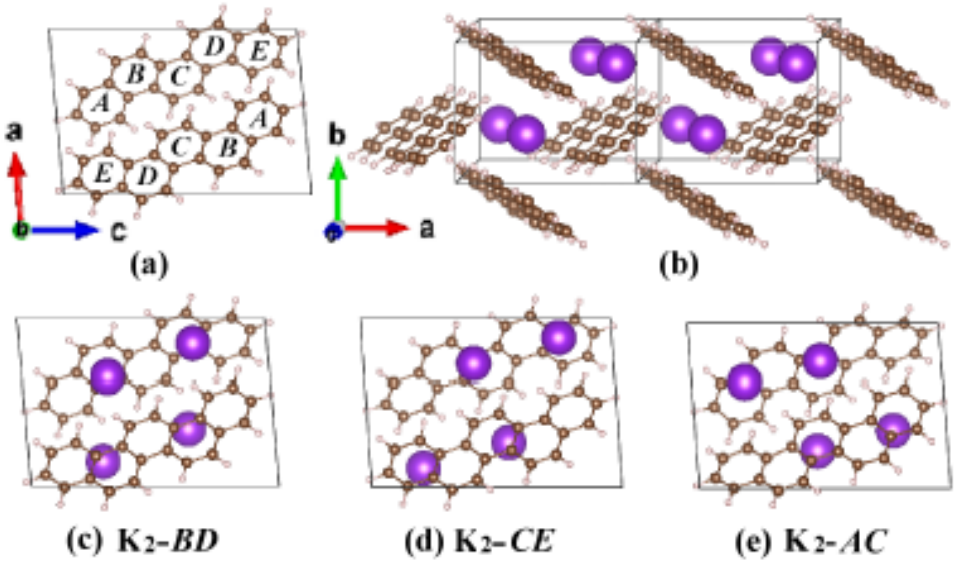
[1] R. Mitsuhashi *et al*, Nature **464**, 76 (2010).

[6] T. Kambe *et al*, Phys. Rev. B **86**, 214507 (2012).

[10] T. Kosugi, T. Miyake, S. Ishibashi, R. Arita, and H. Aoki, Phys. Rev. B **84**, 214506 (2011).

[11] P. L. de Andres, a. Guijarro, and J. A. Vergés, Phys. Rev. B **83**, 245113 (2011).

Possible crystal structures



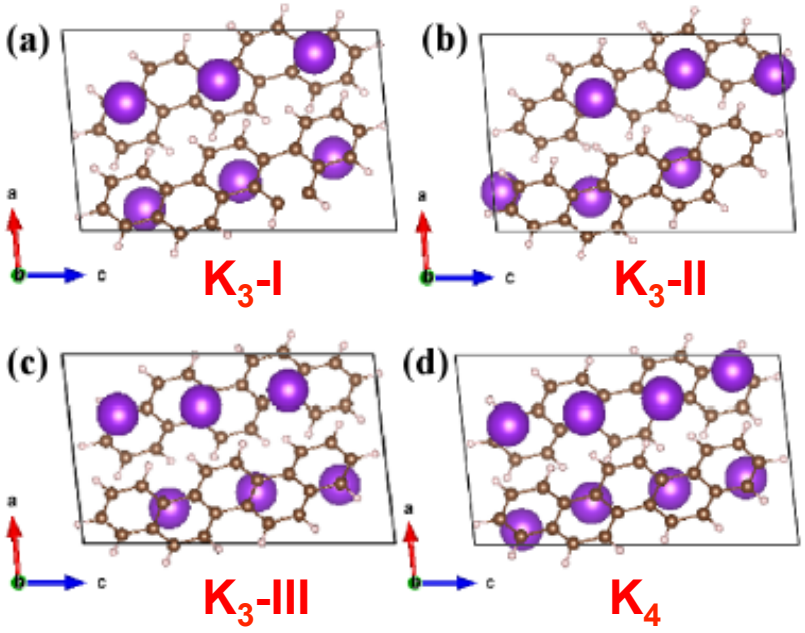


TABLE I. The optimized lattice parameters a, b, c, β, the fraction coordinations of the doped K atoms and the space group of unit cell for K_2picene and K_3picene with different structural phases.

	a (Å)	b (Å)	c (Å)	β (°)	space group
—experiment—					
$K_{2.9}$picene [1]	8.707	5.912	12.97	92.77	$P2_1$
K_3picene [6]	8.571	6.270	14.001	91.68	$P2_1$
K_2-*BD*	8.766	6.818	13.166	95.13	$P2_1$
	(0.3461	0.2917	0.6540)		
	(0.1500	0.3017	0.2981)		
K_2-*CE*	8.752	6.556	13.293	92.98	$P2_1$
	(0.2571	0.3062	0.5452)		
	(0.1073	0.2856	0.1980)		
K_2-*AC*	8.651	6.524	13.306	92.60	$P2_1$
	(0.3150	0.3269	0.8168)		
	(0.2352	0.3291	0.5126)		
K_3-I	8.675	6.770	13.669	95.53	$P2_1$
	(0.3611	0.3057	0.8222)		
	(0.2470	0.2913	0.5183)		
	(0.1098	0.2912	0.2074)		
K_3-II	8.914	6.793	13.534	94.72	$P2_1$
	(0.3227	0.2953	0.6336)		
	(0.1753	0.2949	0.3250)		
	(0.2013	0.2372	0.0257)		
K_3-III	8.523	6.838	14.058	96.67	$P2_1$
	(0.2732	0.3048	0.5729)		
	(0.1904	0.2976	0.2882)		
	(0.3153	0.2897	0.8434)		

Lowest energy

Lowest energy

Formation energy

$$E_{formation} = E_{Kx} - E_{pristine} - E_{dopant}$$

x **stands for the number of K atoms.**
Edopant **is the product of single atom energy in bulk metal and atom number in a unit cell.**

For the K_2-BD phase, the formation energy is -0.330 eV per K atom, which suggests that it is easy to be synthesized in experiment.

The formation energy of the K_3-I phase is -0.295 eV per K atom, comparable to the one for K2picene.

For K_4picene the corresponding formation energy is -0.067 eV per K atom.→ unstable

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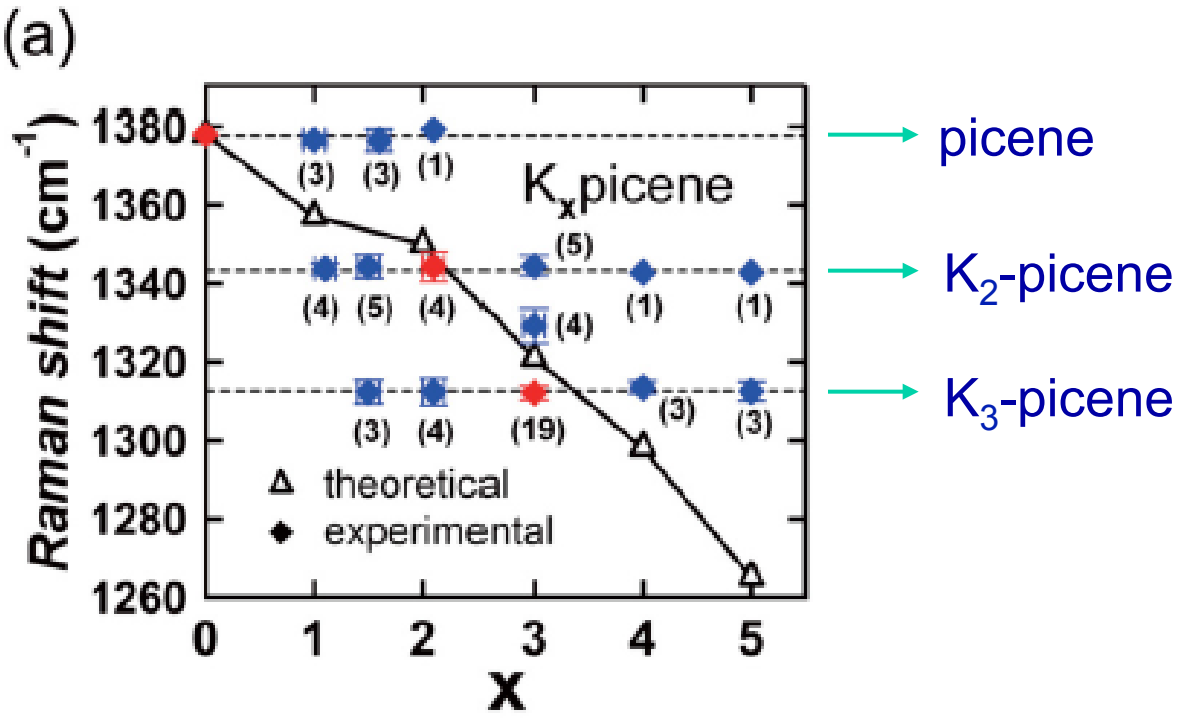
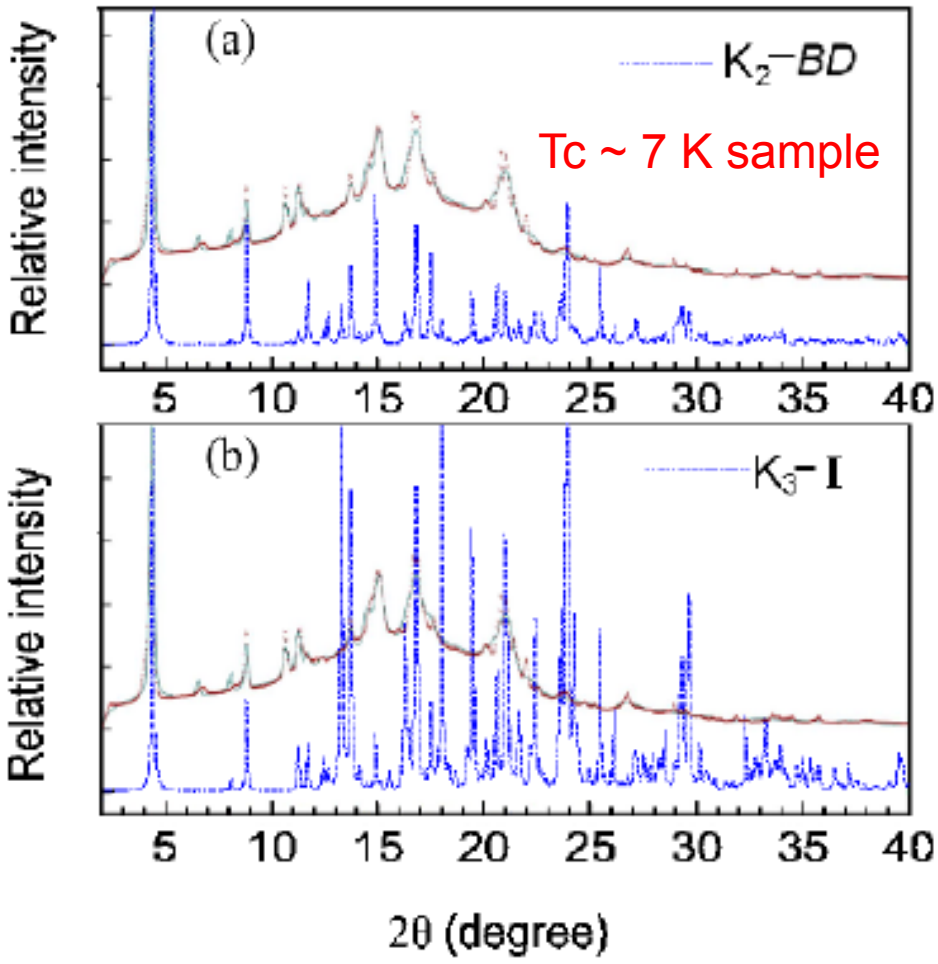
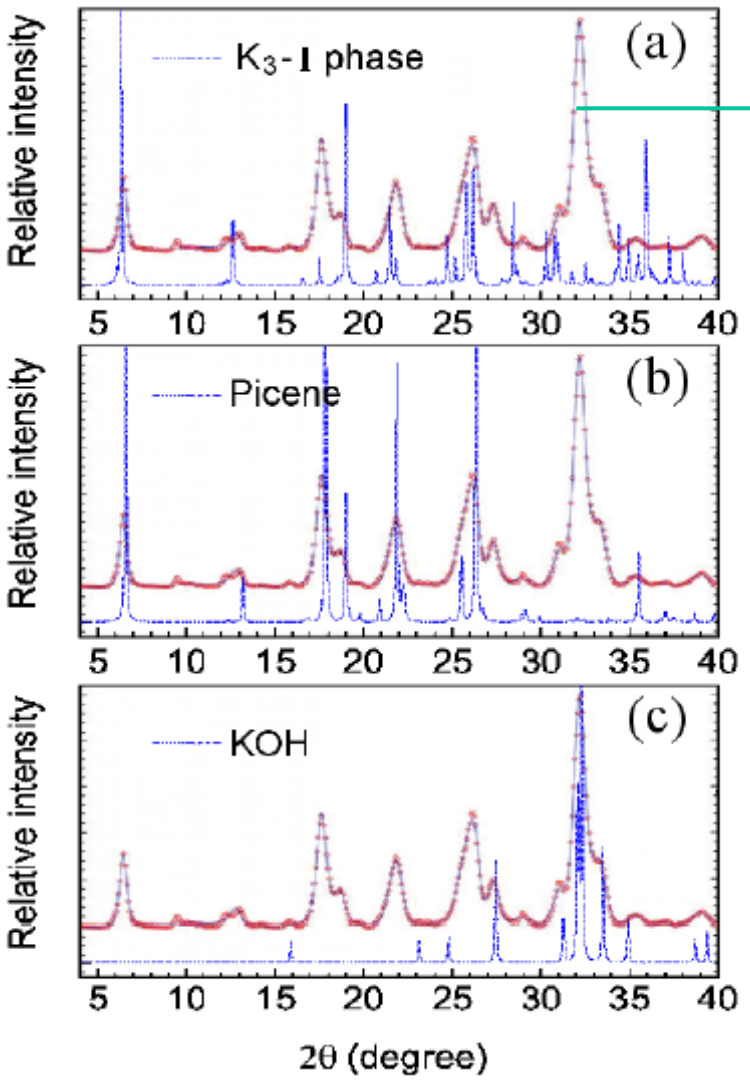


Only K_2 and K_3 picene can be realized!

Comparison of XRD spectra between experiment and theory

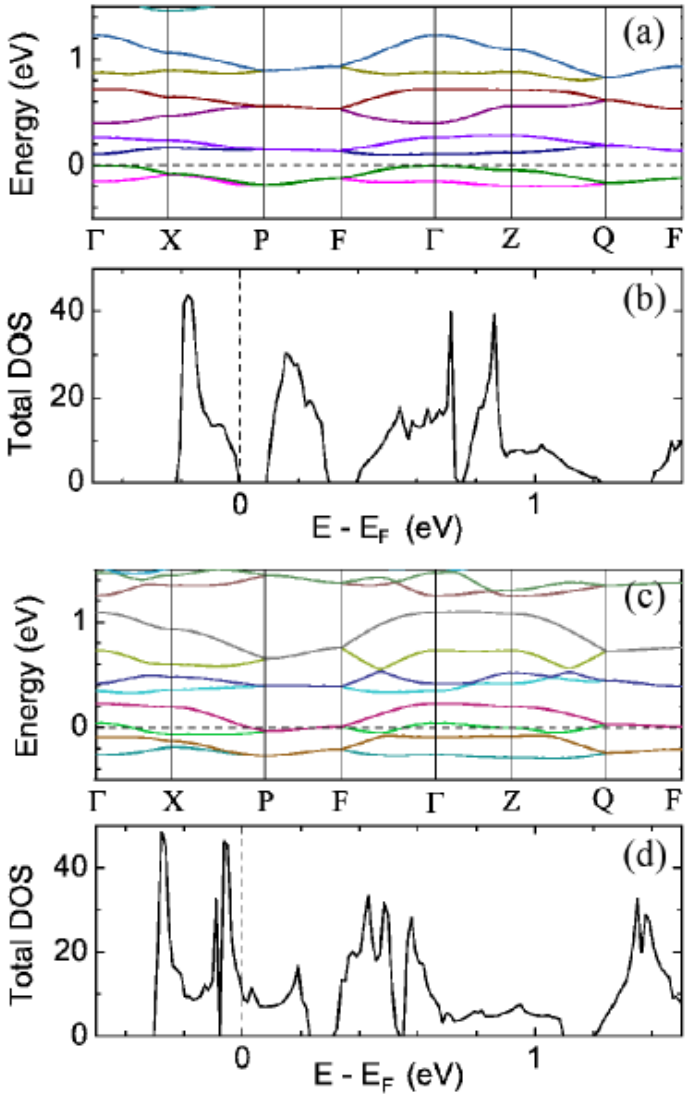


Tc ~ 7 K sample corresponds to K_2-BD.



Tc ~ 18 K sample

Pristine picene and KOH are dominant in the 18 K sample.



K_2-BD semiconducting

K_3-I metallic

FIG. 6. Energy bands and density of states for K_2-*BD* phase (a) (b) and K_3-I (c) (d). Fermi energy is set to zero.

Conclusions

- The spin polarized state is realized in the charged aromatic molecules with two added electrons.
- Electron correlation is not enough for superconductivity.
- The ground state of K-doped aromatic hydrocarbons corresponds to an antiferromagnetic state.
- Tc ~ 7K and 18K superconducting phases of K-doped picene correspond to K_2-BD and K_3-I, respectively.

THANK YOU!