Computer Simulations in Physics and Beyond
Sep 06-10/08, 2015, Moscow

Study of Superconductivities in Polycyclic Aromatic Hydrocarbon

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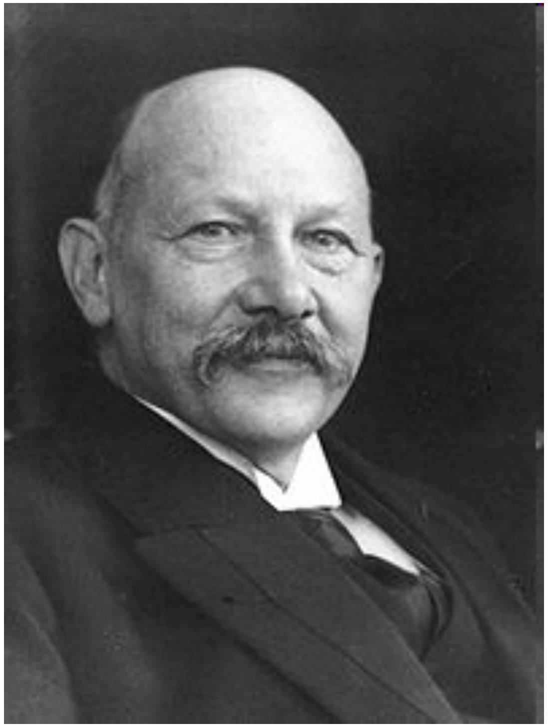
Prof. Z.B. Huang, Mr. L. Du (Hubei Univ. & CSRC)
Dr. X. J. Chen (Carnegie Institute of Washington)

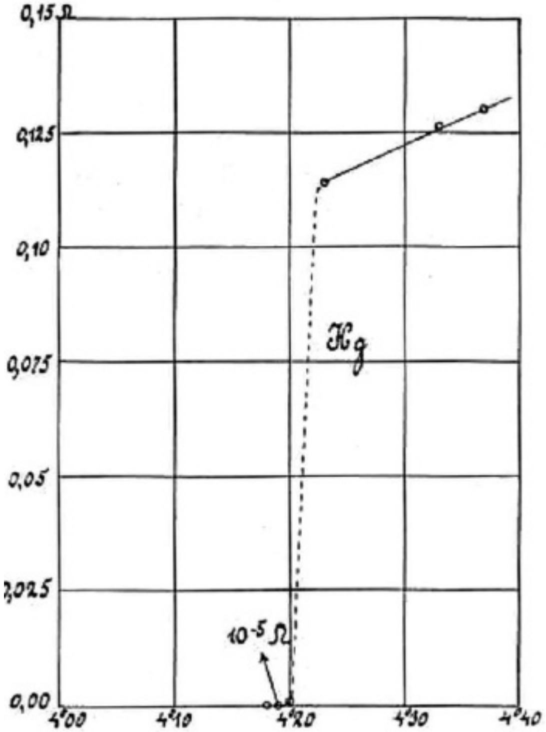
Work supported in part by CAEP, MOST 2011CB922200, NSFC 10974047 and 11174072, and SRFDP 20104208110001.

Outline

- Introduction: organic superconductors and recent discoveries
- Structure studies
- Superconductivity in doped solid Benzene
- An unique superconducting phase in PAHs
- Correlation, Magnetism and Pairing
- Pressure effect
- Summary and discussions

Superconductor





H. Kamerlingh Onnes
Noble Prize 1913

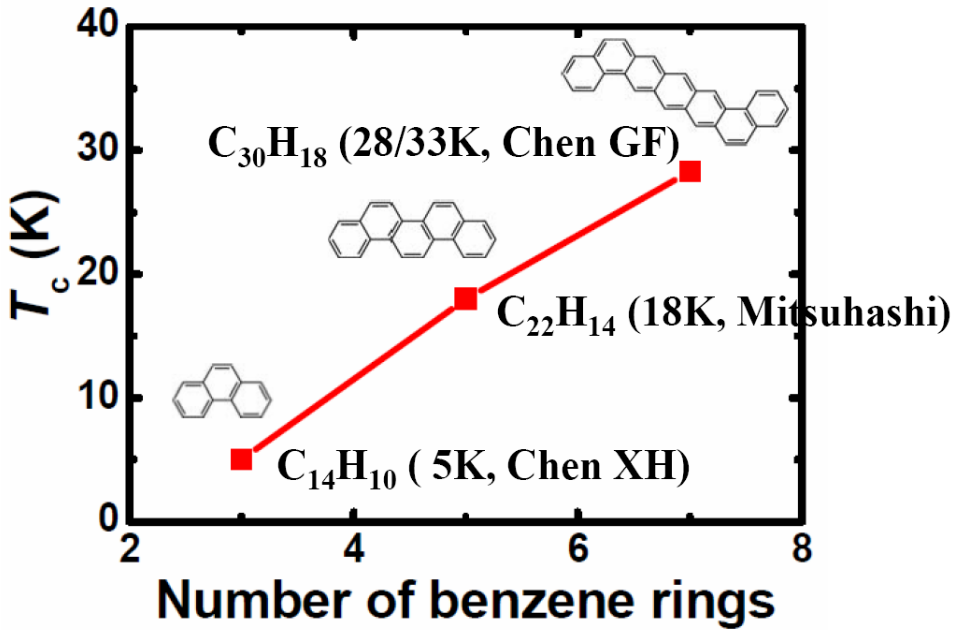
First observation of superconductivity in mercury in 1911.

Since 1911, searching superconductors and understanding their properties are of great fundamental interest in physics, chemistry, and material sciences.

Existing Superconductors

- **Metallic:** normal metals when $T > T_c$.
  Conventional, low $T_c \leq 23.3$K (39K).
- **Ceramic:** complicated behavior when $T > T_c$.
  Novel, high $T_c \approx 165$K, under pressure.
- **Fullerenes:** insulating/semiconducting when $T > T_c$.
  Novel, intermediate $T_c \approx 35$K. (carbon)
- **Mg-B:** metallic, $T_c \approx 39$K
- **Fe-based:** more complicated behavior, high $T_c \approx 55$K; others
- **Organic:** semiconductors when $T > T_c$; $T_c \leq 17$K (before 2005)
  2011, 33K? (carbon)
- SH_2, SH_3, Others?
  Room temperature?

Organic Superconductors



scoveries

Polycyclic Aromatic Hydrocarbon (PAH)

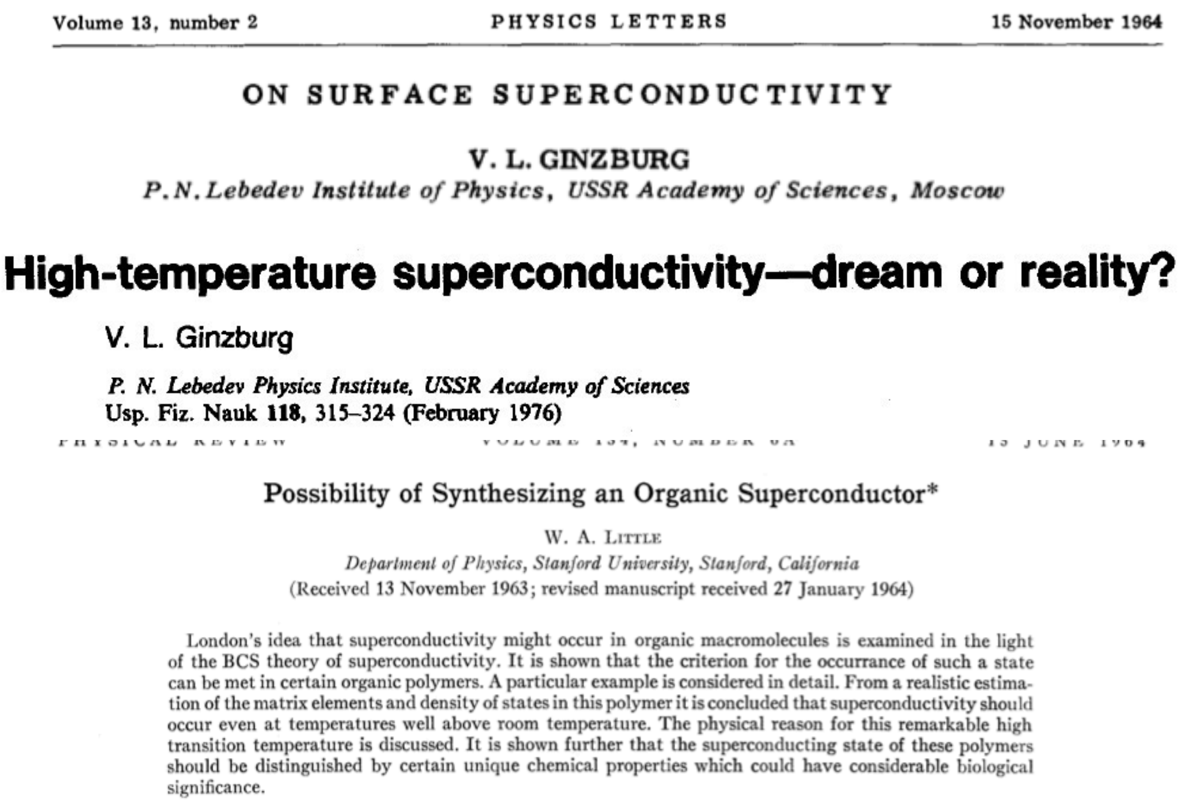
Picene (5-rings, $C_{22}H_{14}$) [1]; (coronene [2]);

Phenanthrene (3-rings, $C_{14}H_{10}$) [3, 4];

Dibenzopentacene (7-rings, $C_{30}H_{18}$) [5].

Superconducting: when doped by alkali-metal

Unconventional superconductivity with higher T_c’s in organic molecules



Volume 13, number 2 PHYSICS LETTERS 15 November 1964

ON SURFACE SUPERCONDUCTIVITY

V. L. GINZBURG
P. N. Lebedev Institute of Physics, USSR Academy of Sciences, Moscow

High-temperature superconductivity—dream or reality?

V. L. Ginzburg

P. N. Lebedev Physics Institute, USSR Academy of Sciences
Usp. Fiz. Nauk **118**, 315–324 (February 1976)

PHYSICAL REVIEW VOLUME 134, NUMBER 6A 15 JUNE 1964

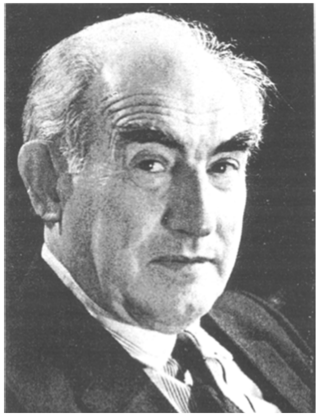
Possibility of Synthesizing an Organic Superconductor*

W. A. Little
Department of Physics, Stanford University, Stanford, California
(Received 13 November 1963; revised manuscript received 27 January 1964)

London’s idea that superconductivity might occur in organic macromolecules is examined in the light of the BCS theory of superconductivity. It is shown that the criterion for the occurrance of such a state can be met in certain organic polymers. A particular example is considered in detail. From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature. The physical reason for this remarkable high transition temperature is discussed. It is shown further that the superconducting state of these polymers should be distinguished by certain unique chemical properties which could have considerable biological significance.

Vitalii Lazarevich Ginzburg

2003 in Physics

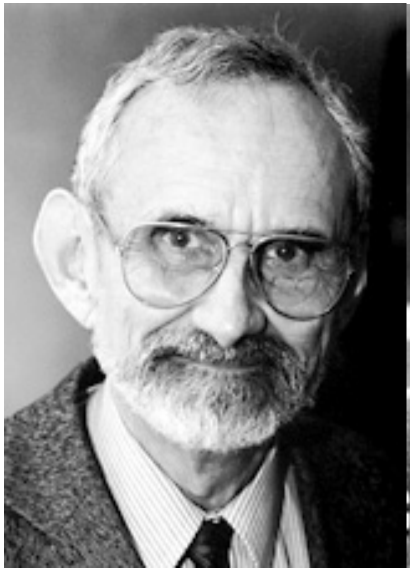


Ginzburg considered nonphonon superconductivity mechanism in the layered systems and initiated search for high temperature superconductors. The idea was based on the interaction of electrons with electron excitations (excitons). The energy of these excitations is much higher than the phonon energy, which can result in substantially higher superconducting transition temperatures.

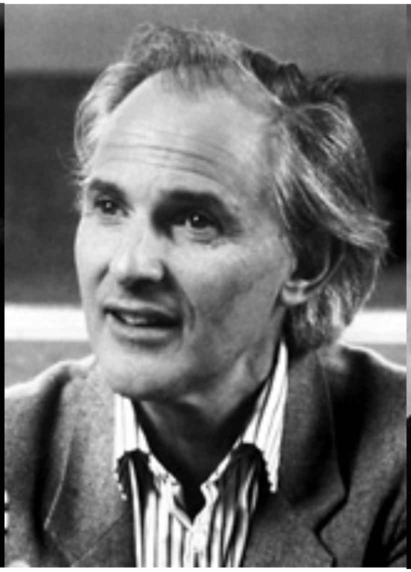
William A. Little

Birth of fullerenes and superconductivity in fullerides

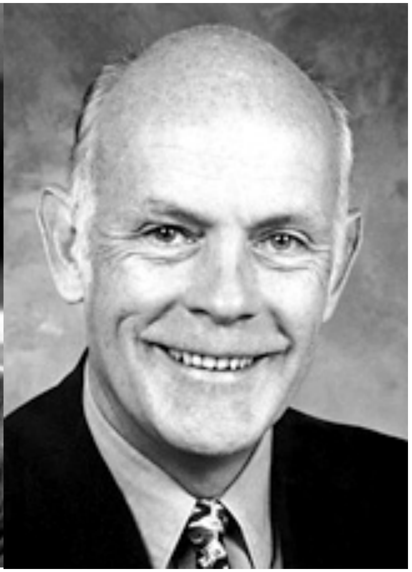
Robert F. Curl Jr.



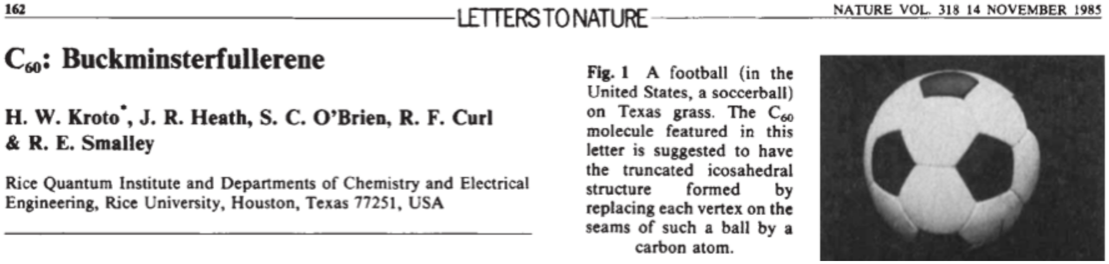
Sir Harold W. Kroto



Richard E. Smalley



The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley "for their discovery of fullerenes".



162 LETTERS TO NATURE NATURE VOL. 318 14 NOVEMBER 1985

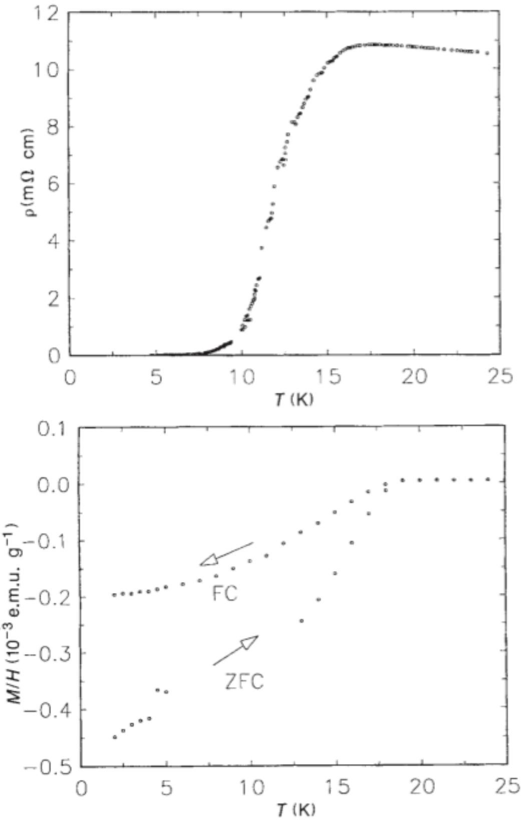
C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

Nature 350, 600 (18 April 1991)



Superconductivity at 18 K in potassium-doped C_{60}

A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez & A. R. Kortan

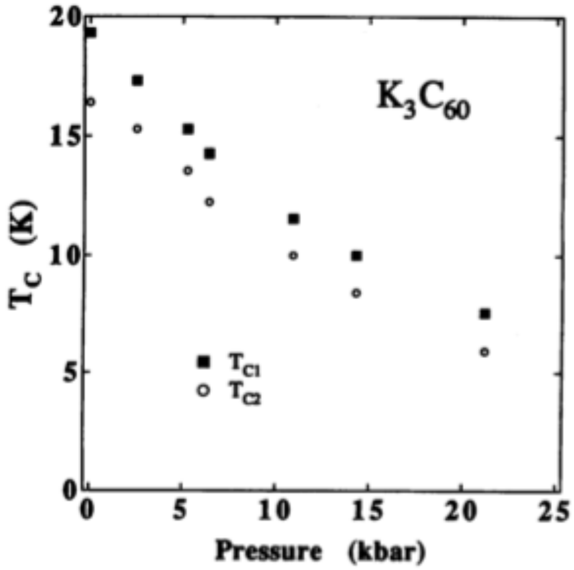
AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070, USA

Pressure effect on SC in fullerides

Pressure Dependence of Superconductivity in Single-Phase K_3C_{60}

G. Sparn, J. D. Thompson, S.-M. Huang, R. B. Kaner, F. Diederich, R. L. Whetten, G. Grüner, K. Holczer

Science 252, 1829 (June 1991).



LETTERS

Bulk superconductivity at 38 K in a molecular system

ALEXEY Y. GANIN[1]*, YASUHIRO TAKABAYASHI[2]*, YAROSLAV Z. KHIMYAK[1], SERENA MARGADONNA[3], ANNA TAMAI[3], MATTHEW J. ROSSEINSKY[1†] AND KOSMAS PRASSIDES[2†]

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[2] Department of Chemistry, University of Durham, Durham DH1 3LE, UK
[3] School of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, UK
*These authors contributed equally to this work
†e-mail: M.J.Rosseinsky@liverpool.ac.uk; K.Prassides@durham.ac.uk

Nature Mater. 7, 367 (2008).

Superconductivity at 33 K in $Cs_xRb_yC_{60}$

K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo & S. Kuroshima,

Fundamental Research Laboratories, NEC Corporation, Tsukuba 305, Japan

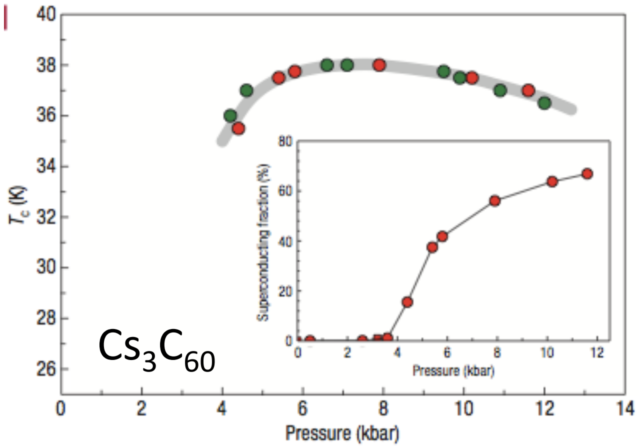
Nature 352, 222 (July 1991).

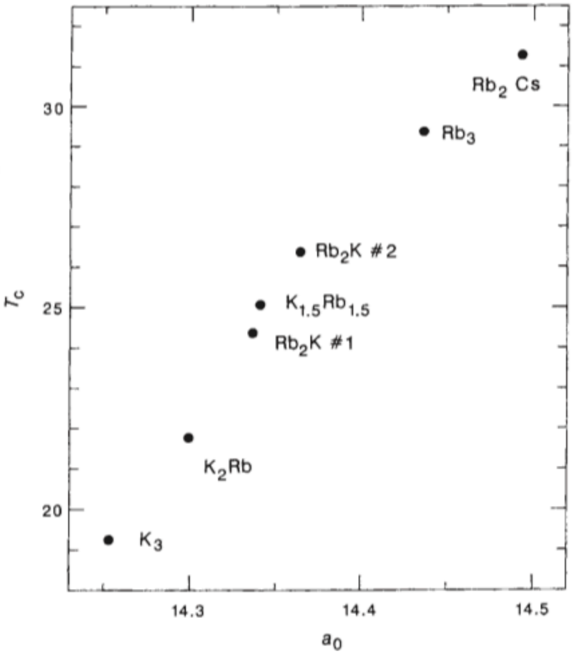
Superconductivity at 30 K in caesium-doped C_{60}

Stephen P. Kelty, Chia-Chun Chen & Charles M. Lieber*

Department of Chemistry and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

Nature 352, 223 (July 1991).





Relation of structure and superconducting transition temperatures in A_3C_{60}

R. M. Fleming, A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, R. C. Haddon, S. M. Zahurak & A. V. Makhija

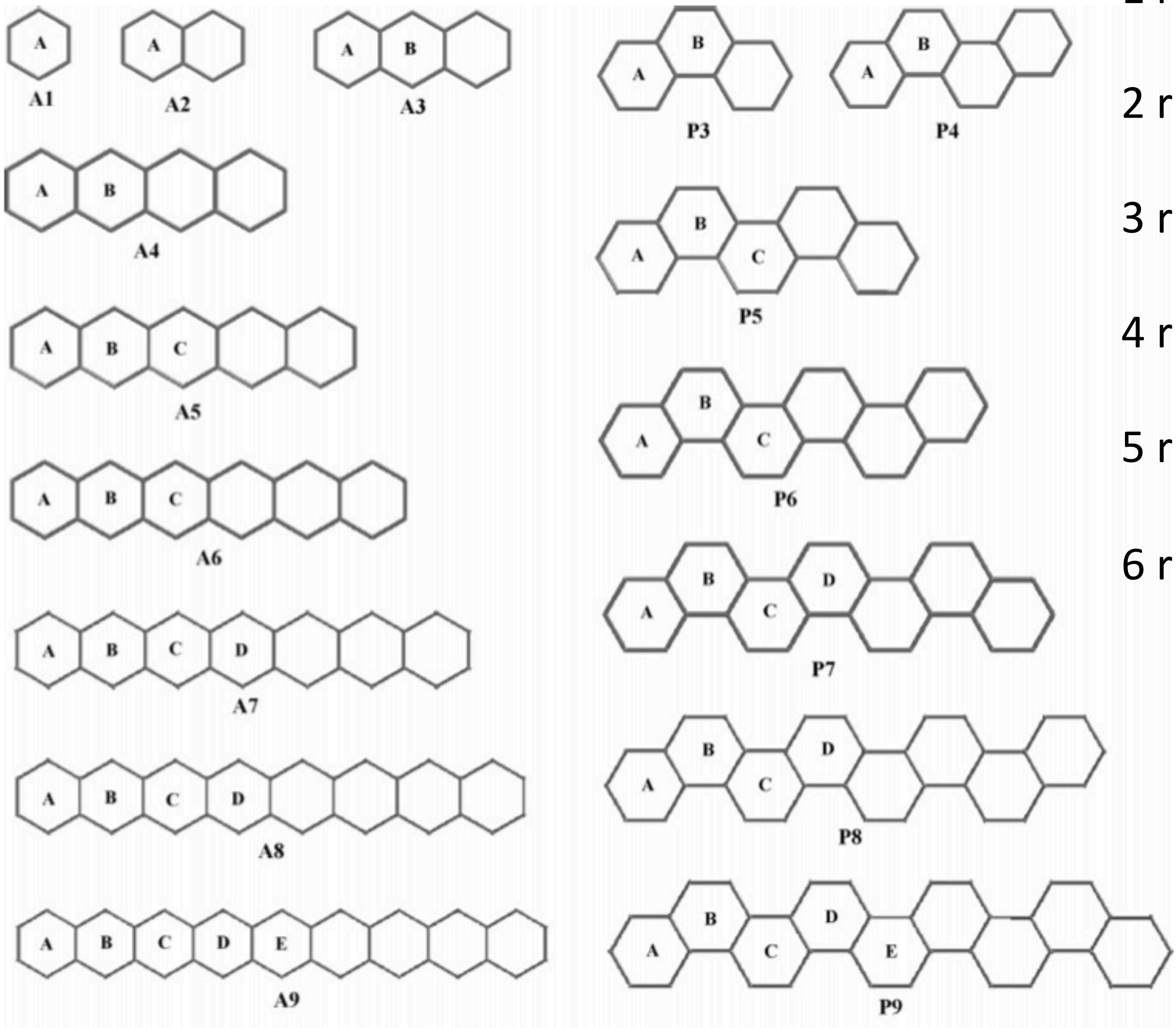
AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

Nature 352, 787 (August 1991).

Interests in aromatic hydrocarbons

Acene series

Phenacene series



1 ring: benzene

2 rings: naphthalene

3 rings: anthracene, phenanthrene

4 rings: tetracene, chrysene

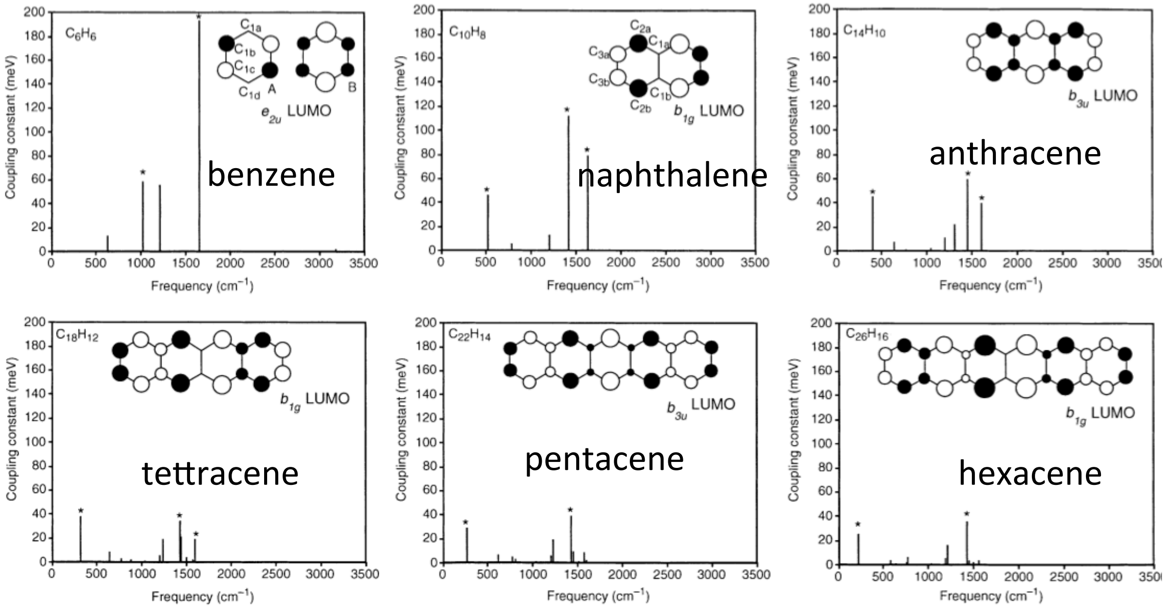
5 rings: pentacene, picene

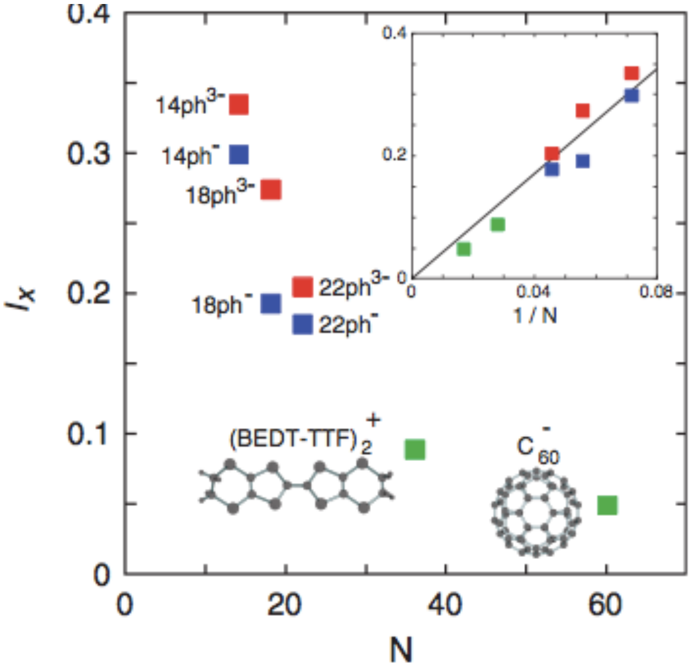
6 rings: hexacene, coronene

Electronic and optoelectronic applications:

light-emitting devices, lasers, field-effect transistors, solar cells, or photodetectors.

Predicted superconductivity in acenes and phenacenes





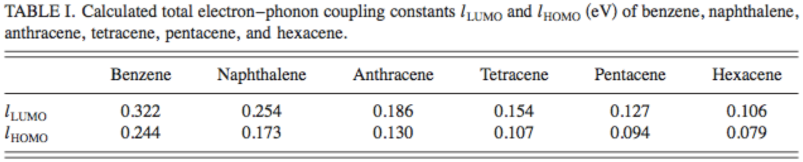


TABLE I. Calculated total electron–phonon coupling constants l_{LUMO} and l_{HOMO} (eV) of benzene, naphthalene, anthracene, tetracene, pentacene, and hexacene.

	Benzene	Naphthalene	Anthracene	Tetracene	Pentacene	Hexacene
l_{LUMO}	0.322	0.254	0.186	0.154	0.127	0.106
l_{HOMO}	0.244	0.173	0.130	0.107	0.094	0.079

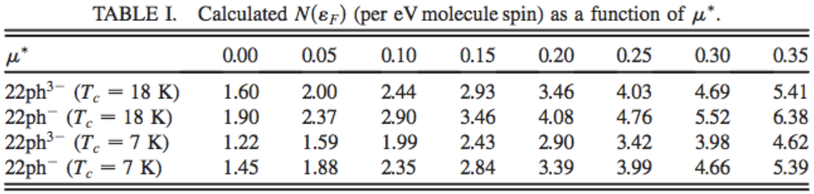


TABLE I. Calculated $N(\varepsilon_F)$ (per eV molecule spin) as a function of μ^*.

μ^*	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35
$22ph^{3-}$ ($T_c = 18$ K)	1.60	2.00	2.44	2.93	3.46	4.03	4.69	5.41
$22ph^-$ ($T_c = 18$ K)	1.90	2.37	2.90	3.46	4.08	4.76	5.52	6.38
$22ph^{3-}$ ($T_c = 7$ K)	1.22	1.59	1.99	2.43	2.90	3.42	3.98	4.62
$22ph^-$ ($T_c = 7$ K)	1.45	1.88	2.35	2.84	3.39	3.99	4.66	5.39

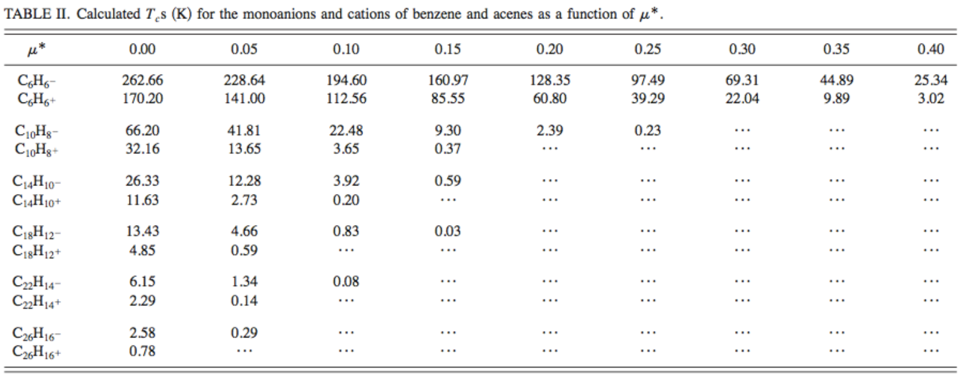


TABLE II. Calculated T_cs (K) for the monoanions and cations of benzene and acenes as a function of μ^*.

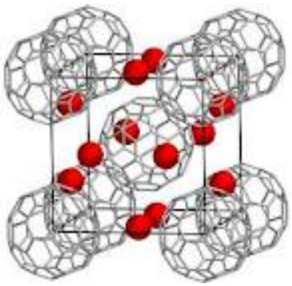
μ^*	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
$C_6H_{6^-}$	262.66	228.64	194.60	160.97	128.35	97.49	69.31	44.89	25.34
$C_6H_{6^+}$	170.20	141.00	112.56	85.55	60.80	39.29	22.04	9.89	3.02
$C_{10}H_{8^-}$	66.20	41.81	22.48	9.30	2.39	0.23	···	···	···
$C_{10}H_{8^+}$	32.16	13.65	3.65	0.37	···	···	···	···	···
$C_{14}H_{10^-}$	26.33	12.28	3.92	0.59	···	···	···	···	···
$C_{14}H_{10^+}$	11.63	2.73	0.20	···	···	···	···	···	···
$C_{18}H_{12^-}$	13.43	4.66	0.83	0.03	···	···	···	···	···
$C_{18}H_{12^+}$	4.85	0.59	···	···	···	···	···	···	···
$C_{22}H_{14^-}$	6.15	1.34	0.08	···	···	···	···	···	···
$C_{22}H_{14^+}$	2.29	0.14	···	···	···	···	···	···	···
$C_{26}H_{16^-}$	2.58	0.29	···	···	···	···	···	···	···
$C_{26}H_{16^+}$	0.78	···	···	···	···	···	···	···	···

)

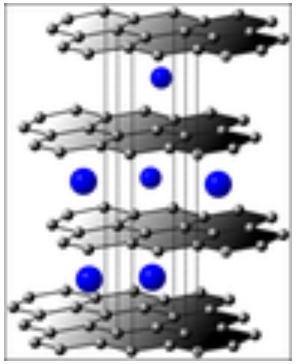
T. Kato et al., JCP 115, 8592 (2001); Syn. Metals 126, 75 (2002); PRL 107, 077001 (2011).

Organic Superconductor

- Quasi-one-dimensional: $C_{10}H_{12}Se$
- Two-dimensional: $C_{10}H_{10}C_8$
- C_{60}
  - Cs_3C_{60}: Tc=40 K at 1.5 GPa
  - K_3C_{60} : Tc=20K



- Graphite intercalation compounds
  - CaC_6: Tc=11.5 K
  - YbC_6: Tc=6.5 K



Picene ($C_{22}H_{14}$) (2009-03-14, 2010-01-20)

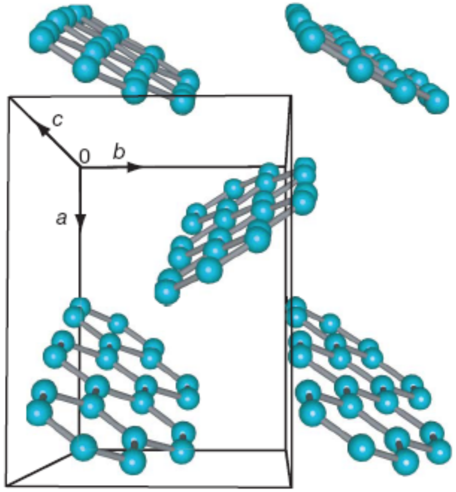
nature Vol 464 | 4 March 2010 | doi:10.1038/nature08859

LETTERS

First organic hydrocarbon superconductor

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]



T_C~ 7--18K

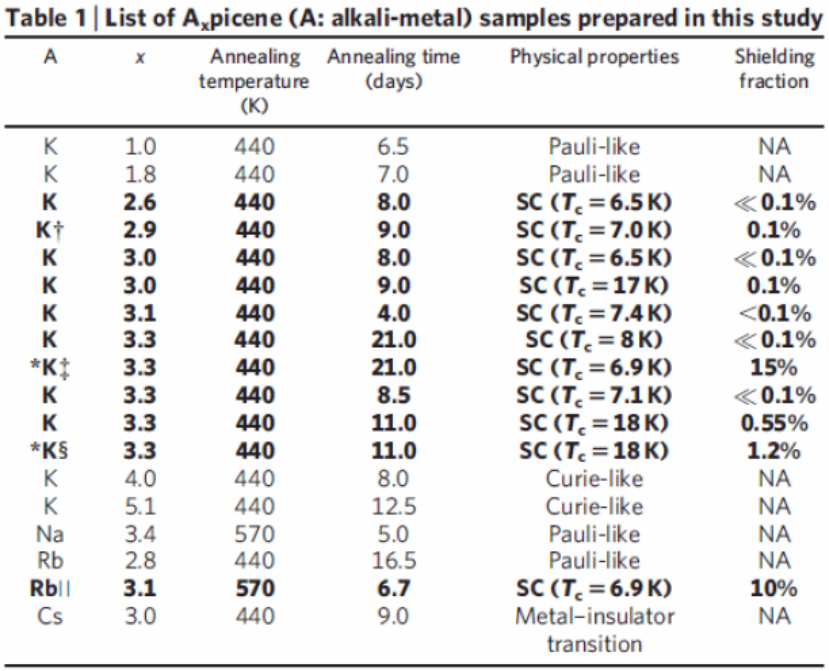


Table 1 | List of $A_x$picene (A: alkali-metal) samples prepared in this study

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

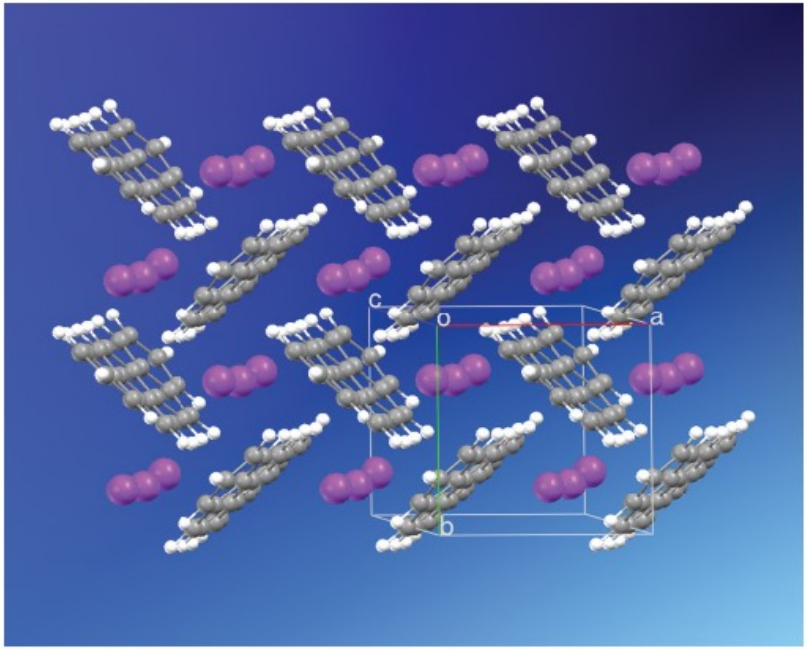
Organic SC

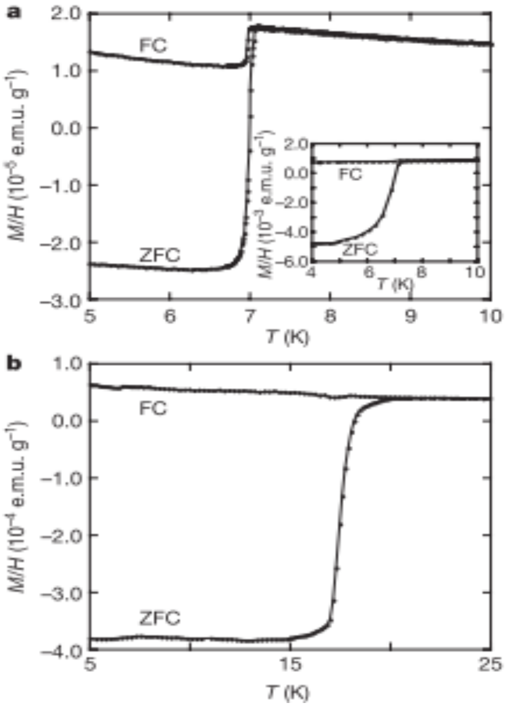
nature Vol 464 | 4 March 2010 | doi:10.1038/nature08859

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

Phenanthrene ($C_{14}H_{10}$) (2011-07-13, 09-21)

NATURE COMMUNICATIONS | ARTICLE

Superconductivity at 5 K in alkali-metal-doped phenanthrene

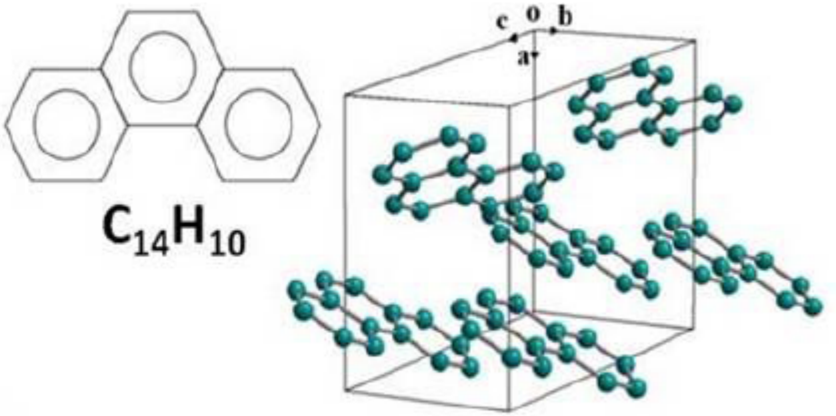
X.F. Wang, R.H. Liu, Z. Gui, Y.L. Xie, Y.J. Yan, J.J. Ying, X.G. Luo & X.H. Chen

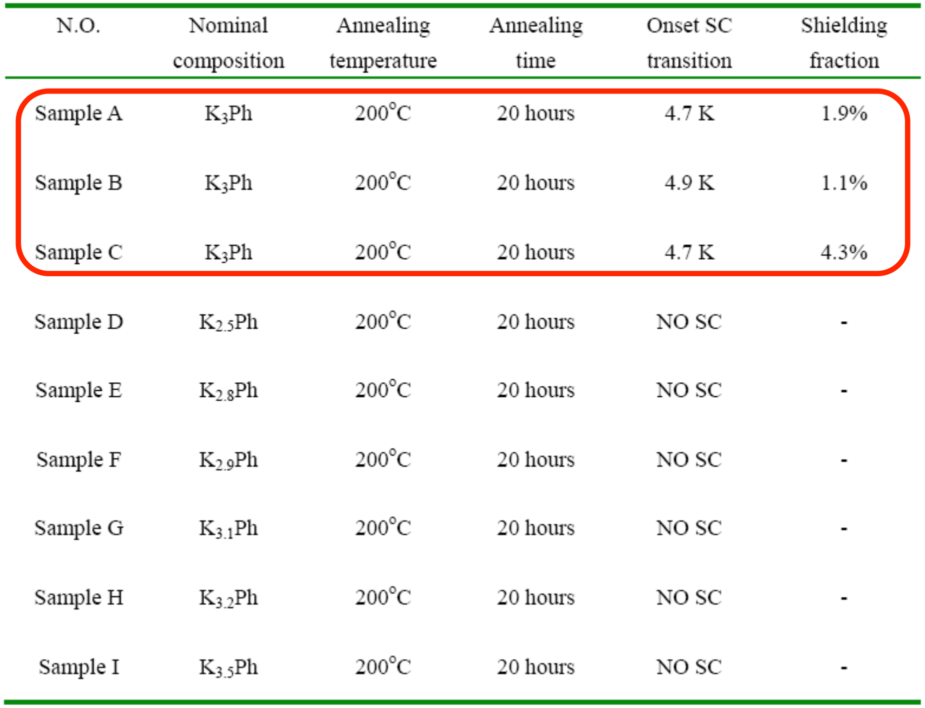
Affiliations | Contributions | Corresponding author

Nature Communications 2, Article number: 507 | doi:1

Received 13 July 2011 | Accepted 21 September 2011

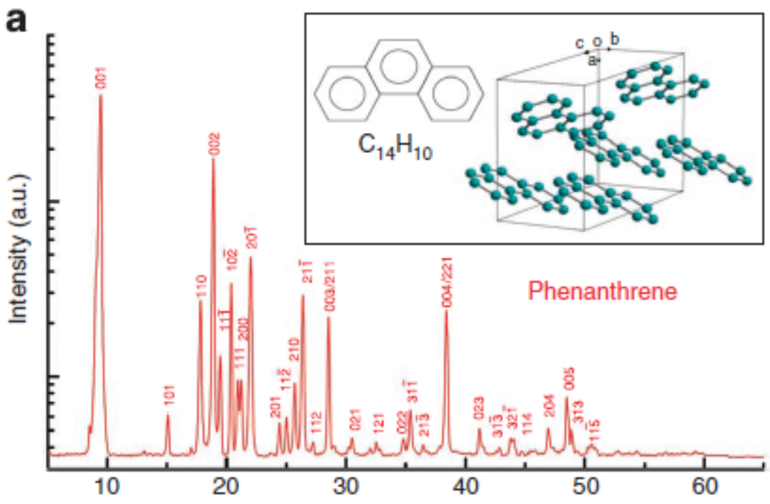
(Submitted on 20 Feb 2011)
arXiv:1102.4075v1

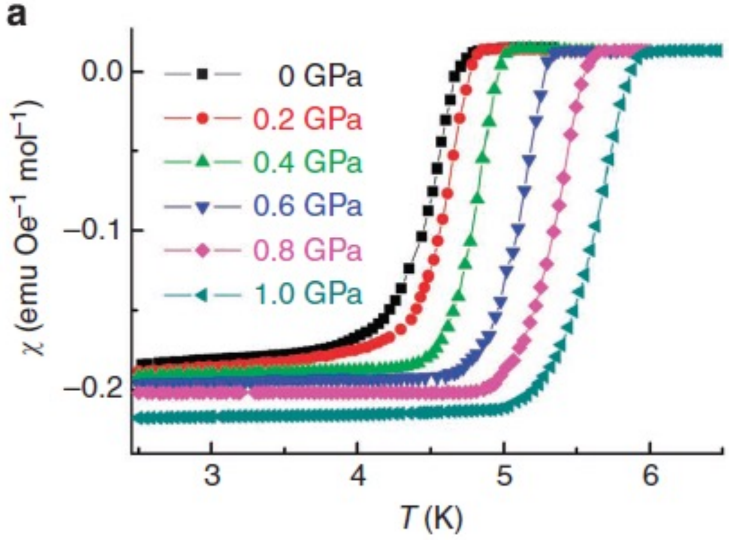


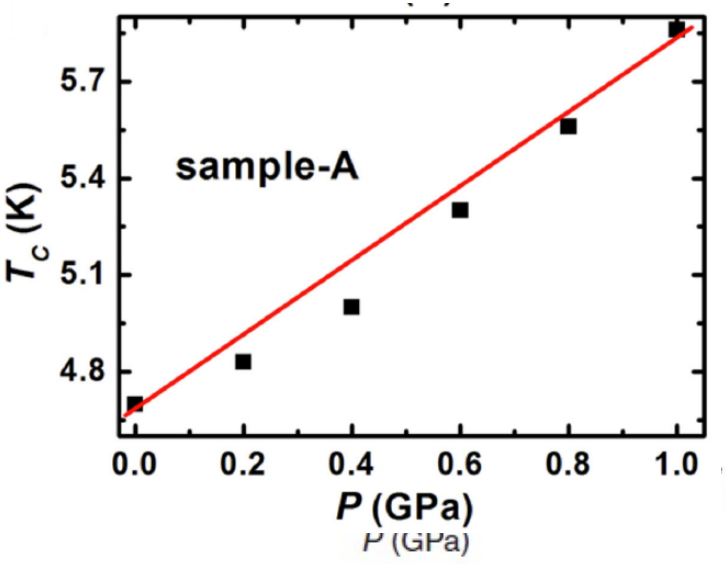


N.O.	Nominal composition	Annealing temperature	Annealing time	Onset SC transition	Shielding fraction
Sample A	K_3Ph	200°C	20 hours	4.7 K	1.9%
Sample B	K_3Ph	200°C	20 hours	4.9 K	1.1%
Sample C	K_3Ph	200°C	20 hours	4.7 K	4.3%
Sample D	$K_{2.5}Ph$	200°C	20 hours	NO SC	-
Sample E	$K_{2.8}Ph$	200°C	20 hours	NO SC	-
Sample F	$K_{2.9}Ph$	200°C	20 hours	NO SC	-
Sample G	$K_{3.1}Ph$	200°C	20 hours	NO SC	-
Sample H	$K_{3.2}Ph$	200°C	20 hours	NO SC	-
Sample I	$K_{3.5}Ph$	200°C	20 hours	NO SC	-

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

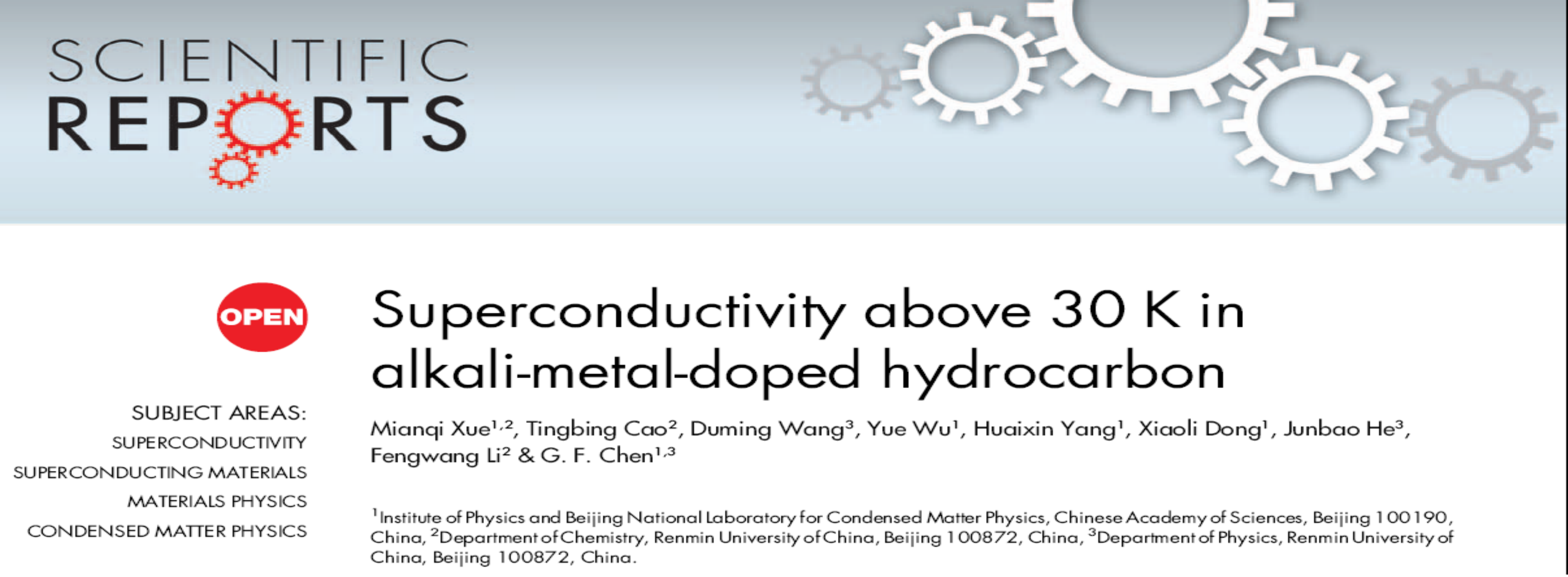






$T_c \sim 5$ K

At 1 GPa, 20% increase of T_c



SCIENTIFIC REPORTS

OPEN

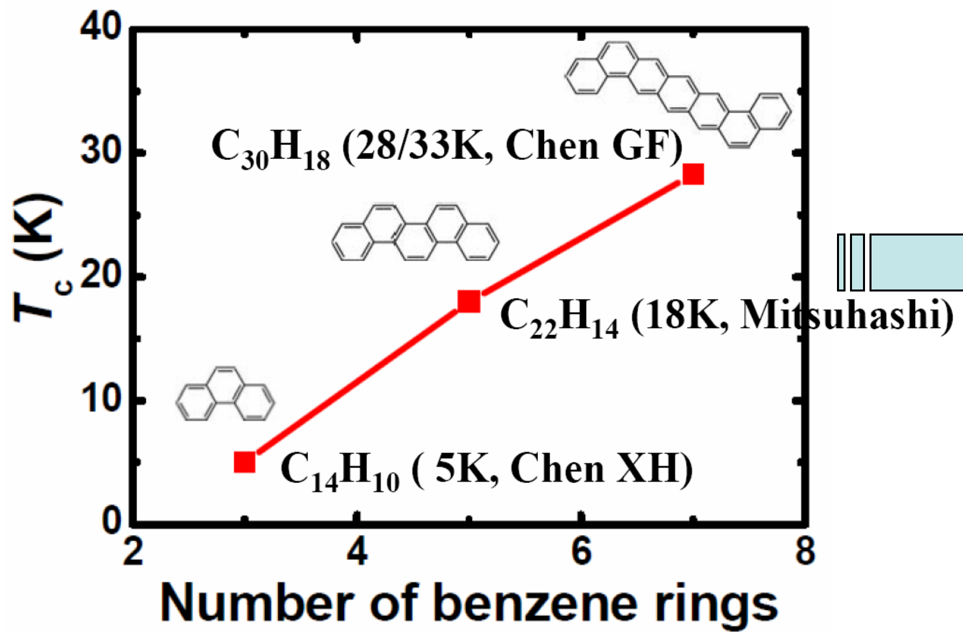
SUBJECT AREAS:
SUPERCONDUCTIVITY
SUPERCONDUCTING MATERIALS
MATERIALS PHYSICS
CONDENSED MATTER PHYSICS

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]

[1]Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China, [2]Department of Chemistry, Renmin University of China, Beijing 100872, China, [3]Department of Physics, Renmin University of China, Beijing 100872, China.

Organic Superconductors



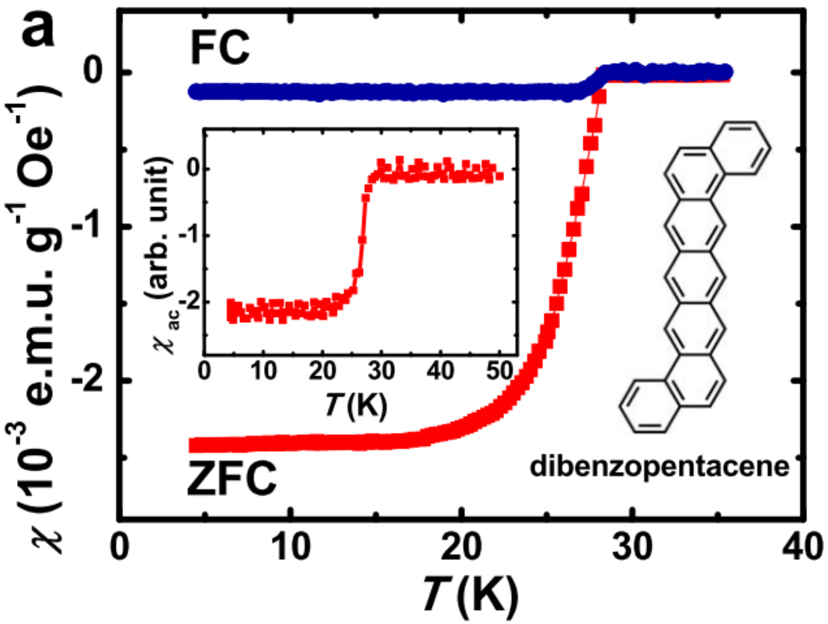
After Copper- and Iron-base superconductivity, a new superconductor family is discovered.

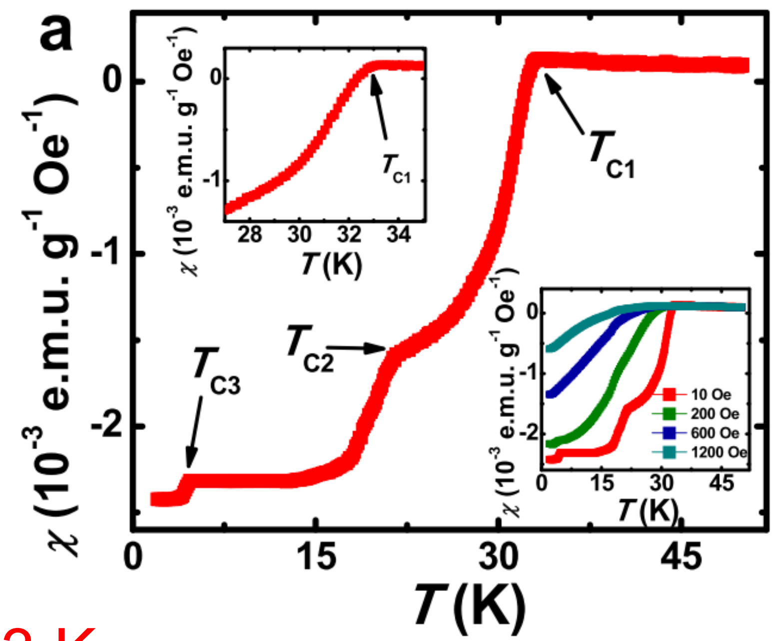
(Submitted on 3 Nov 2011)
arXiv:1111.0820v1

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

PCCP

Dynamic Article Links ▶

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 16476–16493

www.rsc.org/pccp

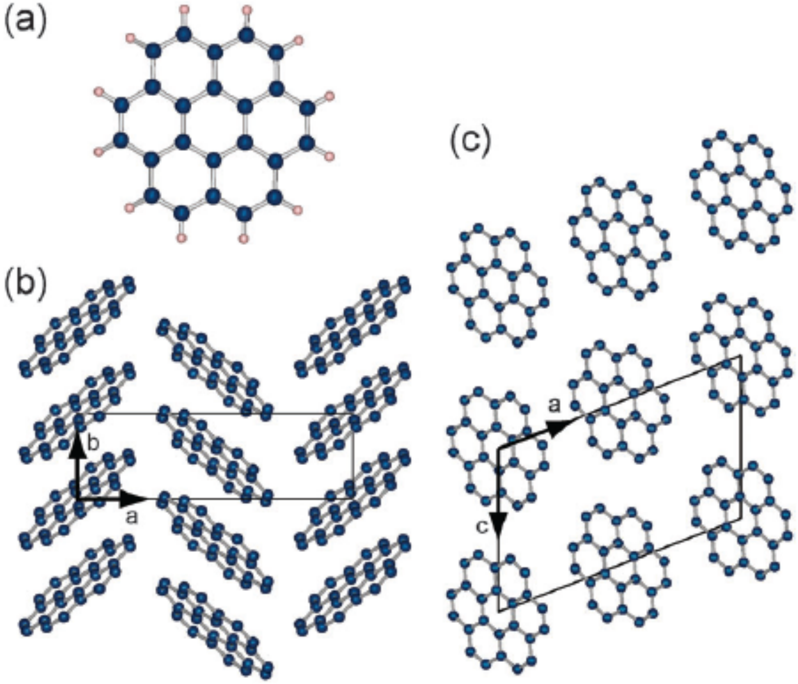
PERSPECTIVE

Metal-intercalated aromatic hydrocarbons: a new class of carbon-based superconductors

Yoshihiro Kubozono,*[ab] Hiroki Mitamura,[a] Xuesong Lee,[a] Xuexia He,[a] Yusuke Yamanari,[c] Yosuke Takahashi,[c] Yuta Suzuki,[c] Yumiko Kaji,[a] Ritsuko Eguchi,[a] Koki Akaike,[a] Takashi Kambe,[c] Hideki Okamoto,[d] Akihiko Fujiwara,[e] Takashi Kato,[f] Taichi Kosugi[gh] and Hideo Aoki[g]

Received 29th March 2011, Accepted 15th July 2011
DOI: 10.1039/c1cp20961b

$T_C \sim 15K$



Zhong GH, Zhang Chao, Yan XW, Wang XH, Han JX

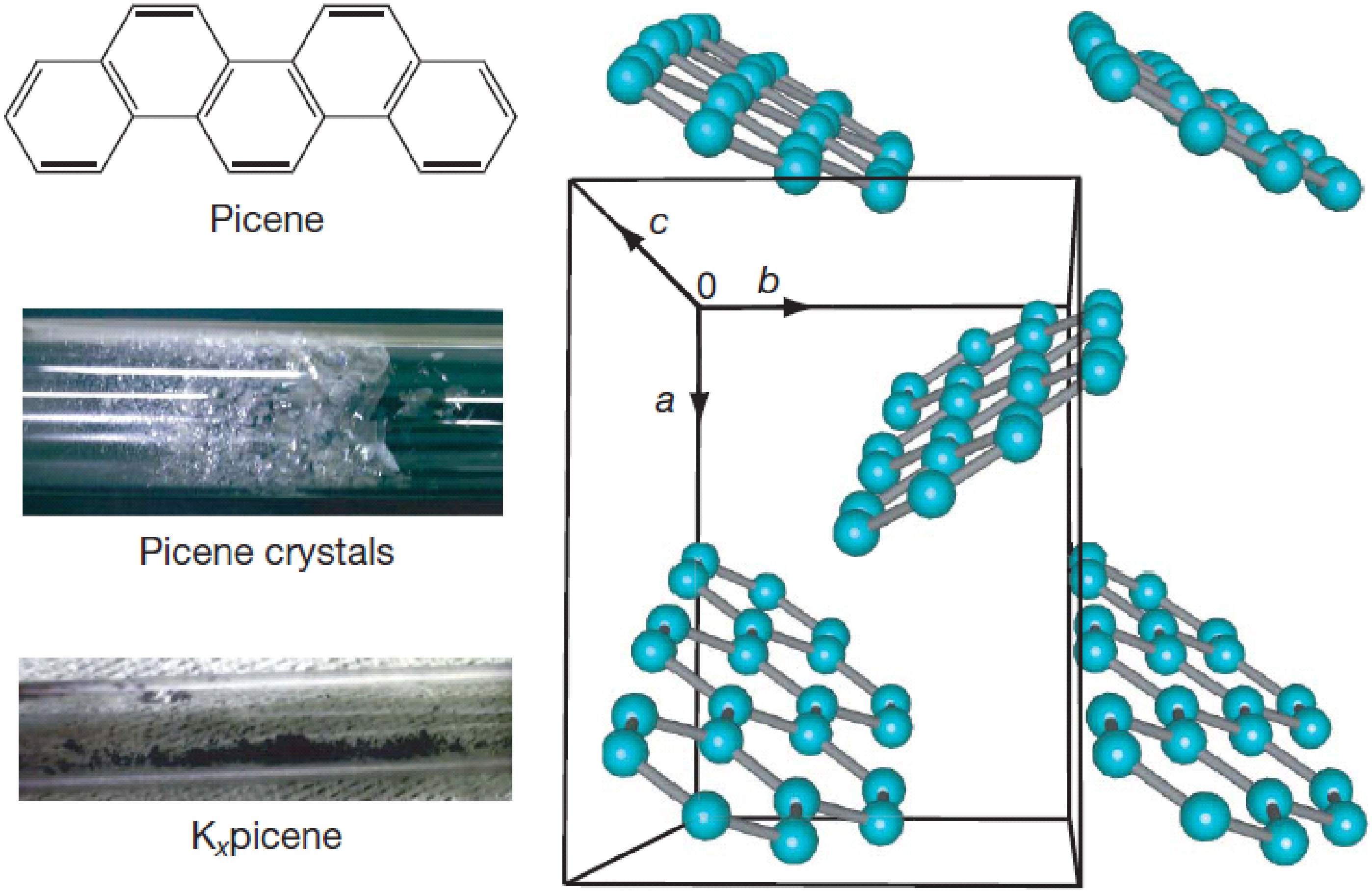
Structure Studies

1. Previous studies
2. Issues and Methodology
3. Undoped: van der Waals interaction
4. **Doped cases:** (reported last year)
    - **K-doped (Tc = 7K and 18K)**
    - La-doped (*d*-electron at Fermi surface)

Previous Studies

1. Undoped, P = 1 atm, most are experimentally known, some ;
2. Doped $C_{22}H_{14}$, some studies;
3. Doped $C_{14}H_{10}$, some studies;
4. Doped $C_{30}H_{18}$ and others, no studies;
5. …
6. Few results as functions of pressure.

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



Picene

Picene crystals

$K_x$picene

Figure 1 | Molecular structure, crystal structure and physical appearance of picene. Photographs show pristine picene (top; white) and $K_x$picene (bottom; black).

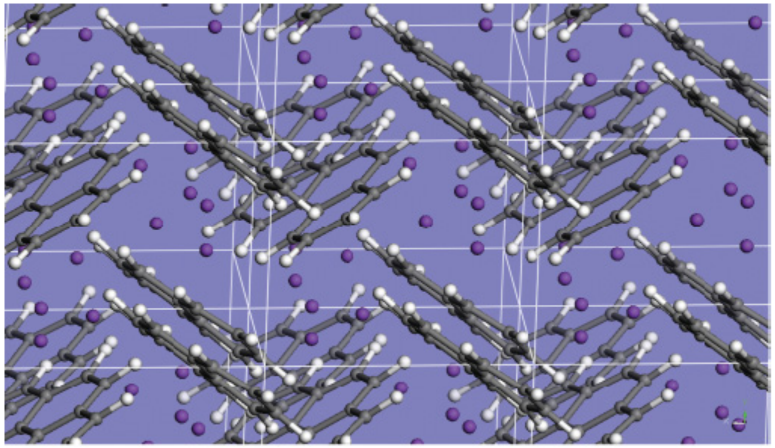
$C_{14}H_{10}$ (theory)

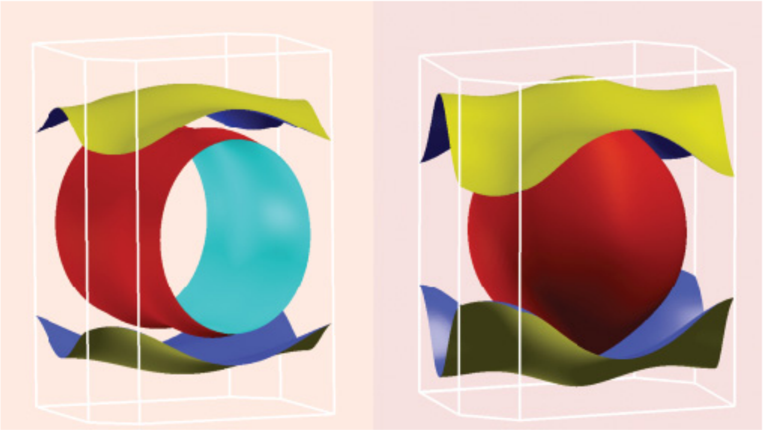
PHYSICAL REVIEW B **84**, 144501 (2011)

Ab initio electronic and geometrical structures of tripotassium-intercalated phenanthrene

P. L. de Andres,[1,*] A. Guijarro,[2] and J. A. Vergés[3]
[1]*Donostia International Physics Center (DIPC), Paseo Manuel Lardizabal 4, E-20018 San Sebastian, Spain*
[2]*Departamento de Quimica Organica and Instituto Universitario de Sintesis Organica, Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*
[3]*Departamento de Teoria y Simulacion de Materiales, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, E-28049 Madrid, Spain*

(Received 26 July 2011; published 3 October 2011)





Two sheets Fermi surface -> 1D & 2D Characters

$C_{22}H_{14}$ (ab initio)

First-Principles Electronic Structure of Solid Picene

Taichi KOSUGI[1,2], Takashi MIYAKE[2,4], Shoji ISHIBASHI[2],
Ryotaro ARITA[3,4], and Hideo AOKI[1]

Journal of the Physical Society of Japan
Vol. 78, No. 11, November, 2009, 113704

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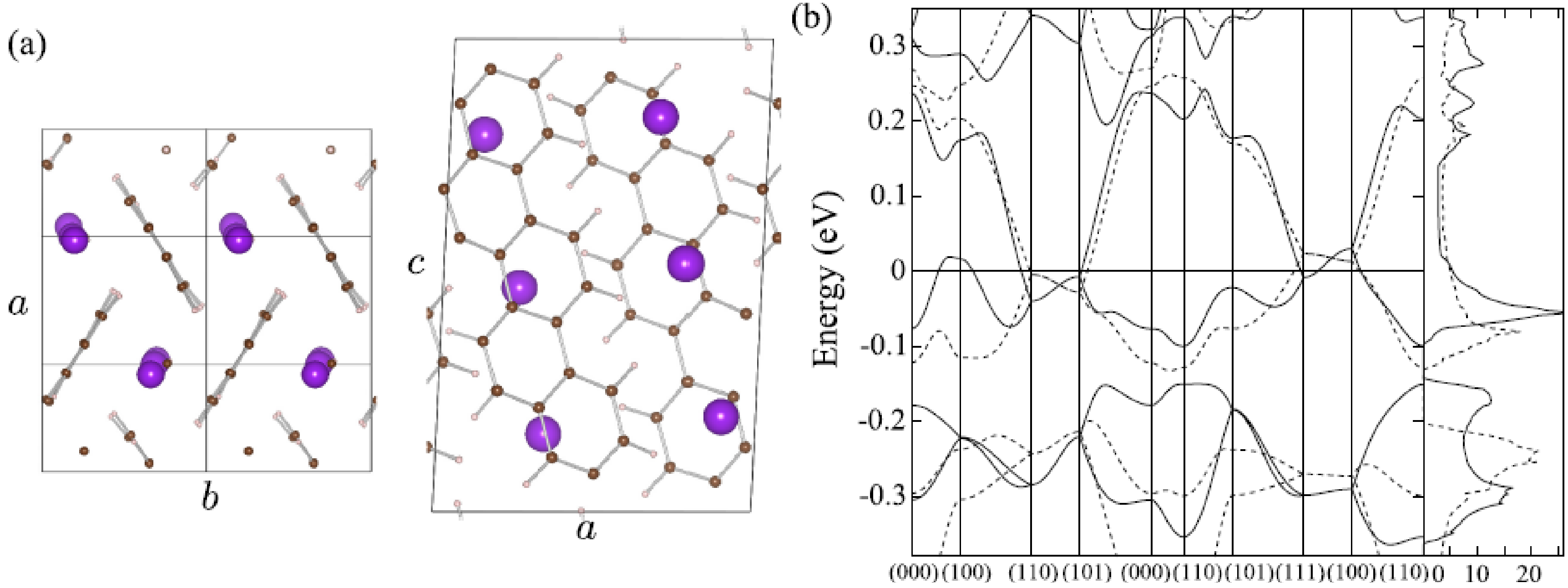
(Received August 14, 2009; accepted August 21, 2009; published November 10, 2009)



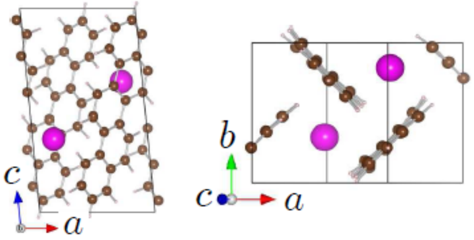
$C_{22}H_{14}$ (ab initio)

arXiv:1109.2059v1
(Submitted on 9 Sep 2011)

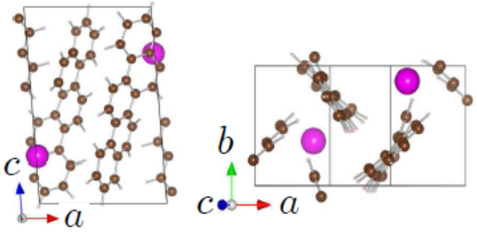
First-principles structural optimization and electronic structure of picene superconductor for various potassium-doping levels

Taichi Kosugi[1], Takashi Miyake[1,2], Shoji Ishibashi[1], Ryotaro Arita[2,3,4], and Hideo Aoki[5]
[1] *Nanosystem Research Institute "RICS", AIST, Umezono, Tsukuba 305-8568, Japan*
[2] *Japan Science and Technology Agency (JST), CREST, Honcho, Kawaguchi, Saitama 332-0012, Japan*
[3] *Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8656, Japan*
[4] *Japan Science and Technology Agency (JST), PRESTO, Kawaguchi, Saitama 332-0012, Japan and*
[5] *Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033, Japan*

K_1picene (A)



K_1picene (B)

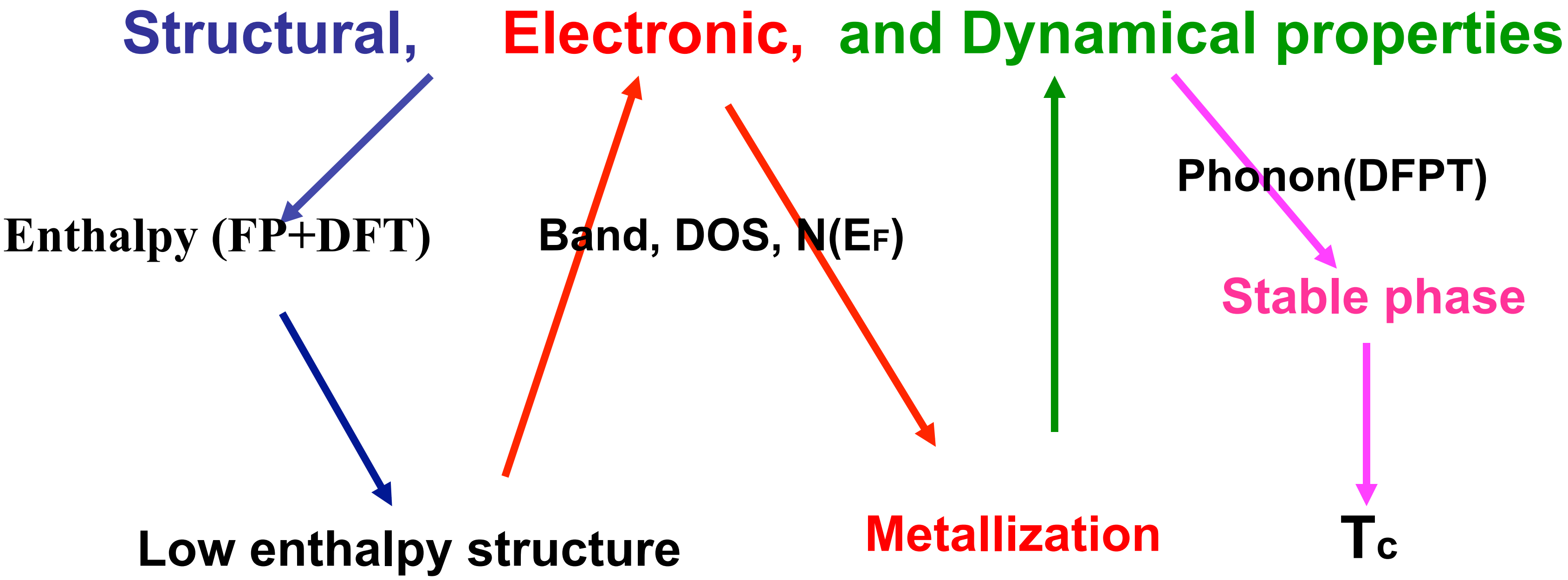


Searching Optimal Structure is nontrivial

Issues

- How to find structural of global minimum?
- How to take care of electron-electron correlations?
- How to select (generate) pseudo potential?
- How to deal with van der Waals force?
- **The position of doped K, La, etc.?**
- Computational speed up, e.g., calculation of Phonon spectrum, high throughput computation, etc.
- …

Computational Approach



Structural, Electronic, and Dynamical properties

Enthalpy (FP+DFT)

Low enthalpy structure

Band, DOS, $N(E_F)$

Metallization

Phonon(DFPT)

Stable phase

T_c

- **Issues: Structure phase transition; Metallization pressure; Electronic and Dynamic properties; Superconductivity.**
- **Codes: VASP, CASTEP, Quantum Espresso, etc.**
- **When determining stable structure, zero point energy included.**

XRD/Raman: solving the structure, theory vs experiment.

Methodology

- Structure optimization: DFT with Generalized Gradient Approximation (GGA), implemented in the VASP (Vienna *ab initio* simulation package) with projected augmented wave (PAW) Norm-conserving pseudo-potential
- Quantum-ESPRESSO package (www.pwscf.org) with Vanderbilt type ultra soft pseudo-potential and GGA is used to calculate electron-phonon interaction and superconducting parameter

Method (undoped and K-doped)

- Package: VASP.
- Method: PAW.
- Exchange correlation potential: LDA, GGA-PBE, PBE-vdW, Heyd-Scuseria-Ernzerhof (HSE).
- Cutoff energy: 600 eV.
- K-point: Monkhorst-Pack k-point grids, separation 0.02 Å^{-1}; convergence thresholds, 10^{-5} eV in energy and 0.005 eV/Å in force; A conjugate-gradient algorithm was used to relax the ions into their instantaneous ground state.
- DOS calculations: tetrahedron method.

Pristine Solid phenanthrene ($C_{14}H_{10}$)

Method	a	b	c	β	V
Expt 1	8.453	6.175	9.477	98.28	489.6
Expt 2	8.472	6.166	9.467	98.01	
Other's Theo.	8.05	5.96	9.16	96.8	
LDA	8.102 -4.2%	5.731 -7.2%	9.018 -4.8%	96.82 -1.5%	415.74 -15.1%
PBE	8.273 -2.1%	7.450 +20.6%	10.278 +8.5%	115.49 +17.5%	571.78 +16.8%
revPBE, vdW	8.801 +4.1%	6.065 -1.8%	9.440 -0.3%	98.16 -0.1%	499.10 +1.9%
optPBE, vdW	8.506 +0.6%	5.936 -4.0%	9.304 -1.8%	97.19 -1.1%	465.63 -4.9%
optB88, vdW	8.344	5.808	9.214	96.83	443.33
optB86b, vdW	8.230 -2.6%	5.880 -4.8%	9.240 -2.5%	96.58 -1.7%	444.54 -9.2%
rPW86, vdW	8.314 -1.6%	5.969 -3.3%	9.254 -2.4%	97.31 -0.9%	455.53 -7.0%
rPW86, vdW2	8.547 +1.1%	5.997 -2.9%	9.323 -1.6%	98.00 -0.2%	473.25 -3.3%
DFT-D2	8.129	5.794	9.133	96.53	427.29

Pristine Solid picene ($C_{22}H_{14}$)

Method	a	b	c	β	V
Expt	**8.480**	**6.154**	**13.515**	**90.46**	**705.27**
LDA	**8.194** **-3.4%**	**5.736** **-6.8%**	**13.055** **-3.4%**	**89.30** **-1.3%**	**613.51** **-13.0%**
PBE	**9.461** **+11.6%**	**6.320** **+2.7%**	**13.706** **+1.4%**	**92.43** **+2.1%**	**818.80** **+16.1%**
revPBE, vdW	**8.821** **+4.0%**	**6.103** **-0.8%**	**13.553** **-0.3%**	**90.93** **+0.5%**	**729.52** **+3.4%**
optPBE, vdW	8.543	5.984	13.401	90.00	685.04
optB88, vdW	8.408	5.829	13.293	89.44	651.40
optB86b, vdW	8.330	5.878	13.342	89.20	653.20
rPW86, vdW	8.436	5.975	13.353	90.01	673.03
rPW86, vdW2	**8.572** **+1.1**	**6.038** **-1.9%**	**13.420** **-0.7%**	**90.43** **-0.0%**	**694.70** **-1.5%**
DFT-D2	**8.222**	**5.773**	**13.255**	**89.02**	**629.07**

Pristine Solid 1,2;8,9-dibenzopentacene ($C_{30}H_{18}$)

Method	a	b	c	β	V
LDA	**6.279**	**7.381**	**21.225**	**122.35**	**831.00**
PBE	**6.792**	**7.972**	**22.134**	**123.24**	**1002.36**
revPBE, vdW	**6.704**	**7.943**	**21.885**	**122.63**	**981.47**
optPBE, vdW					
optB88, vdW	6.477	7.368	21.422	122.01	866.85
optB86b, vdW					
rPW86, vdW	6.642	7.419	21.461	121.77	899.06
rPW86, vdW2	**6.597**	**7.728**	**21.690**	**122.54**	**932.27**
DFT-D2	**6.316**	**7.319**	**21.392**	**122.28**	**836.14**

Summary of Undoped Cases

1. For $C_{14}H_{10}$ and $C_{22}H_{14}$, the optimized crystal structures based on LDA and PBE are both far away from the experiments. The volume obtained by LDA/PBE is smaller/larger than the experimental one.

2. Crystal structures agreeable with experimental values could be obtained after considering the van der Waals interactions for $C_{14}H_{10}$ and $C_{22}H_{14}$, indicating the importance of the vdW interactions. We also noted the effect of correlations involved, e.g., programs revPBE and rPW86.

3. Based on our experience with the vdW, we predicted the crystal structure of $C_{30}H_{18}$, to be confirmed by the experiment.

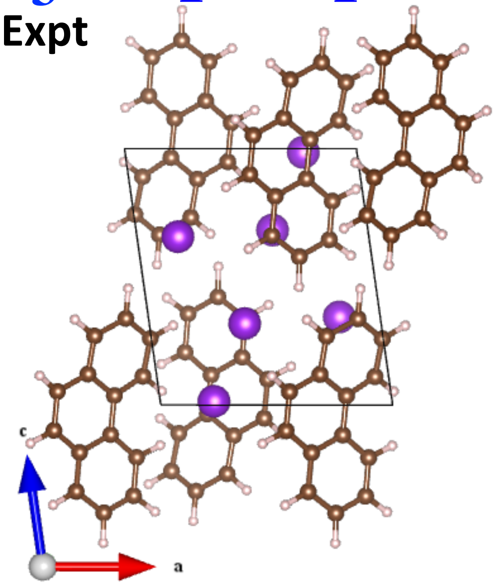
4. We also studied structures of other hydrocarbons.

Doped Cases

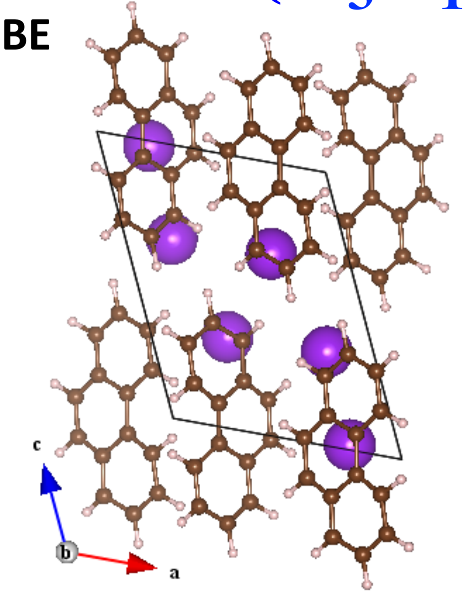
1. We carried out the PBE-, LDA-, and vdW-included calculations and checked out dozens of configurations for $K_3C_{14}H_{10}$ and $K_3C_{22}H_{14}$.
2. LDA-S1 gave the most common structure during the optimization, LDA-S2 gave the most stable structure, while LDA-S3 and LDA-S4 gave two configurations closer to the experimental case.
3. The vdW interaction is weak.
4. **The positions of K atoms are hard to locate.**
5. For $K_3C_{30}H_{18}$, calculations are very expensive, yet no experiments to compare.

K_3-doped phenanthrene ($K_3C_{14}H_{10}$)

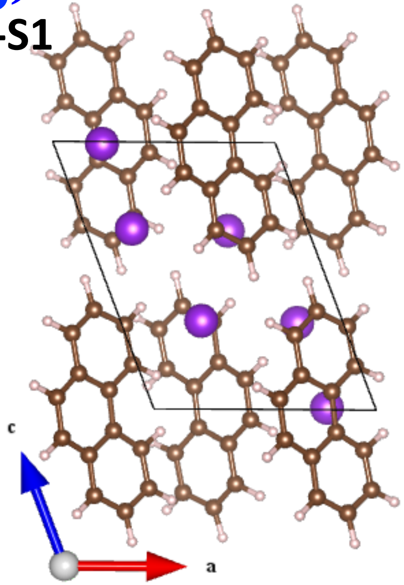
Expt



PBE

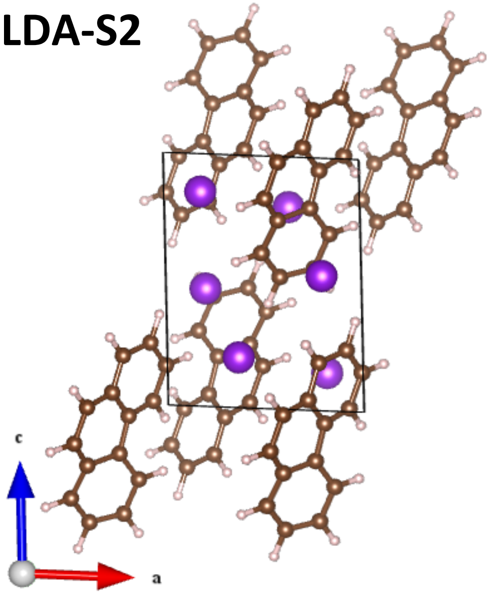


LDA-S1



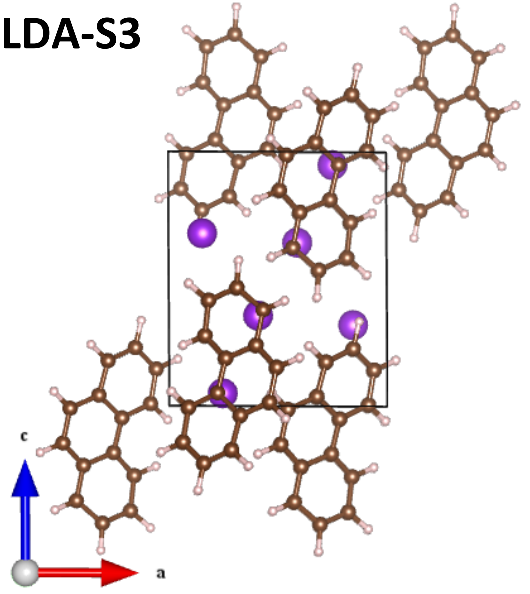
-360.47565 eV

LDA-S2



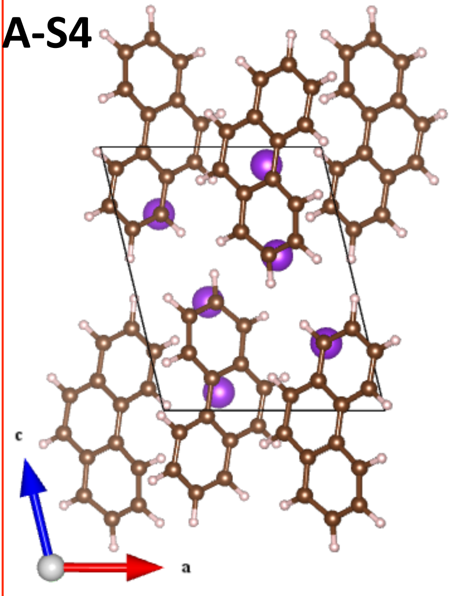
-360.76000 eV

LDA-S3



-360.04223 eV

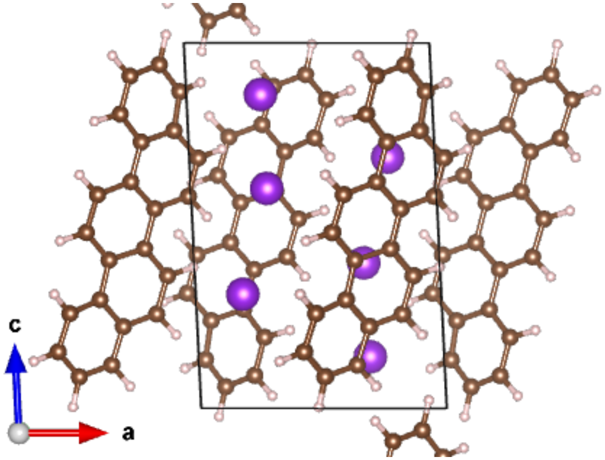
LDA-S4



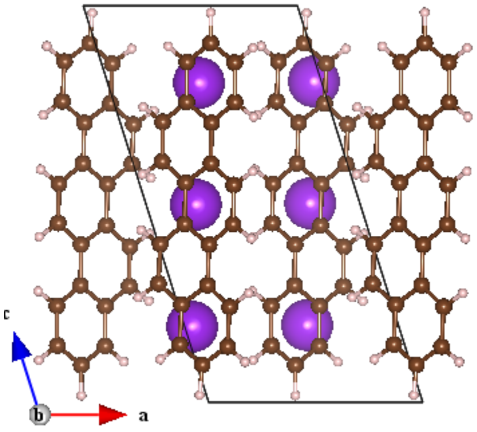
-360.02803 eV

K_3-doped picene ($K_3C_{22}H_{14}$)

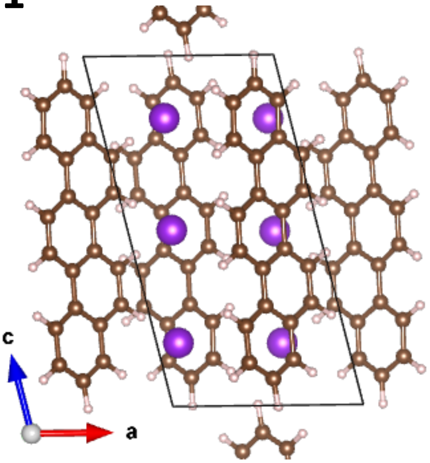
Exp



PBE

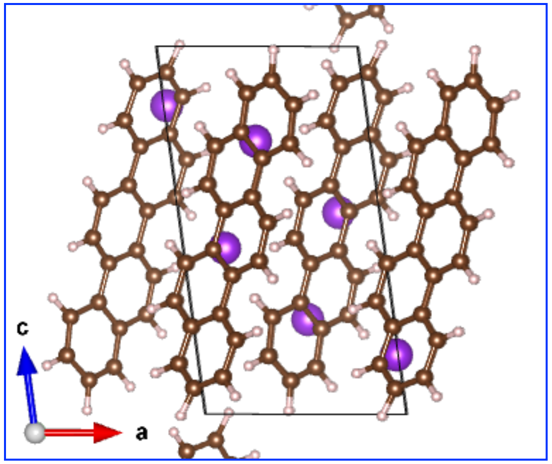


LDA-S1



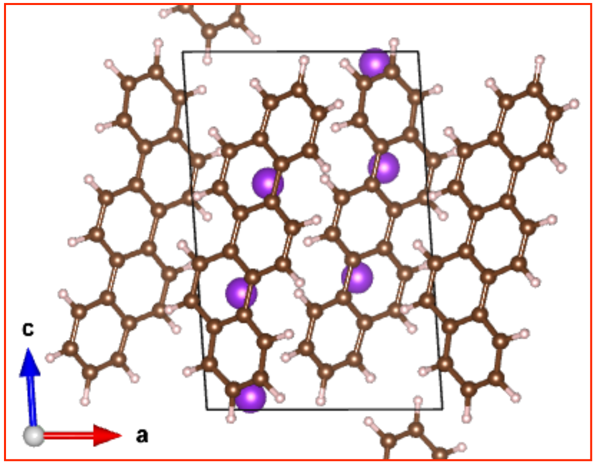
-550.94285 eV

LDA-S2



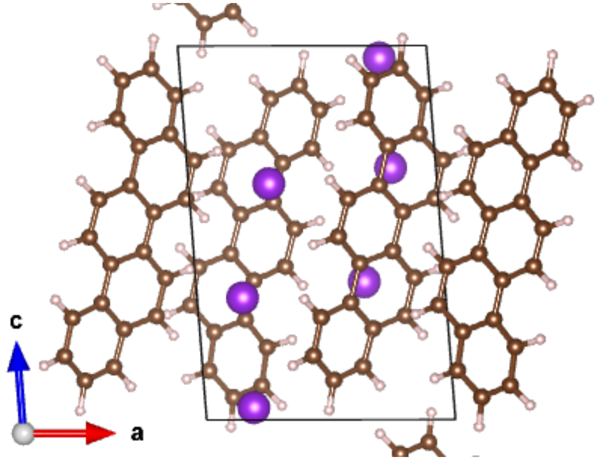
-551.09229 eV

LDA-S3



-550.04097 eV

optB86b,vdW

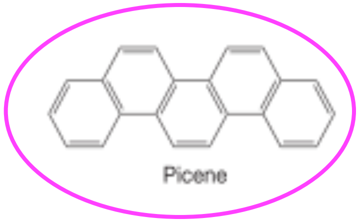


-550.56712 eV

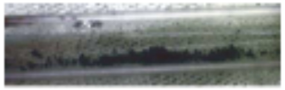
Identify two superconducting phases in potassium-doped picene, why two Tc?

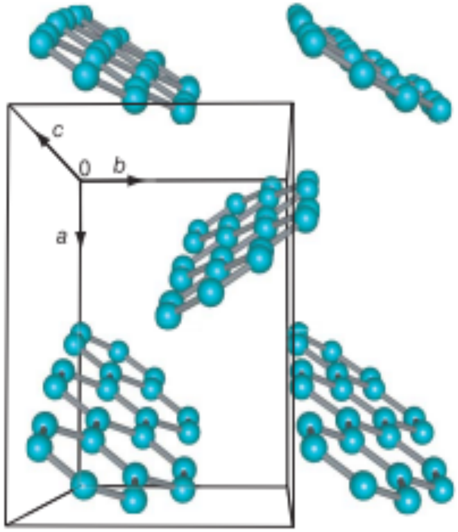
Superconductivity in alkali-metal-doped picene

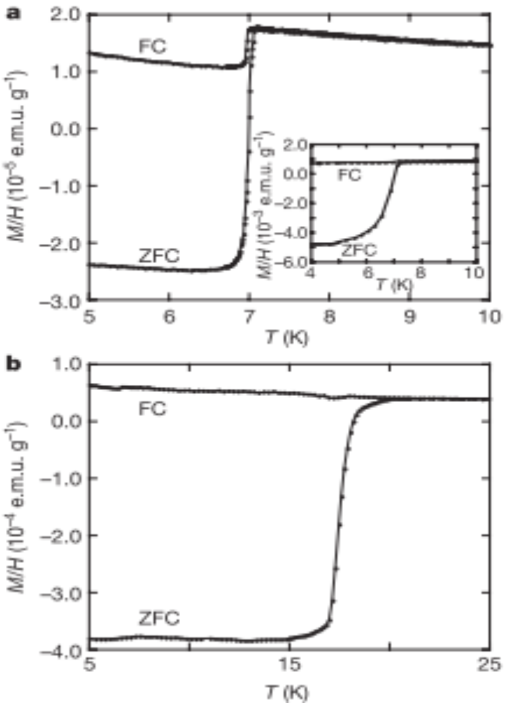
Ryoji Mitsuhashi[1], Yuta Suzuki[2], Yusuke Yamanari[2], Hiroki Mitamura[1], Takashi Kambe[2], Naoshi Ikeda[2], Hideki Okamoto[3,4], Akihiko Fujiwara[5], Minoru Yamaji[6], Naoko Kawasaki[1], Yutaka Maniwa[7] & Yoshihiro Kubozono[1]


Picene


Picene crystals


K_3picene





Tc = 7K

Tc = 18 K

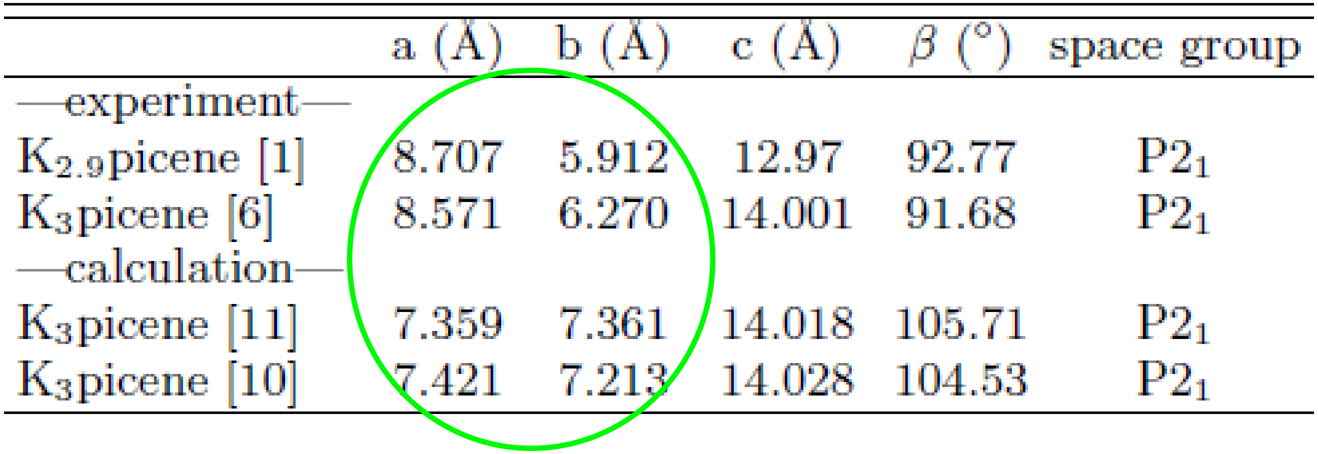
Picene ($C_{22}H_{14}$) (experiment)

Concerned Issues

1. Why there exist multiple superconducting phases?
2. What are the crystal and electronic structures for each phase?

Previous Studies

Lattice parameters: experiment and theory



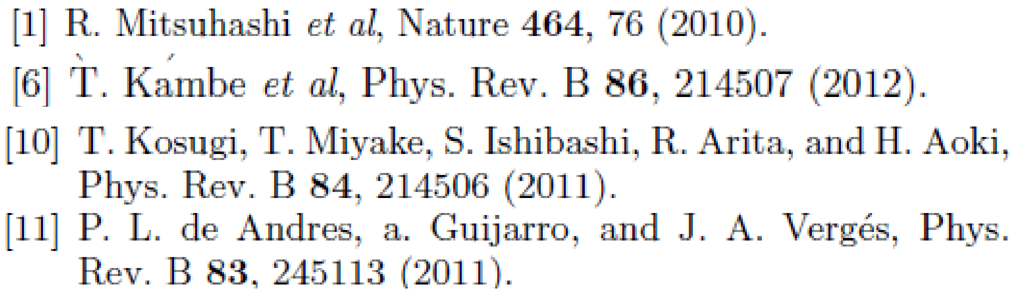
	a (Å)	b (Å)	c (Å)	β (°)	space group
—experiment—					
$K_{2.9}$picene [1]	8.707	5.912	12.97	92.77	$P2_1$
K_3picene [6]	8.571	6.270	14.001	91.68	$P2_1$
—calculation—					
K_3picene [11]	7.359	7.361	14.018	105.71	$P2_1$
K_3picene [10]	7.421	7.213	14.028	104.53	$P2_1$

→ Tc ~ 7K

→ Tc ~ 18K

(LDA)

Large discrepancies for a and b axises!



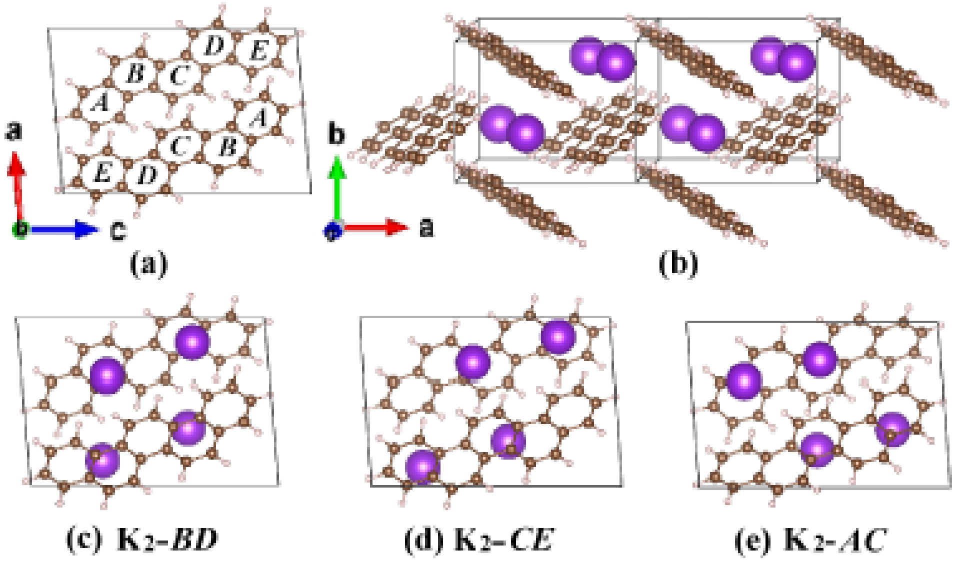
[1] R. Mitsuhashi *et al*, Nature **464**, 76 (2010).

[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).

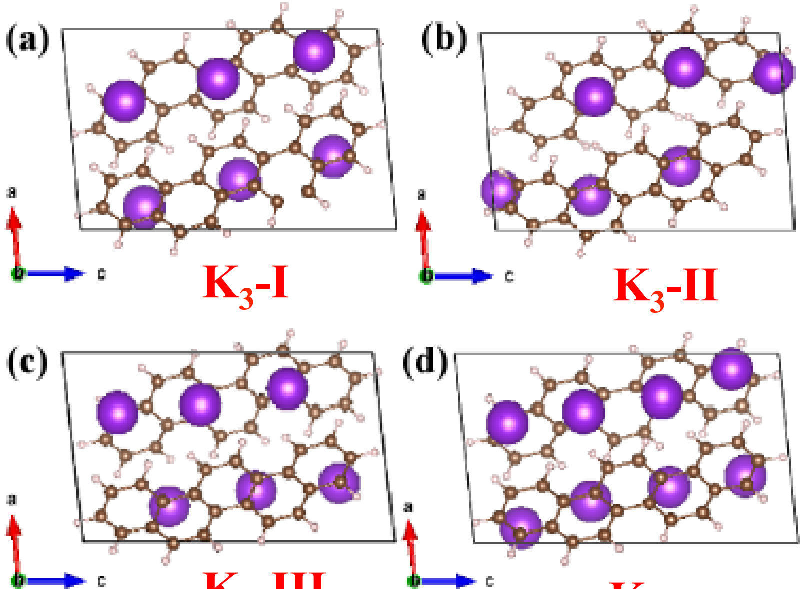
[11] P. L. de Andres, a. Guijarro, and J. A. Vergés, Phys. Rev. B **83**, 245113 (2011).

Possible Crystal Structures



(a) (b)

(c) K_2-*BD* (d) K_2-*CE* (e) K_2-*AC*



K_3-I K_3-II

K_3-III K_4

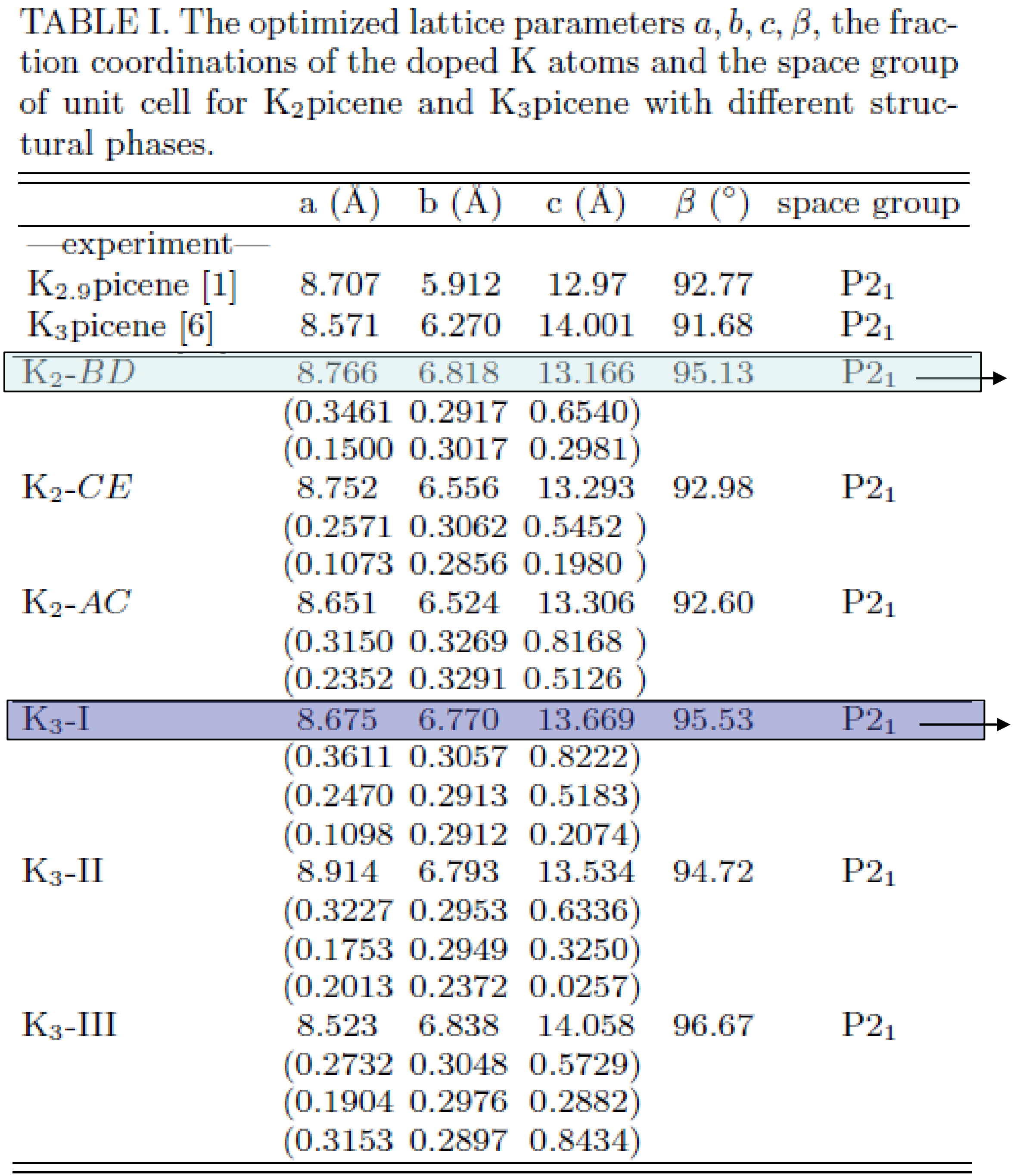


TABLE I. The optimized lattice parameters a, b, c, β, the fraction coordinations of the doped K atoms and the space group of unit cell for K_2picene and K_3picene with different structural phases.

	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

Stability: Formation Energy

$$E_{formation} = E_{Kxpicene} - E_{picene} - E_{Kx}$$

x stands for the number of K atoms.

K_2-BD: $E_{formation}$ = -0.330 eV per K atom.

K_3-I: $E_{formation}$ = -0.295 eV per K atom.

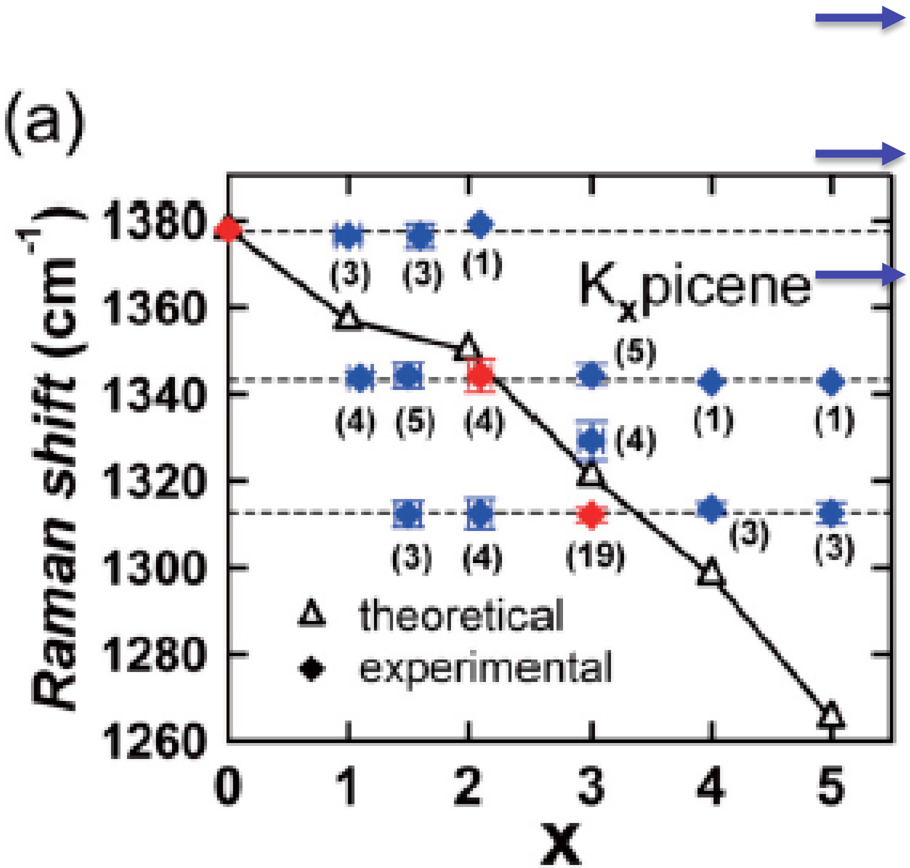
K_4picene: $E_{formation}$ = -0.067 eV per K atom,

→ unstable

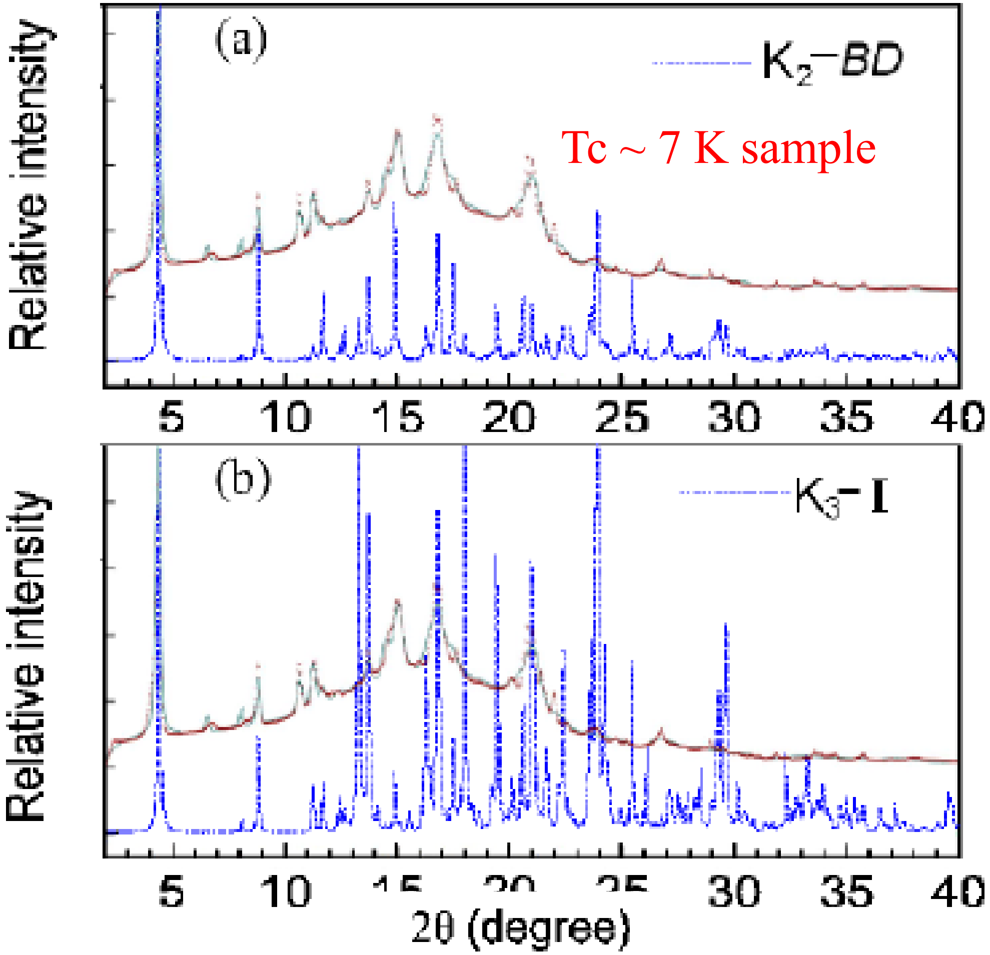
Experiment

Only K_2 picene and K_3 picene can be realized!

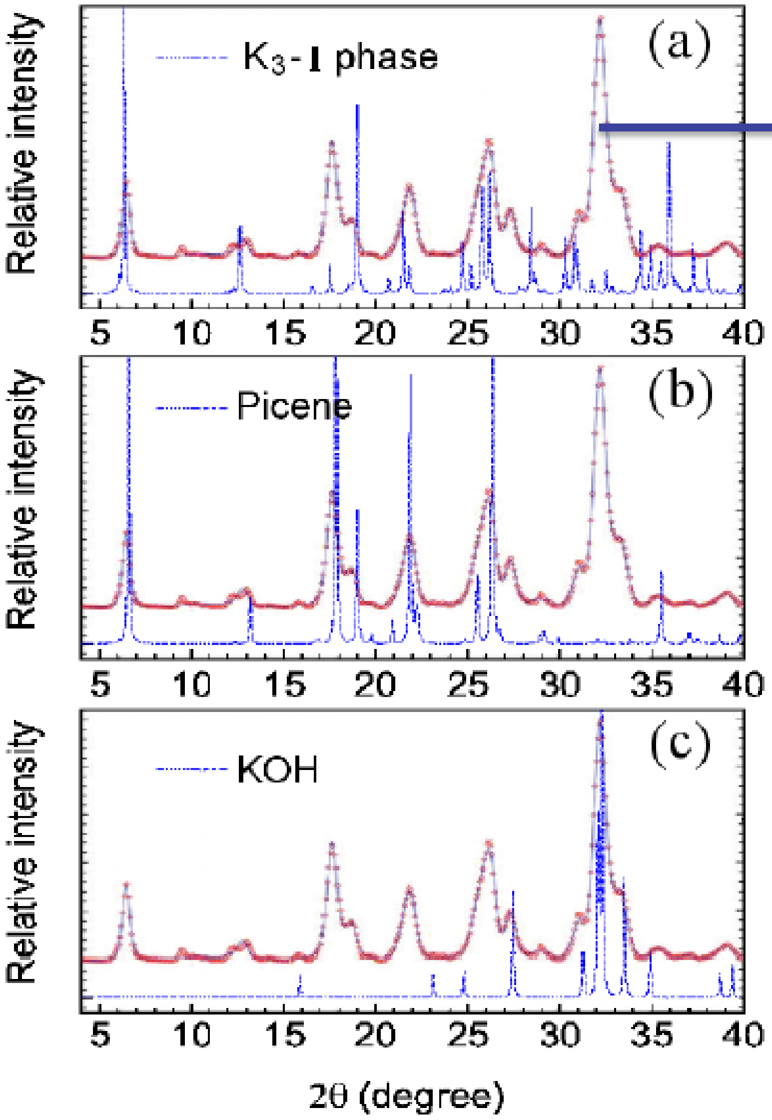
PHYSICAL REVIEW B 86, 214507 (2012)



XRD spectra between experiment and theory



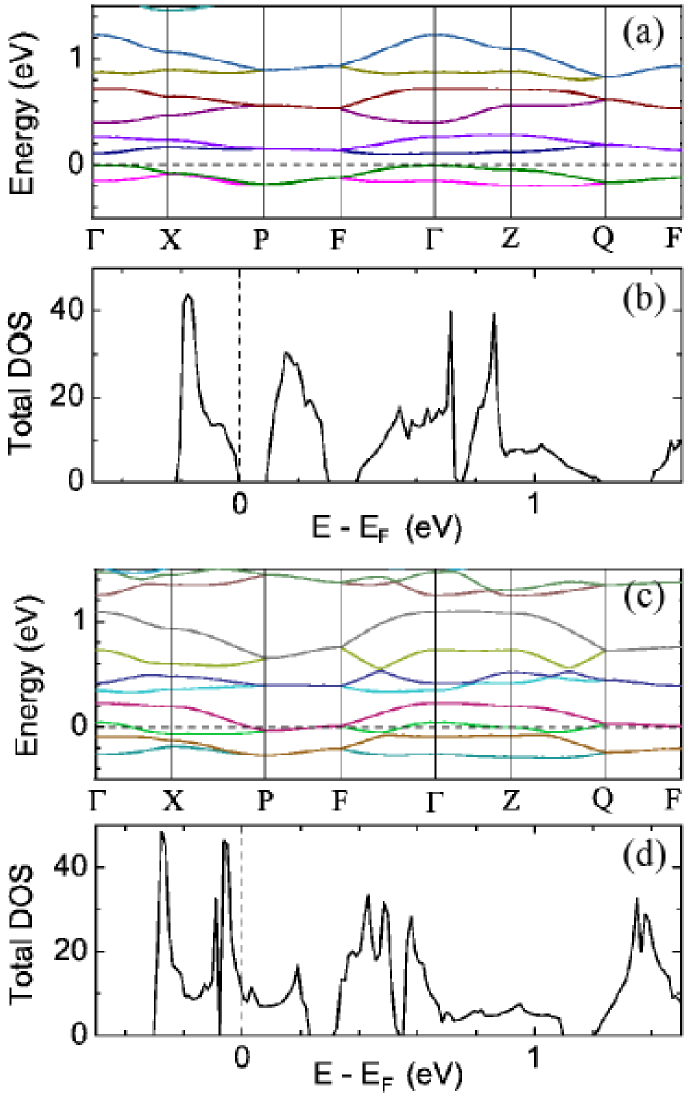
Tc ~ 7 K sample corresponds to K_2-BD.



Tc ~ 18 K sample

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

Band Structure



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.

Superconductivity at Tc = 7K

The K_2-*BD* phase is a semiconductor with an energy gap of 0.1 eV, which can be regarded as the parent compound for the T*c* = 7 K SC phase.

Superconductivity can be induced either through a deviation of K concentration from 2 in the K_2-*BD* phase, similar to semiconductor doping, or by a transfer of electrons from K atoms on the polycrystalline boundary to the picene molecules.

Superconductivity at Tc = 18K

The K3-I phase is a metal with relatively high DOS value of 10.4 states/eV per unit cell at the Fermi level, which could lead to superconductivity with T*c*=18 K.

Brief Summary

- For undoped hydrocarbon compounds, crystal structures of $C_{14}H_{10}$ and $C_{22}H_{14}$ are experimentally known, but $C_{30}H_{18}$ are still under investigating.
- For K-doped cases, few structures are known. Searching optimal structures are non-trivial.
- By carrying out XRD studies, we gave reasonable explanations on two Tc phases observed in $C_{22}H_{14}$.
- Usual DFT studies on crystal structure do not provide results agree well with experiments. **Different searching algorithms** may find their values here.

Superconductivity in Doped Solid Benzene

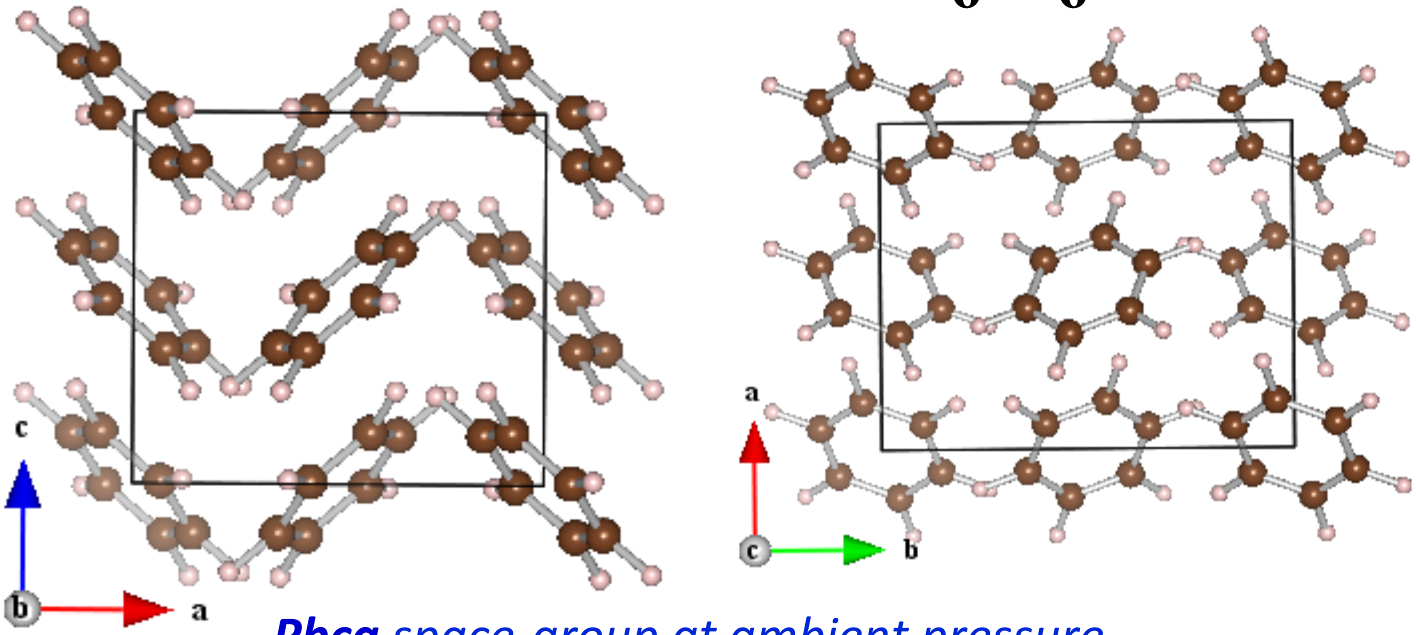
The 5-7K SC phase

- Motivation and issues
- Brief review on solid benzene relevant phases
- Doping into solid benzene: possible structures, formation energy, band structure, Fermi surface, superconductivity, etc.

Concerned Issues

- All aromatic hydrocarbons are made of benzene rings, could one benzene ring, as the unit cell, also superconducting?
- Solid benzene has a rich phase diagram with several phases as functions of temperature and pressure, it would be interesting to see if it superconducts, and moreover, if T_c increases under pressure.
- If a single benzene ring superconducts, will it be of common feature for all aromatic hydrocarbons?

Solid Benzene C_6H_6



Pbca *space-group at ambient pressure*

four C_6H_6 f.u. in unit cell.

Kozhin, V. M., Kitaigorodskii, A. I.: Zh. Fiz. Khim. 29 (1955) 2074.

Thiery, M. M.; Leger, J. M. J. Chem. Phys. 1988, 89, 4255–4271

Ciabini, L.; Gorelli, F. A.; Santoro, M.; Bini, R.; Schettino, V.; Mezouar, M. Phys. Rev. B 2005, 72, 094108

Ciabini, L.; Santoro, M.; Gorelli, F. A.; Bini, R.; Schettino, V.; Raugei, S. Nature Mater. 2007, 6, 39–43.

Doping Potassium

- It has low melting point, easy to make.
- Doping potassium is common to all PAHs.
- The interaction between benzene molecule and K+ ion has been observed experimentally and studied theoretically by E L’opez et al.

E. L’opez, J. M. Lucas, J. de Andr’es, M. Albert, J. M. Bofill, D. Bassi, and A. Aguilar, Phys. Chem. Chem. Phys. **13**, 15977 (2011).

Crystal Structure of $K_xC_6H_6$

- We obtained the most stable configurations of after optimization for each doping concentration: (a) x=1; (b) x=2; (c) x=3, viewing from different directions.
- Accuracy check: (a) we used LDA to obtain crystal structure, within 5% of the experimental result; (b) Our calculated band gap of 4.1 eV is in good agreement with the previous result:

X. D. Wen, R. Homann, and N. W. Ashcroft, JACS 133, 9023 (2011).

Formation Energy of $K_xC_6H_6$

$$E_{formation} = E_{Kxpicene} - E_{picene} - E_{Kx}$$

x stands for the number of K atoms.

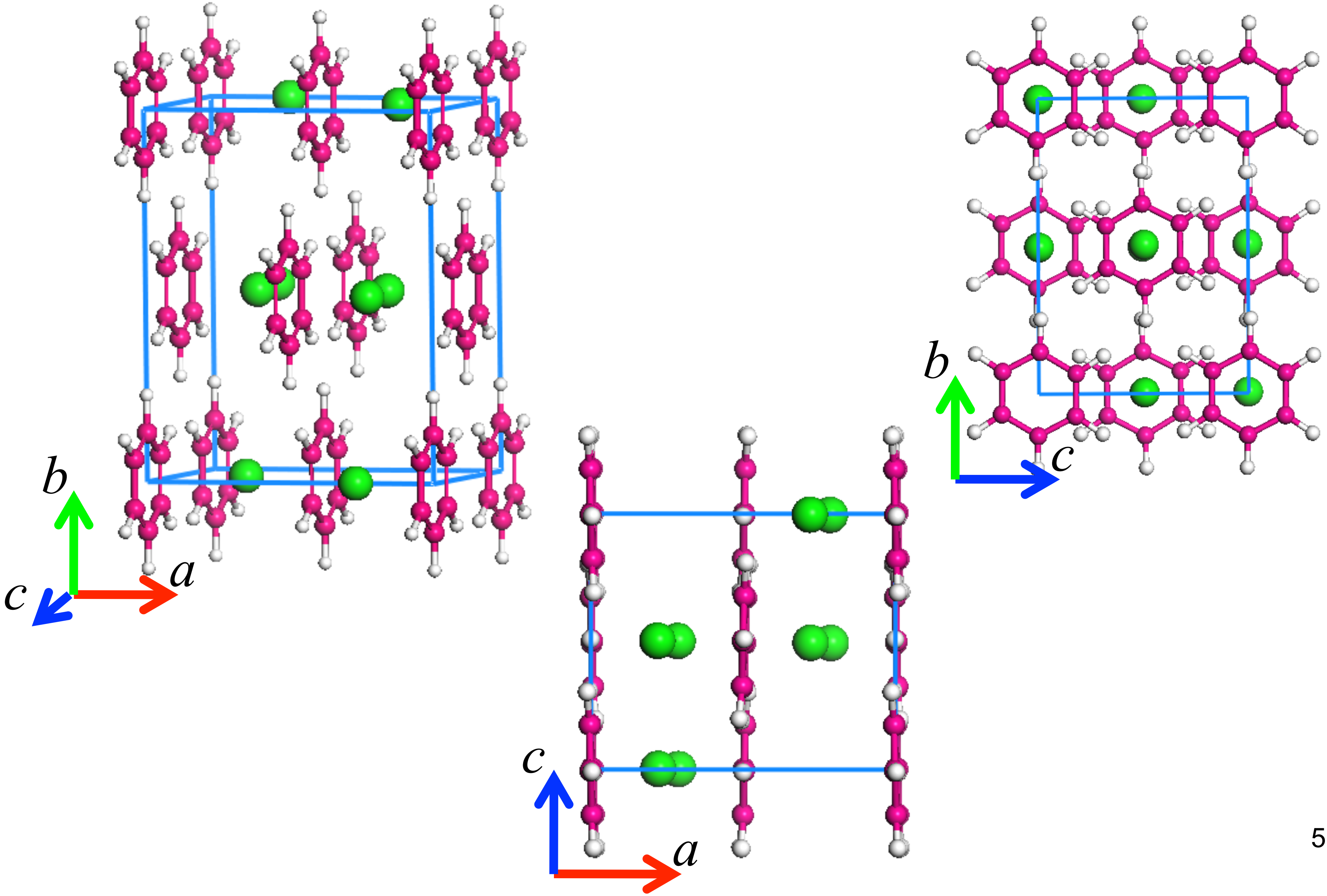
$K_1C_6H_6$: $E_{formation}$ = 0.35 eV per K atom.

$K_2C_6H_6$: $E_{formation}$ = -1.49 eV per K atom.

$K_3C_6H_6$: $E_{formation}$ = 0.51 eV per K atom,

→ $K_2C_6H_6$ is the most stable one to realize

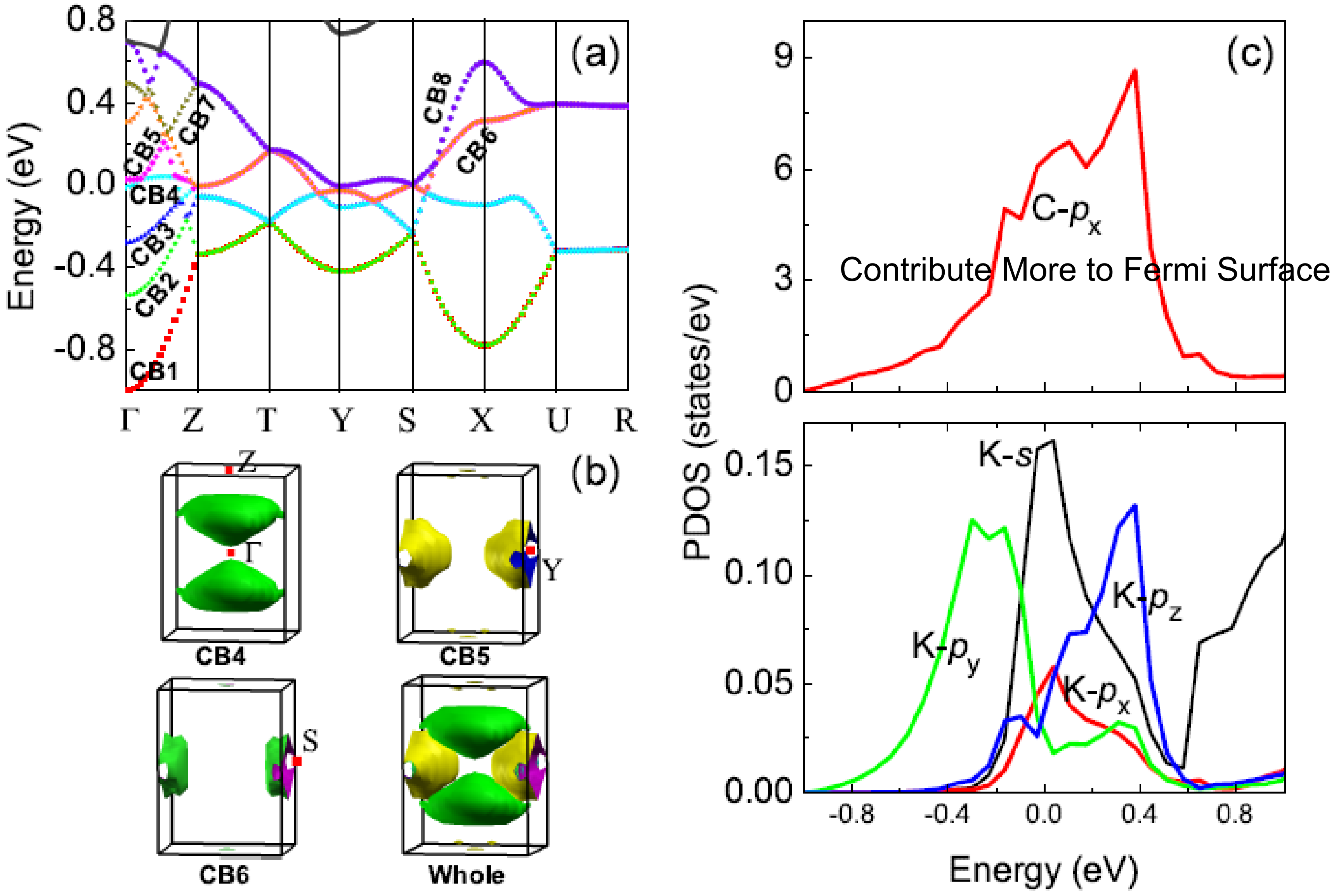
$K_2C_6H_6$: Crystal Structure



Crystal Structure

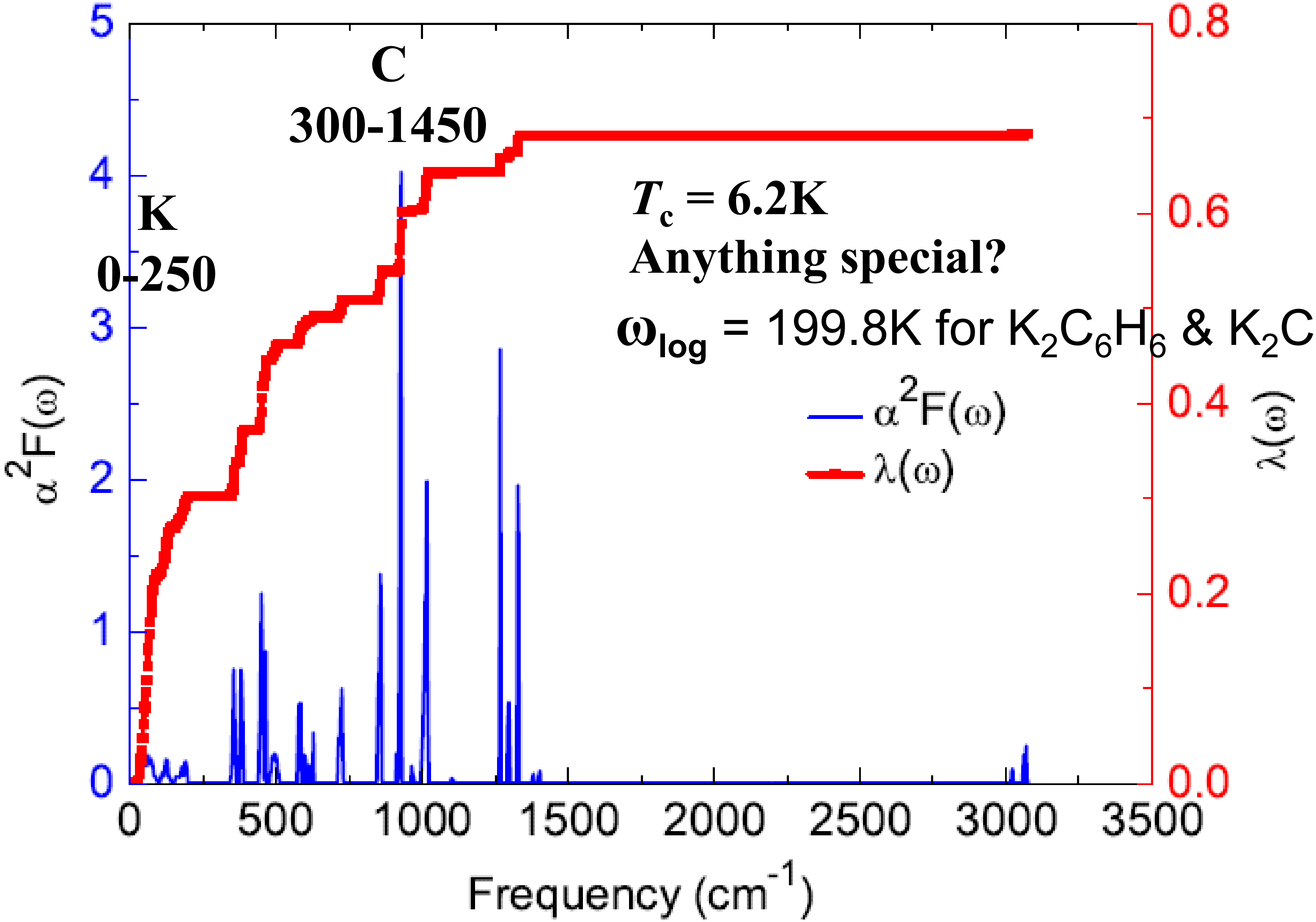
- All doped structures has the Pbca symmetry, but with different rotation of the benzene rings.
- The layered structure is similar to YbC_6 & CaC_6, they both superconduct.

$K_2C_6H_6$: Band structure, Fermi surface, and PDOS



Contribute More to Fermi Surface

$K_2C_6H_6$: Eliashberg spectral function $\omega^2 F(\omega)$ & the electron-phonon coupling integral $\lambda(\omega)$



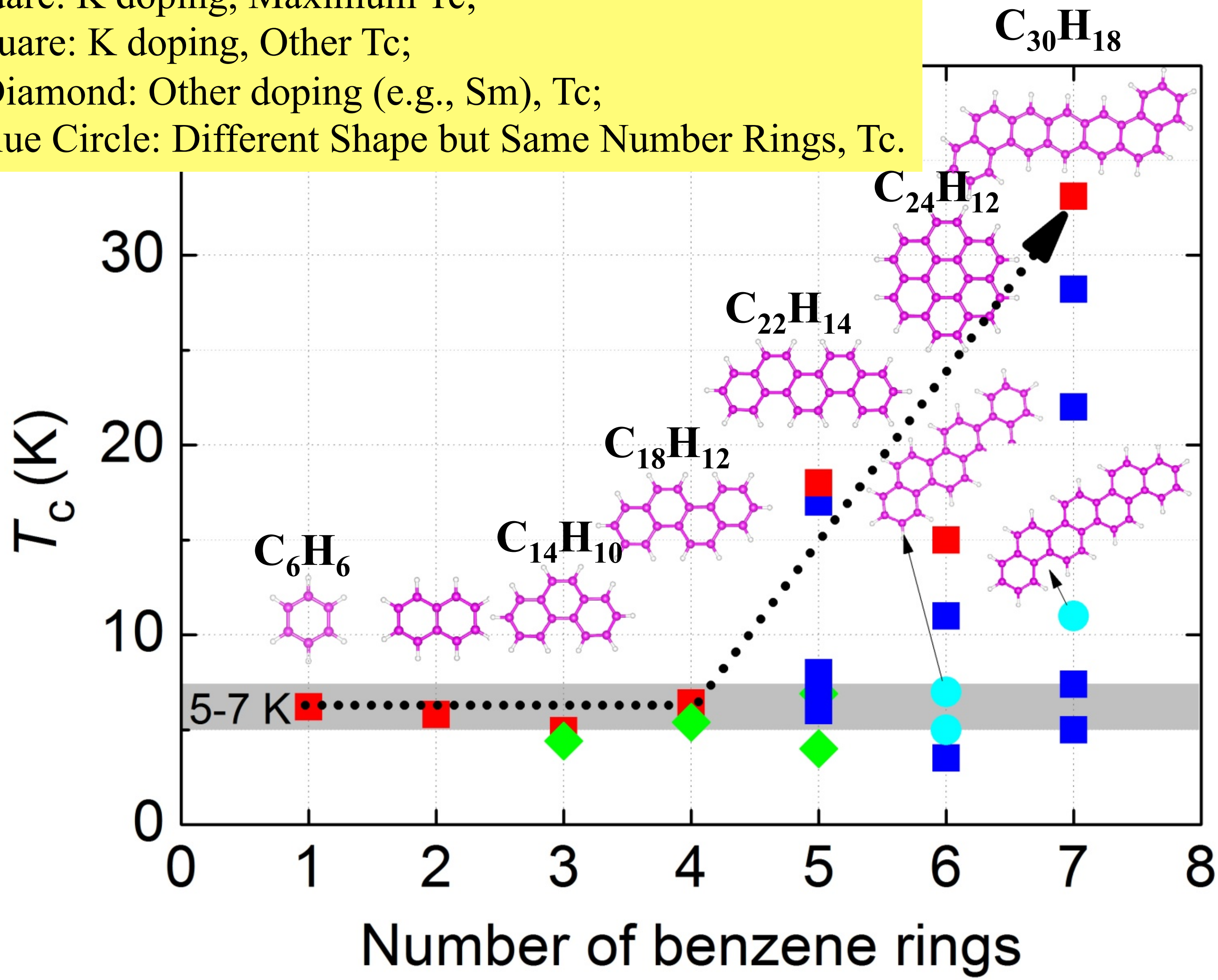
T_c = 6.2K

Anything special?

ω_{log} = 199.8K for $K_2C_6H_6$ & $K_2C_{22}H_{14}$

T_c versus number of benzene rings

Red Square: K doping, Maximum Tc;
Blue Square: K doping, Other Tc;
Green Diamond: Other doping (e.g., Sm), Tc;
Light Blue Circle: Different Shape but Same Number Rings, Tc.



An unique SC Phase?

- For the two-ring case, detail calculations show that the system becomes metal when charge fluctuations occur, very similar to $K_2C_{22}H_{14.}$
- There seems exist a common superconducting phase with T_c about 5-7K.
- How about higher T_c?

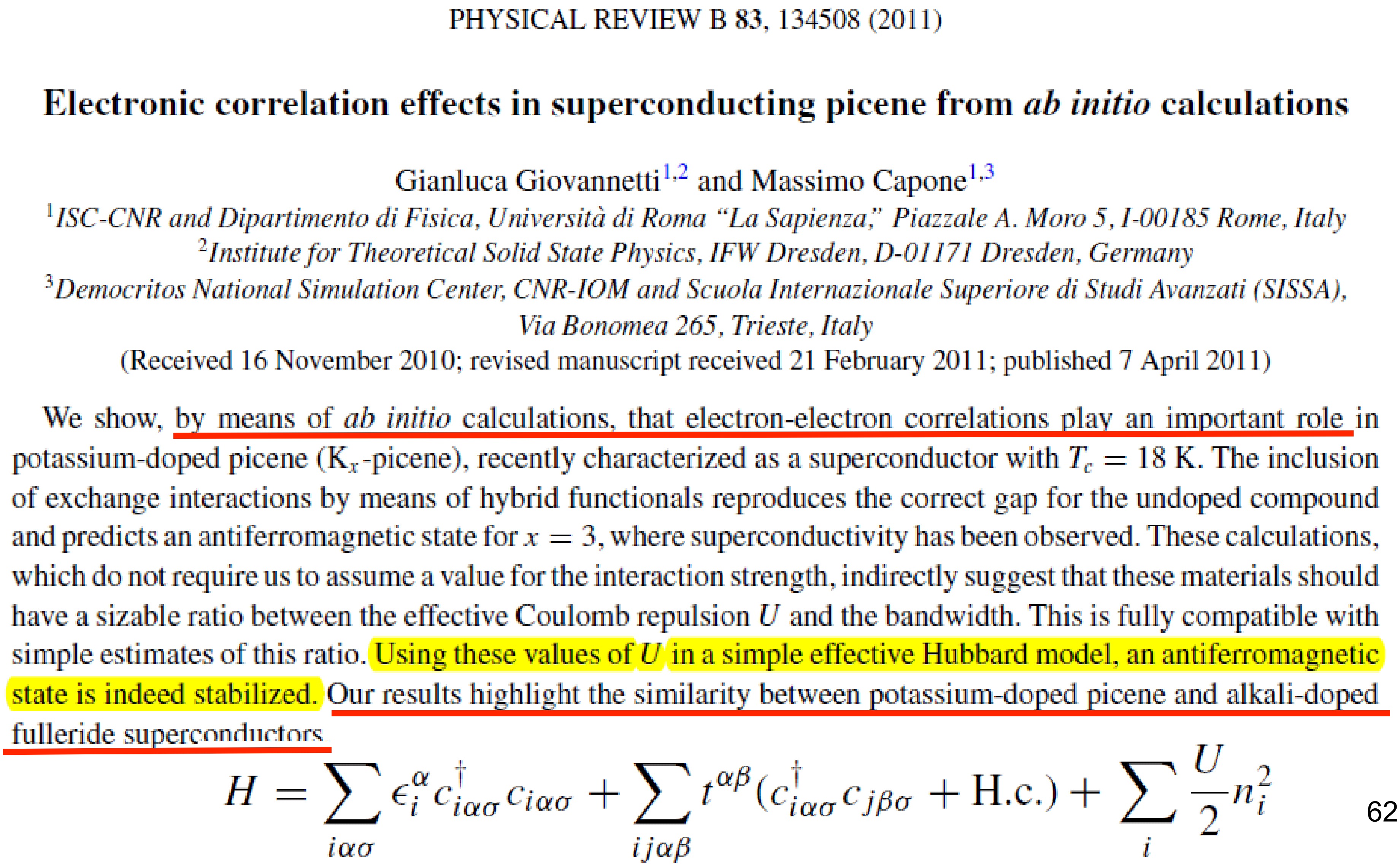
Correlation Effect

Electron-Electron Correlation (EC)?

Measure of correlation?

Magnetism?

Previous Results: $C_{22}H_{14}$ (theory)



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

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

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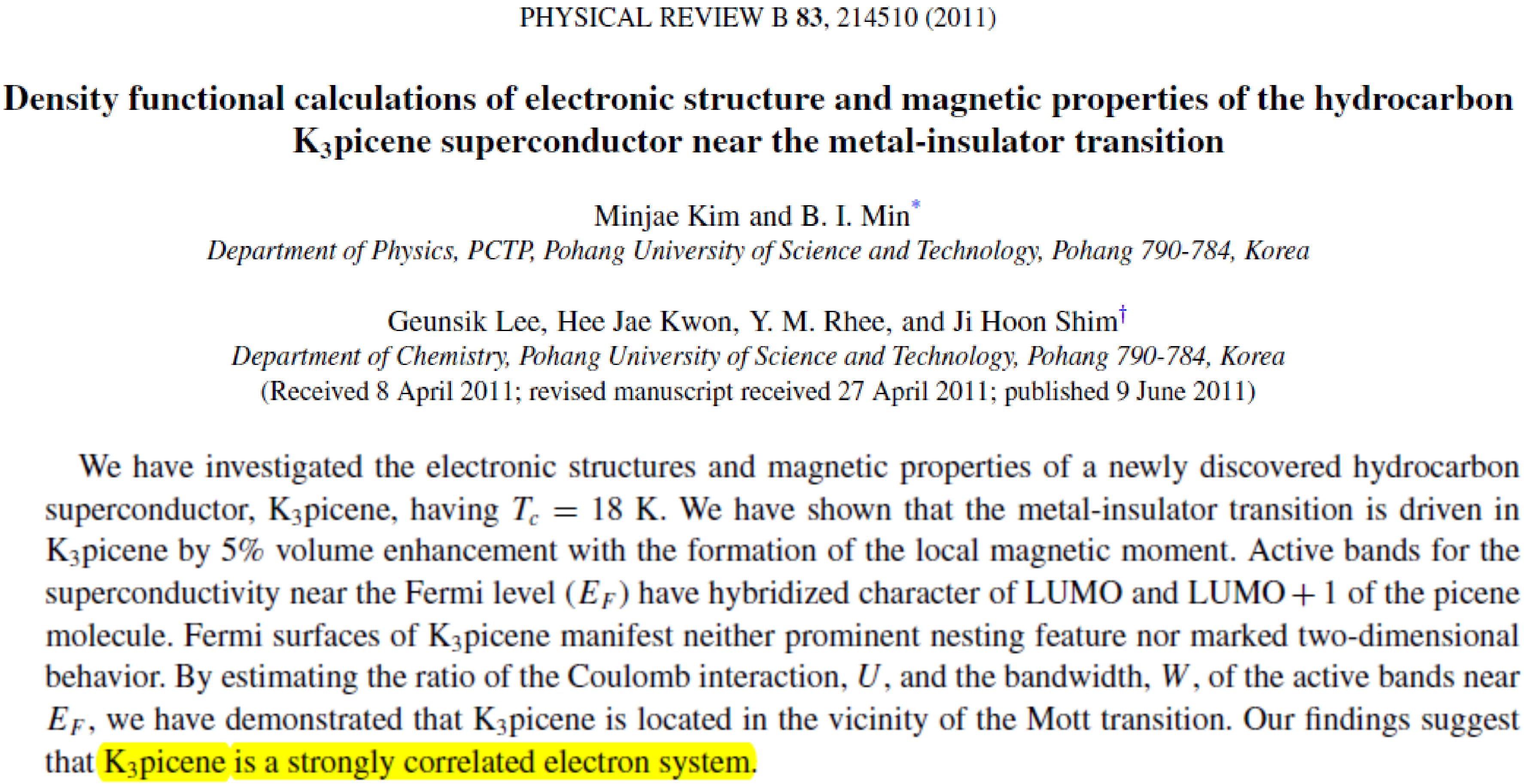
[2] *Institute for Theoretical Solid State Physics, IFW Dresden, D-01171 Dresden, Germany*
[3] *Democritos National Simulation Center, CNR-IOM and Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Bonomea 265, Trieste, Italy*
(Received 16 November 2010; revised manuscript received 21 February 2011; published 7 April 2011)

We show, by means of *ab initio* calculations, that electron-electron correlations play an important role in potassium-doped picene (K_x-picene), recently characterized as a superconductor with $T_c = 18$ K. The inclusion of exchange interactions by means of hybrid functionals reproduces the correct gap for the undoped compound and predicts an antiferromagnetic state for $x = 3$, where superconductivity has been observed. These calculations, which do not require us to assume a value for the interaction strength, indirectly suggest that these materials should have a sizable ratio between the effective Coulomb repulsion U and the bandwidth. This is fully compatible with simple estimates of this ratio. Using these values of U in a simple effective Hubbard model, an antiferromagnetic state is indeed stabilized. Our results highlight the similarity between potassium-doped picene and alkali-doped fulleride superconductors.

$$H = \sum_{i\alpha\sigma} \epsilon_i^{\alpha} c_{i\alpha\sigma}^{\dagger} c_{i\alpha\sigma} + \sum_{ij\alpha\beta} t^{\alpha\beta} (c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} + \mathrm{H.c.}) + \sum_{i} \frac{U}{2} n_i^2$$

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



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

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(Received 8 April 2011; revised manuscript received 27 April 2011; published 9 June 2011)

We have investigated the electronic structures and magnetic properties of a newly discovered hydrocarbon superconductor, K_3picene, having $T_c = 18$ K. We have shown that the metal-insulator transition is driven in K_3picene by 5% volume enhancement with the formation of the local magnetic moment. Active bands for the superconductivity near the Fermi level (E_F) have hybridized character of LUMO and LUMO + 1 of the picene molecule. Fermi surfaces of K_3picene manifest neither prominent nesting feature nor marked two-dimensional behavior. By estimating the ratio of the Coulomb interaction, U, and the bandwidth, W, of the active bands near E_F, we have demonstrated that K_3picene is located in the vicinity of the Mott transition. Our findings suggest that K_3picene is a strongly correlated electron system.

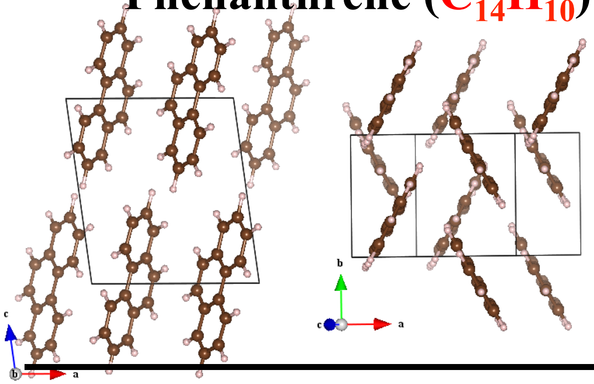
$U/W = 2.83 > 1.73$ (Mott Insulator); CuO_2, $U \sim W = 8t$

Our Studies

- Comparisons of electronic correlation effects for undoped hydrocarbon compounds
- Comparisons of electronic correlation effects and electronic structures
  for doped hydrocarbon compounds

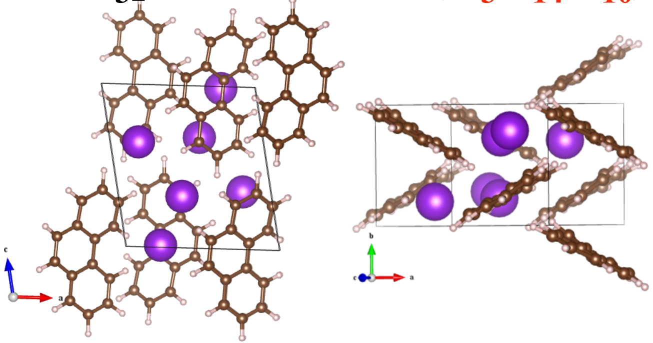
5 Cases Studied

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

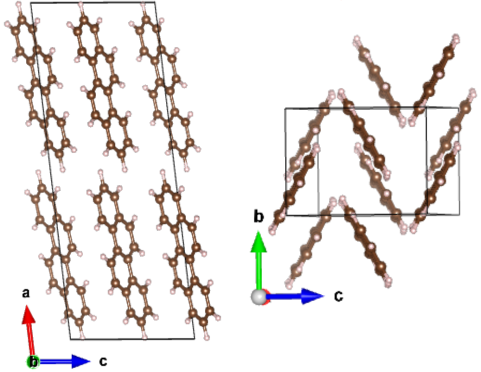


Tri-potassium

K$_3$phenanthrene ($K_3C_{14}H_{10}$)

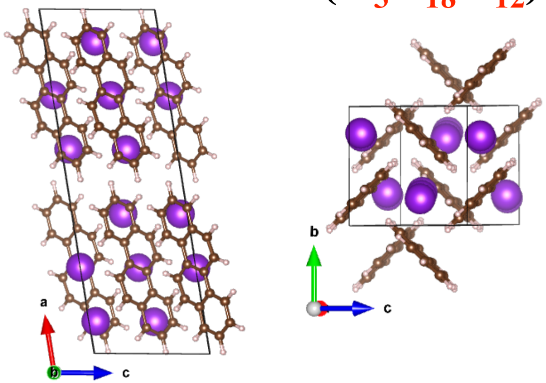


Chrysene ($C_{18}H_{12}$)

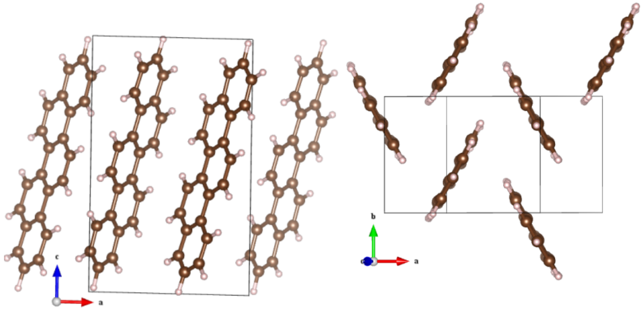


Tri-potassium

K$_3$Chrysene ($K_3C_{18}H_{12}$)

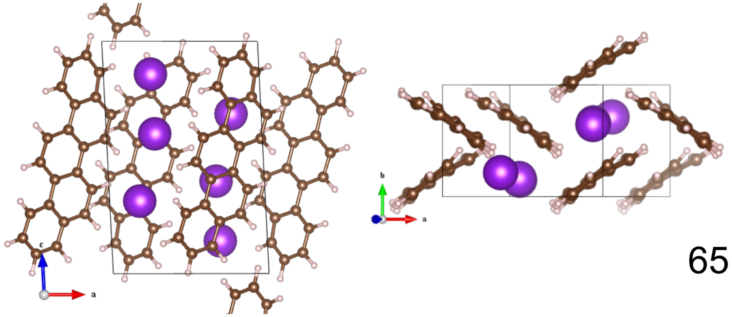


Picene ($C_{22}H_{14}$)



Tri-potassium

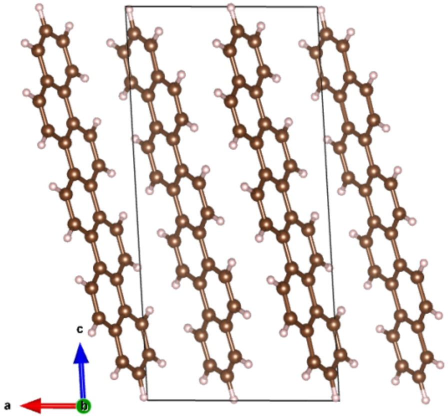
K$_3$picene ($K_3C_{22}H_{14}$)



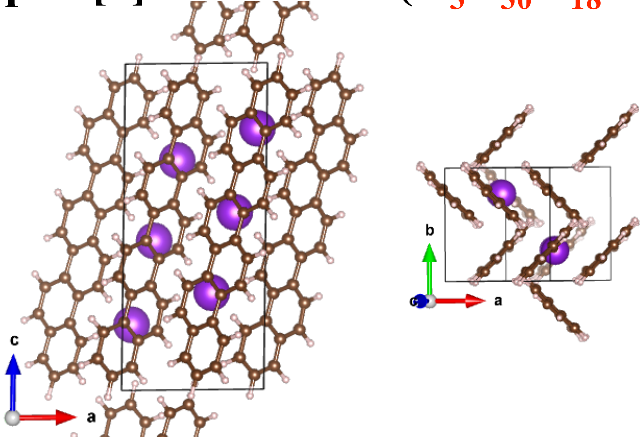
Cases Studied

[7]Phenacenes ($C_{30}H_{18}$-II):

K-doped [7]Phenacenes ($K_3C_{30}H_{18}$-II)

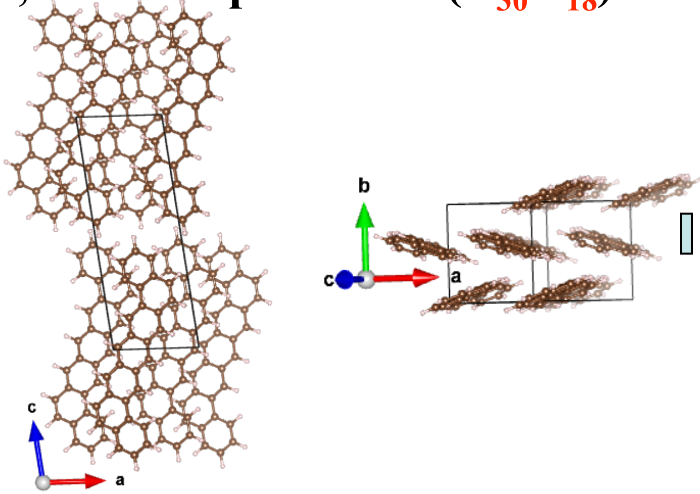


Tri-potassium

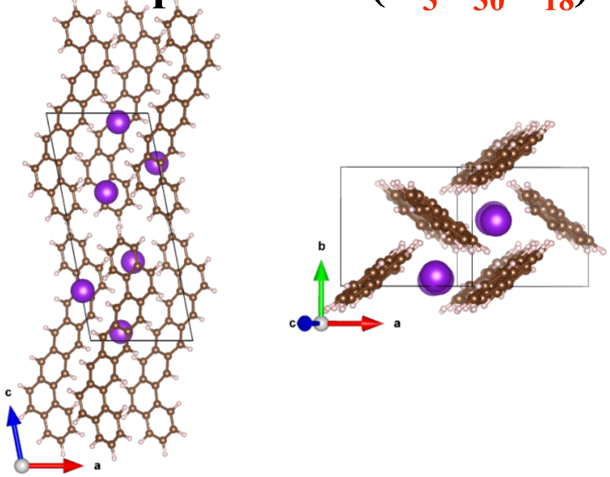


1,2:8,9-dibenzopentacene ($C_{30}H_{18}$)

K-doped 1,2:8,9-dibenzopentacene ($K_3C_{30}H_{18}$)



Tri-potassium



Method

For undoped systems:

- Package: VASP
- Method: PAW
- Exchange correlation potential:

  GGA-PBE, Heyd-Scuseria-Ernzerhof (HSE)
- Cutoff energy: 600 eV
- K-point: 6 x 8 x 6 ($C_{14}H_{10}K_3$), 6 x 8 x 6 ($C_{22}H_{14}K_3$), 4 x 4 x 2 ($C_{30}H_{18}K_3$)
- DOS calculations: tetrahedron method, a Gaussian broadening of 0.02

Method

For K-doped systems:

- Package: WIEN2k
- Method: FP-LAPW
- Exchange correlation potential:

  GGA-PBE, Heyd-Scuseria-Ernzerhof (HSE)
- Cutoff energy: -9.0 Ry
- K-point: 3 x 4 x 3 ($C_{14}H_{10}K_3$), 3 x 5 x 2 ($C_{22}H_{14}K_3$), 5 x 4 x 1 ($C_{30}H_{18}K_3$)
- DOS calculations: tetrahedron method
- R_{MT}: 1.29, 0.67, 2.0 a.u. for C, H , K, respectively

Estimating Correlation

After getting the lattice structure, we obtain the electronic structures by using the generalized gradient approximation (GGA) [1]. To overcome the limitations of PBE-GGA (and LDA) and its shortcoming in the determination of the gap, we repeated the same kind of calculation by using the hybrid functional method (HSE) [2-4].

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[3] J. Heyd and G. E. Scuseria, J. Chem. Phys. **121**, 1187 (2004).
[4] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).

Based on PBE exchange-correlation functional approach [1], the hybrid density functional, which includes a certain amount of HF exchange, could be written as

$$\boxed{\mathrm{E}_{XC}^{\mathrm{HSE}} = \nu\, \mathrm{E}_{X}^{HF} + (1-\nu)\, \mathrm{E}_{X}^{\mathrm{PBE}} + \mathrm{E}_{C}^{\mathrm{PBE}}}$$

Estimating Correlation

$$\boxed{E_{XC}^{\text{HSE}} = \nu E_X^{HF} + (1-\nu) E_X^{\text{PBE}} + E_C^{\text{PBE}}}$$

where the $E^{HF}{}_x$ represents the HF exchange form, the $E^{PBE}{}_x$ corresponds to the PBE exchange form, and the $E^{PBE}{}_c$ is the PBE correlation energy.

The mixing coefficient **ν** represents the amount of exact/DFT exchange, indicating the extend of Fock exchange and reflecting the intensity of electronic correlation (EC).

Introducing a screened Coulomb potential (***μ***)[20] and splitting all terms into their short-range (SR) and long-range (LR) components:

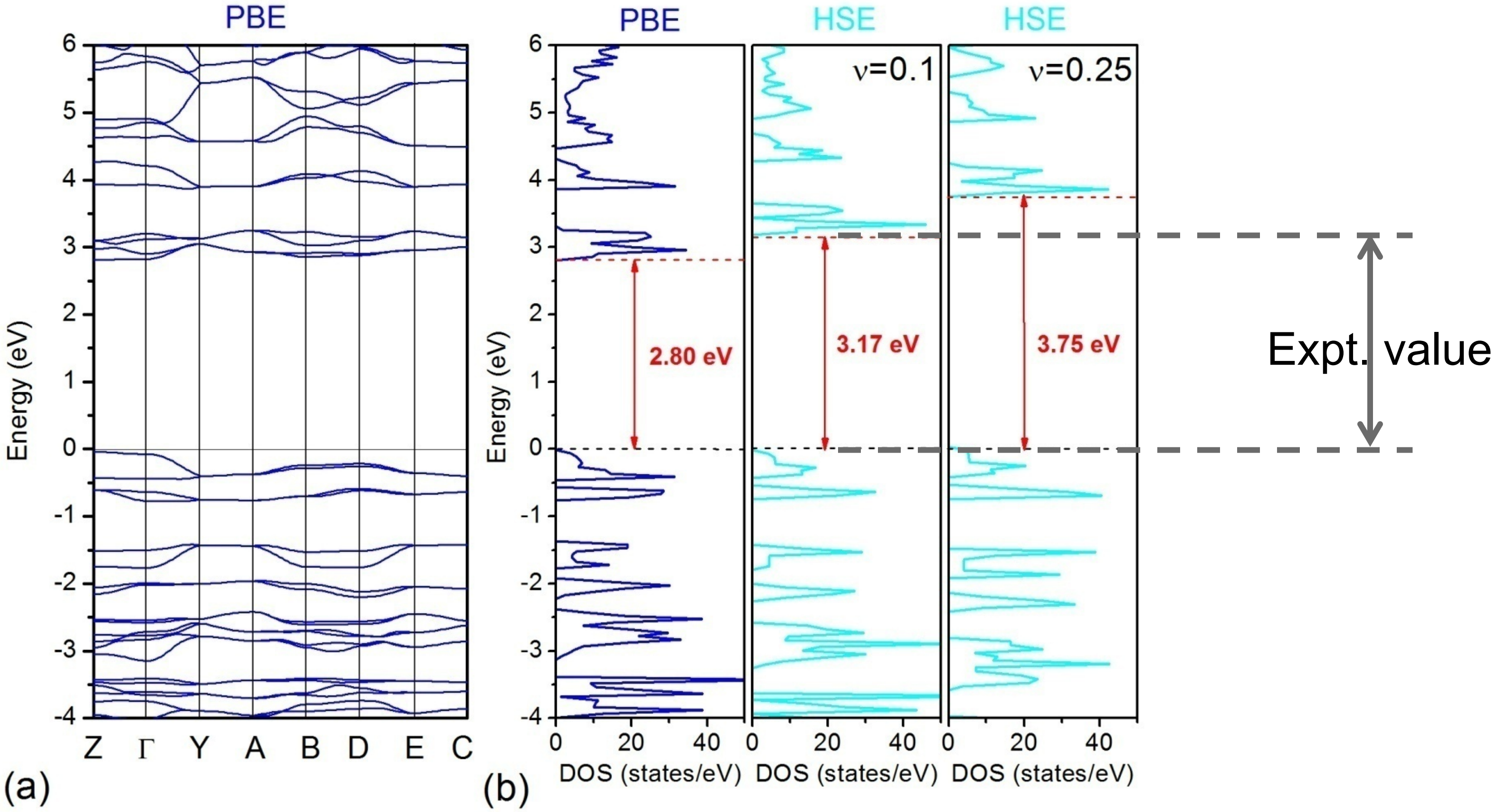
$$\boxed{E_{XC}^{\text{HSE}} = \nu E_X^{HF,\text{SR}}(\mu) + (1-\nu) E_X^{\text{PBE,SR}}(\mu) + E_X^{\text{PBE,LR}}(\mu) + E_C^{\text{PBE}}}$$

Coulomb screen μ varies from the 0.1 Å to 0.2 Å.

ν(representing correlation) varies from 0 (PBE) to 1.

Pure phenanthrene ($C_{14}H_{10}$): Fixing μ =0.2

Based on experimental lattice constants



For phenanthrene, the Band-gap obtained from PBE is 2.80 eV, which is less than the experimental value. Small account (*v*> 0.1) of exact exchange (HSE calculation) is added to correct the error. However, normal HSE calculation (adopted default *v*> 0.25) will overestimate the gap.

Namely, the electronic correlation effect is not neglected in solid phenanthrene.

Experimental Band-gap: 3.16 eV;

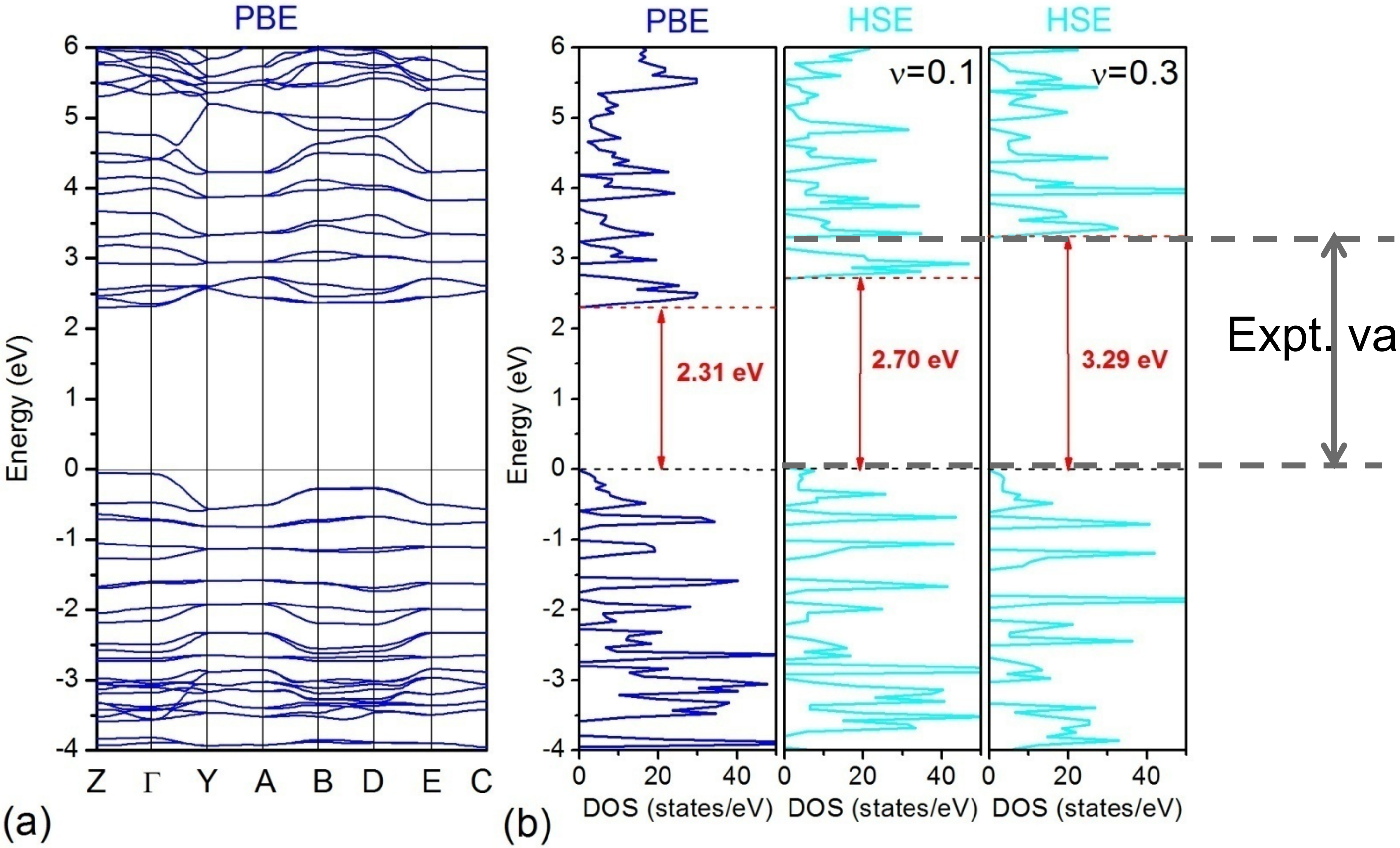
M. T. Bhatti et al., Turk. J. Phys. **24**, 673 (2000).

LDA result: 2.75 eV

P. L. de Andres et al. PRB **84**, 144501 (2011)

Pure picene ($C_{22}H_{14}$): Fixing μ =0.2

Based on experimental lattice constants



For picene, the Band-gap obtained from PBE is only 2.31 eV, the gap is intensively underestimated by PBE. HSE functional induces the increase of gap and furthers with increasing the ratio *ν* of exact/DFT exchange. When *ν* is increased to ~ 0.3, the obtained gap is equal to the experimental value.

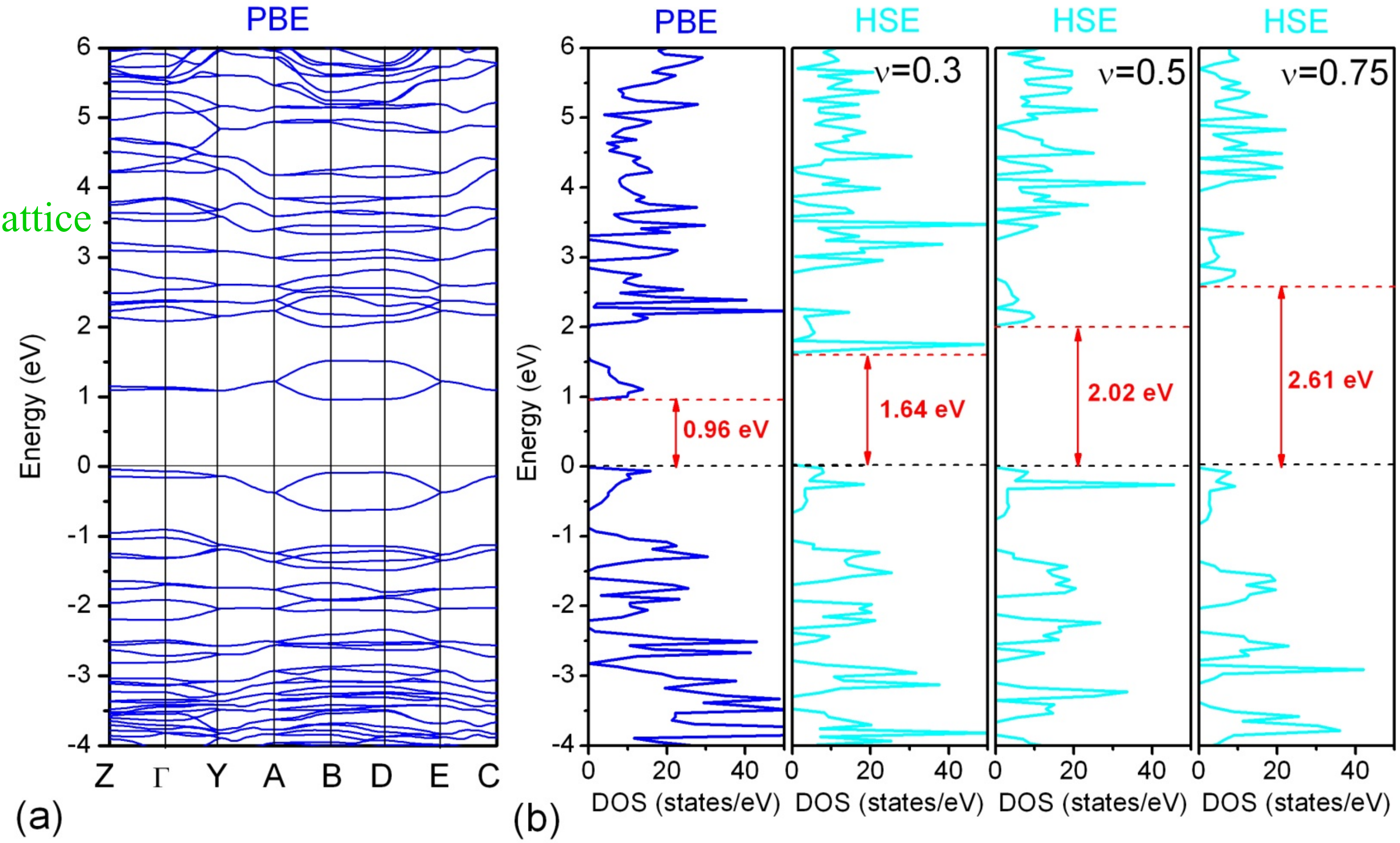
It indicates that the PBE level can not describe the electronic properties of picene truly since the strong electronic correlation effect exists in this system, and more stronger effect than phenanthrene.

Experimental Band-gap: 3.3 eV;
H Okamoto et al., JACS 130, 10470 (2008)

LDA result: 2.36 eV
T. KOSUGI et al., JPSJ 78, 113704 (2009)

Pure 1,2:8,9-dibenzopentacene ($C_{30}H_{18}$): Fixing μ =0.2

Based on optimized lattice constants



For $C_{30}H_{18}$, the Band-gap obtained from PBE is only 0.96 eV, the gap is intensively underestimated by PBE. HSE functional induces the increase of gap and furthers with increasing the ratio *v* of exact/DFT exchange. When *v* reaches > 0.5, the obtained gap is consistant with the experimental implication.

It indicates that the PBE level can not describe the electronic properties of $C_{30}H_{18}$ truly since the strong electronic correlation effect exists in this system, and more stronger effect than $C_{14}H_{10}$ and $C_{22}H_{14}$.

Experimental opitical band-gap: **> 2 eV**;

F. Roth, A. K onig, B. Mahns, B. B uchner, and M. KnupferarXiv:1206.0526v1

Correlation Measure

Reproducing the experimental band gap, the values of $v$andμ parameters are

	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	$C_{30}H_{18}$-B	$C_{30}H_{18}$
E_g (expt.)	3.16	3.3	3.3	3.2	> 2.0
E_g (DFT)	2.80	2.40	2.31	2.04	1.03
v (fix μ=0.1)	0.05	0.18	0.21	0.26	> 0.29
v (fix μ=0.2)	0.10	0.26	0.30	0.37	> 0.48

Results show, the ratio of exact/DFT exchange gets larger with the increase of the number of rings, indicating the electron correlations in this system.

For doped cases, considering electronic correlation effects, we calculate band structures and magnetic moments with *suggested* electronic structures of $K_3C_{14}H_{10}$, $K_3C_{22}H_{14}$, and $K_3C_{30}H_{18}$ in the followings:

Magnetism (doped)

- Un doped $C_{14}H_{10}$, $C_{22}H_{14}$, and $C_{30}H_{18}$ are non-magnetic.
- Doped K_3 – $C_{14}H_{10}$, $C_{22}H_{14}$, and $C_{30}H_{18}$:

Relative energies to magnetic ground state (unit: meV) based on the experimental lattice constants. AFM-1 represents the initial spin antiparalleling in molecular plane formed by three (or five) rings, while AFM-2 marks the initial spin antiparalleling between two molecular layers and paralleling in molecular plane.

	functional	NM	FM	AFM-1	AFM-2	*M*
$K_3C_{14}H_{10}$	PBE	0.5	1.0	7.5	**0**	**0.09**
	HSE	2.0	1.4	7.7	**0**	**0.13**
$K_3C_{22}H_{14}$	PBE	6.2	6.2	6.9	**0**	**0.25**
	HSE	7.9	7.9	10.3	**0**	**0.30**
$K_3C_{30}H_{18}$	PBE	30.6	20.3	57.0	**0**	**0.45**
	HSE	97.2	80.8	103.4	**0**	**0.49**

For $K_3C_{14}H_{10}$, no visible magnetic ground-state, while $K_3C_{30}H_{18}$ seems to have AFM-2 state. Correlation increases with number of benzene

Brief Summary

- For undoped hydrocarbon compounds, the electronic correlation effect (EC) increases from $C_{14}H_{10}$ to $C_{22}H_{14}$ to $C_{30}H_{18}$. It also depends on the geometry.
- For K-doped cases, the flat bands near the Fermi level indicate that EC also follows the same pattern.
- Although the existence of the long-rang magnetic order is still interrogative, the appearance of local magnetic moment and its increase with the number of benzene rings establish that the EC increases with the number of benzene rings in the K-doped systems.

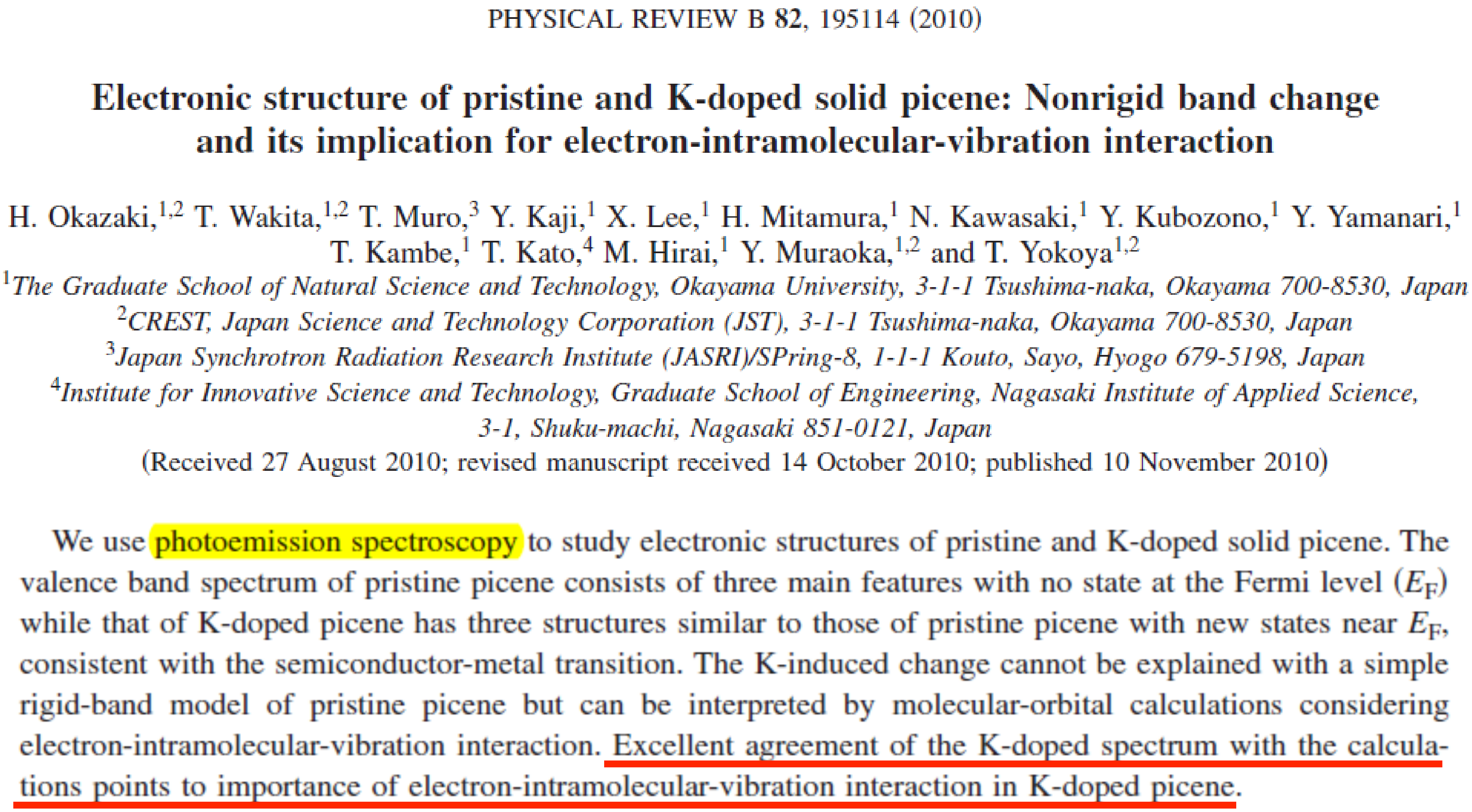
Magnetism and Superconductivity

Model?

Magnetism?

Superconductivity?

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



PHYSICAL REVIEW B **82**, 195114 (2010)

Electronic structure of pristine and K-doped solid picene: Nonrigid band change and its implication for electron-intramolecular-vibration interaction

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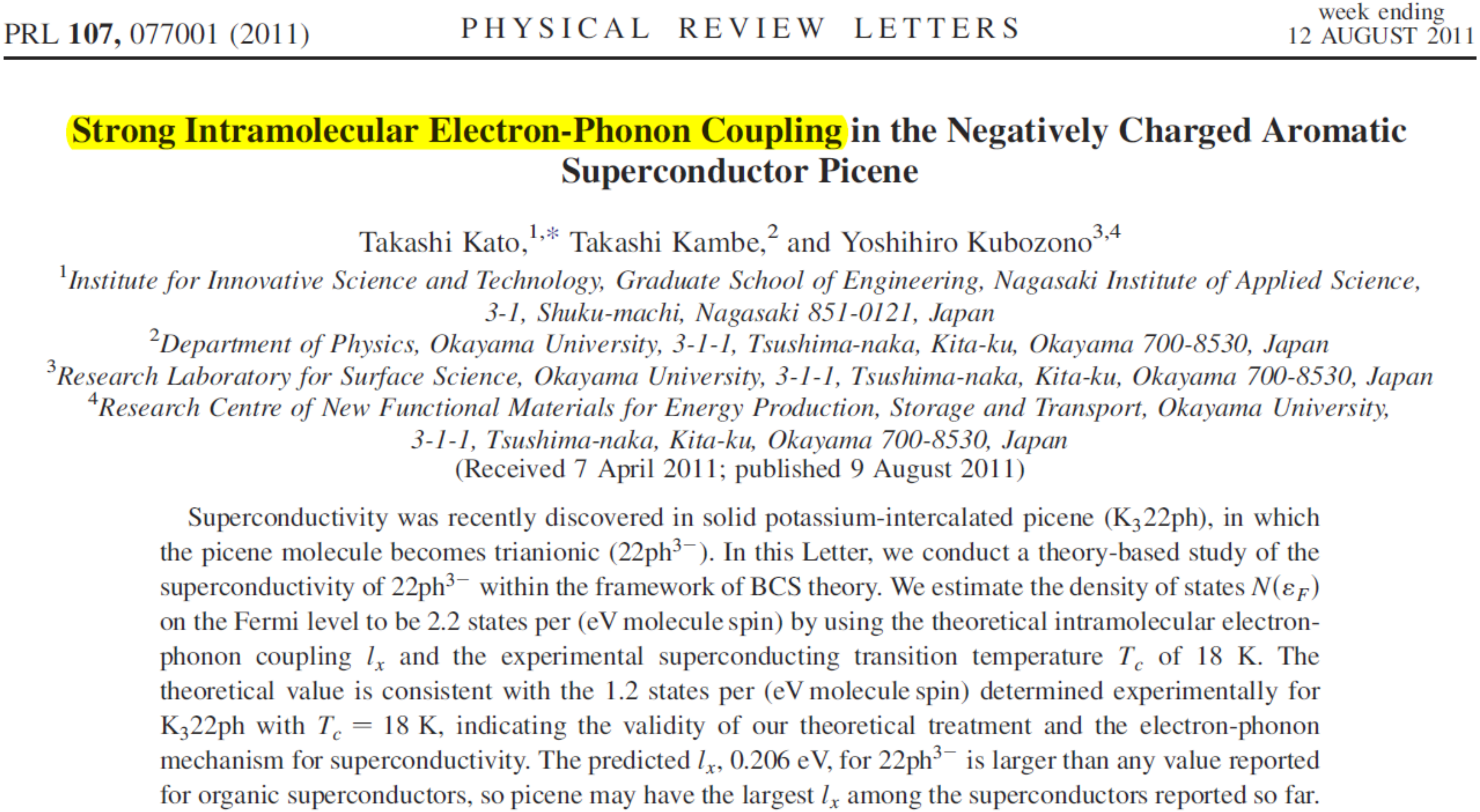
We use photoemission spectroscopy to study electronic structures of pristine and K-doped solid picene. The valence band spectrum of pristine picene consists of three main features with no state at the Fermi level (E_F) while that of K-doped picene has three structures similar to those of pristine picene with new states near E_F, consistent with the semiconductor-metal transition. The K-induced change cannot be explained with a simple rigid-band model of pristine picene but can be interpreted by molecular-orbital calculations considering electron-intramolecular-vibration interaction. Excellent agreement of the K-doped spectrum with the calculations points to importance of electron-intramolecular-vibration interaction in K-doped picene.

Electron-phonon interaction exists

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



PRL **107,** 077001 (2011) PHYSICAL REVIEW LETTERS week ending 12 AUGUST 2011

Strong Intramolecular Electron-Phonon Coupling in the Negatively Charged Aromatic Superconductor Picene

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Superconductivity was recently discovered in solid potassium-intercalated picene ($K_3$22ph), in which the picene molecule becomes trianionic ($22ph^{3-}$). In this Letter, we conduct a theory-based study of the superconductivity of $22ph^{3-}$ within the framework of BCS theory. We estimate the density of states $N(\varepsilon_F)$ on the Fermi level to be 2.2 states per (eV molecule spin) by using the theoretical intramolecular electron-phonon coupling l_x and the experimental superconducting transition temperature T_c of 18 K. The theoretical value is consistent with the 1.2 states per (eV molecule spin) determined experimentally for $K_3$22ph with $T_c = 18$ K, indicating the validity of our theoretical treatment and the electron-phonon mechanism for superconductivity. The predicted l_x, 0.206 eV, for $22ph^{3-}$ is larger than any value reported for organic superconductors, so picene may have the largest l_x among the superconductors reported so far.

Electron-phonon interaction is important

$C_{22}H_{14}$ (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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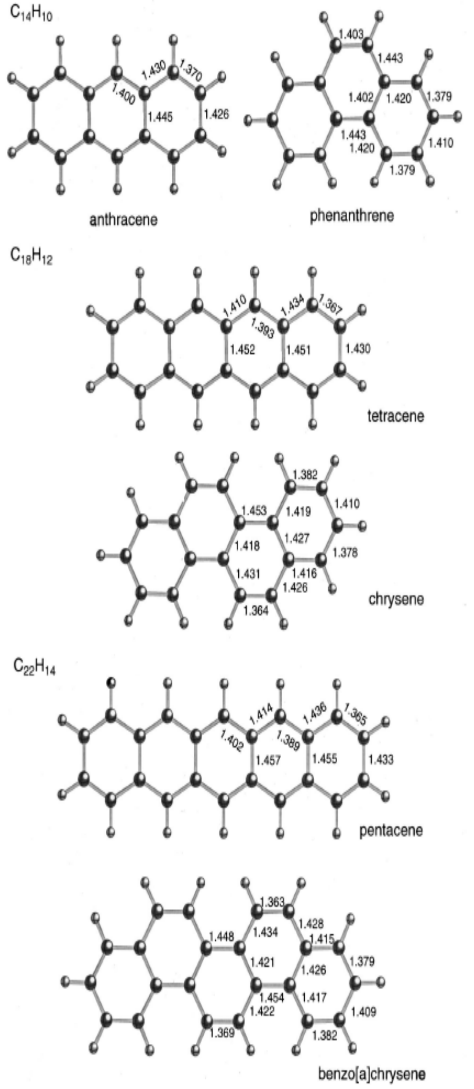
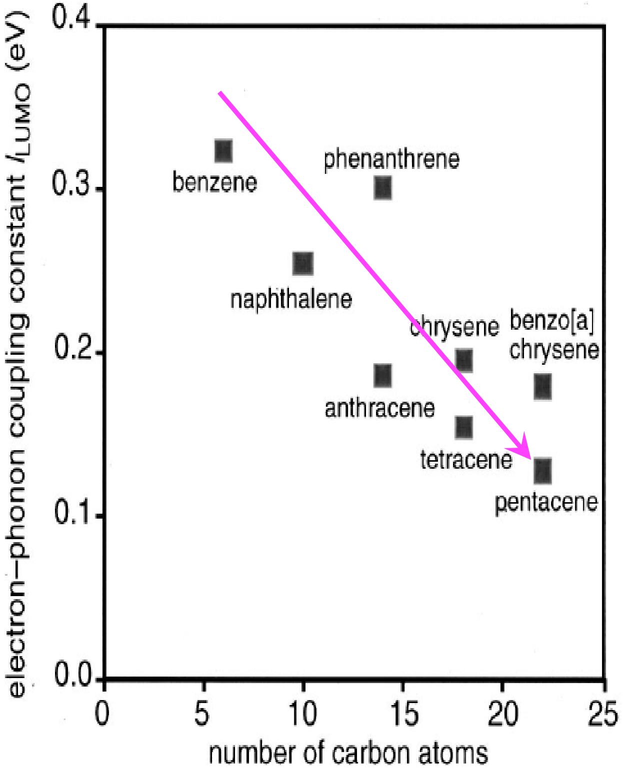
$\lambda = 0.73$, $\omega_{\log} = 18.0$ meV (208 K)
Intercalant and intermolecular phonon modes contribute substantially (40%) to λ as also shown by the **isotope exponents** of potassium (0.19) and carbon (0.31).

Other calculations: $\lambda = 0.88/1.41$, $\omega_{\log} = 207/240\ \mathrm{cm}^{-1}$
(Note that intramolecular phonons dominate in C_{60})

Electron-Phonon alone is not enough





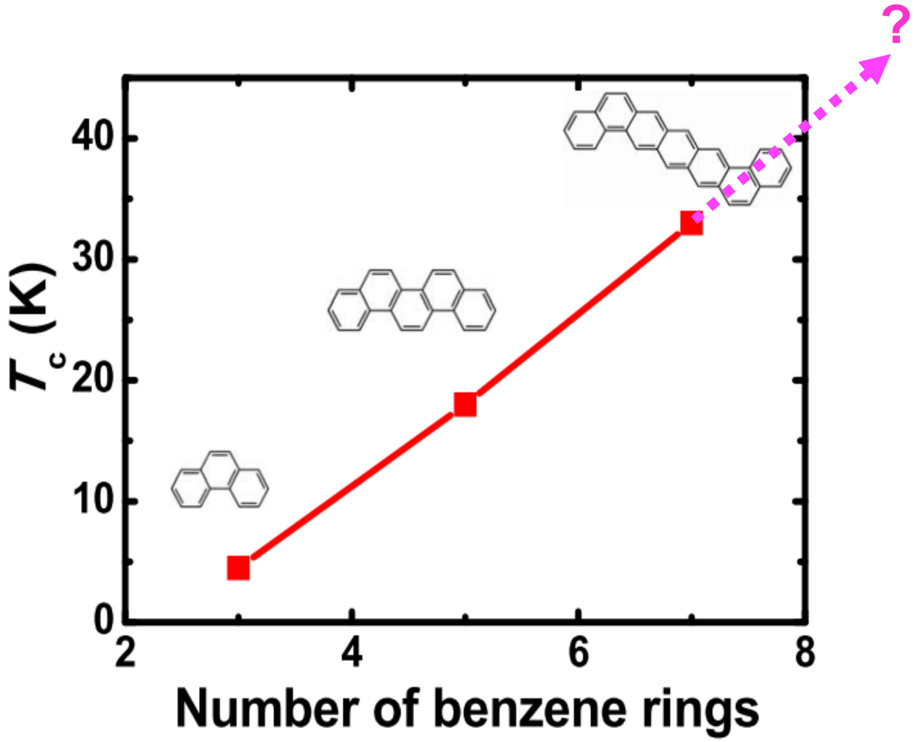
T. Kato et al., J. Chem. Phys. 116, 3420 (2002).

Brief Summary

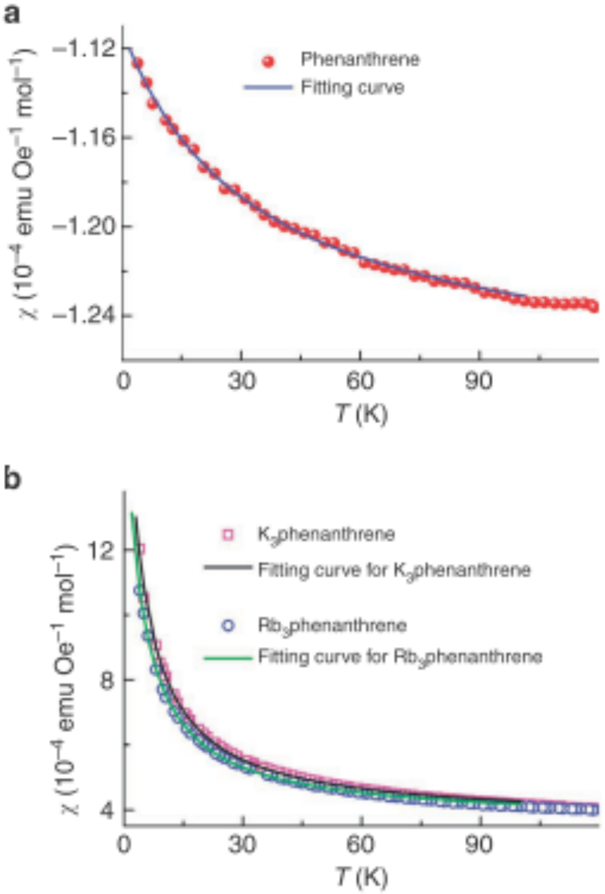
- Electron-phonon interaction does play role, but may not be able to explain the experiments;
- We have seen that electron-electron correlation increases with the number of benzene rings;
- Electron-electron interaction is larger than the bandwidth near the Fermi energy, indicating that correlation should be taken into account.

Issues to Address

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



High magnetic susceptibility



T_c increases with increasing the Number of benzene rings!

Curie-Weiss magnetic behavior

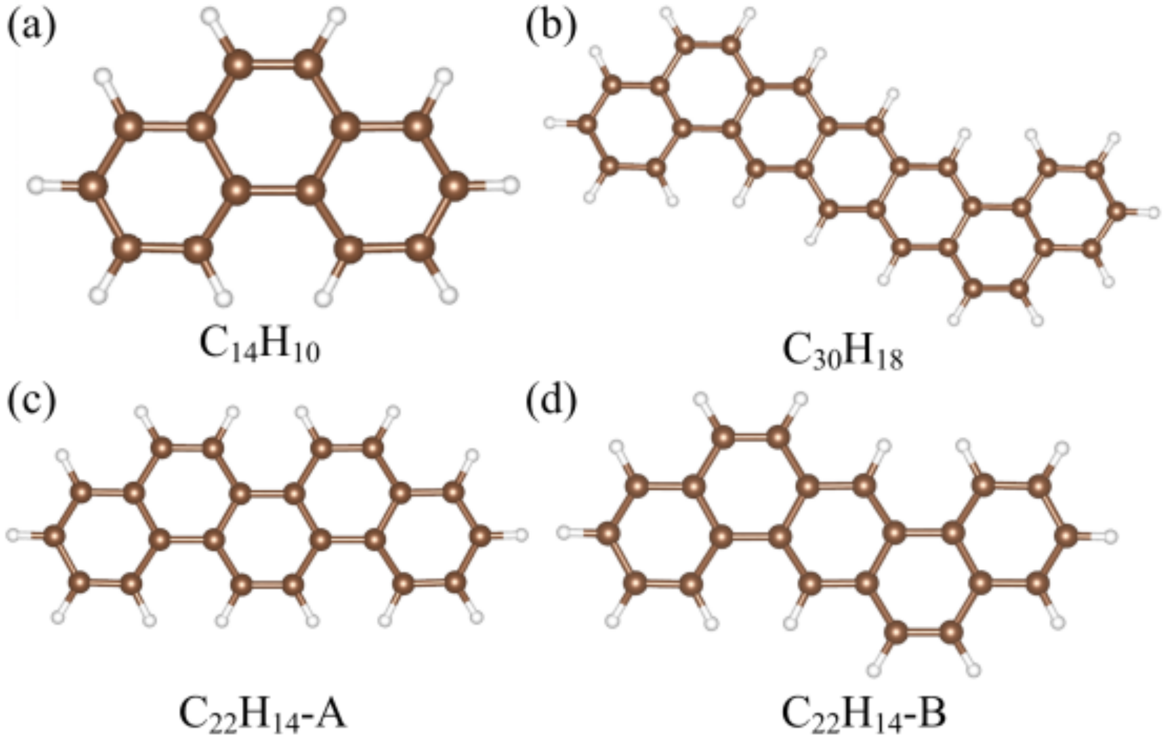
→ local spin!

ED/QMC Calculation

- Try the simplest model to address the following issues: (1) origin of the local spin? (2) electron correlation contributes to superconductivity?
- Non-perturbative studies on simple systems
- Results:
  - magnetic instability
  - electron pairing instability

Starting point: a Hubbard-like Model

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

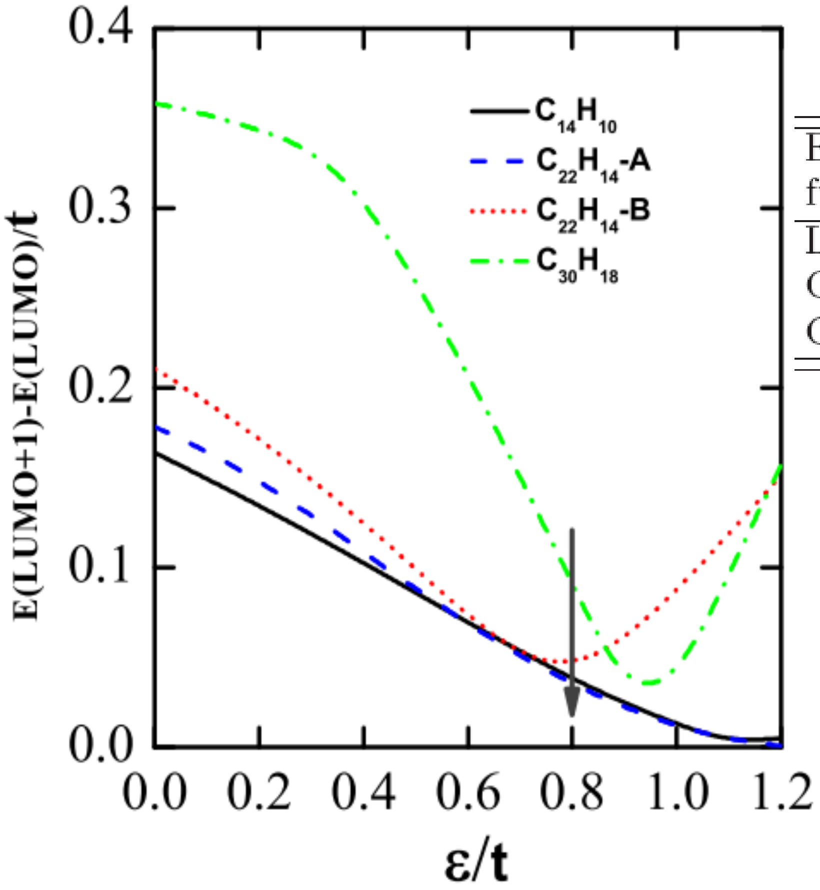


t ~ 2.7-3.0 eV
U ~ 6-10 eV
U/t ~ 2-3

ε? (~ t)

Electron-phonon interaction could be accounted by ***t* (1 + *αx*)**

The Parameter ε



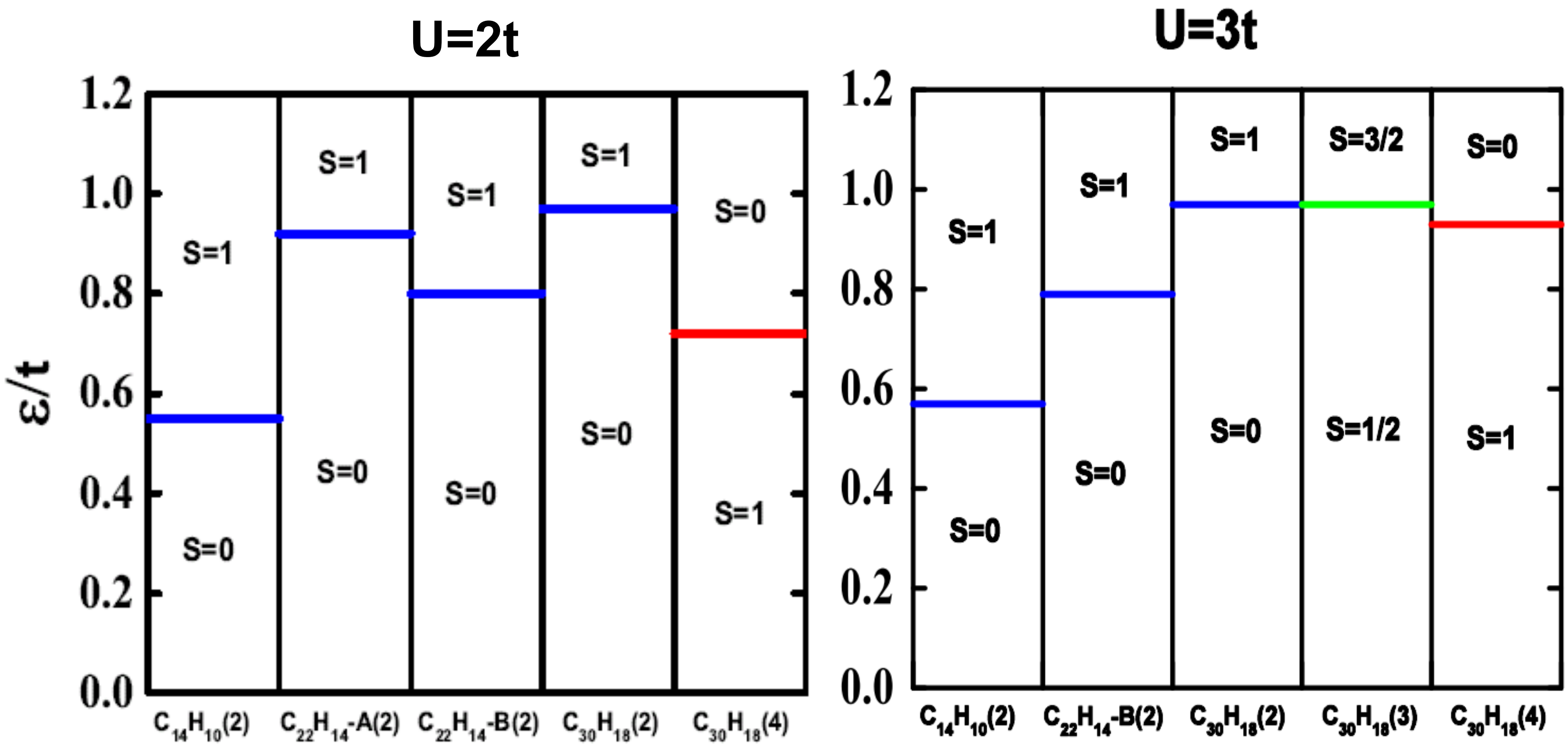
$$\Delta E_{LUMO} = E(LUMO+1) - E(LUMO)$$

Exchange-correlation function	$\Delta E_{\mathrm{LUMO}}(C_{14}H_{10})$	$\Delta E_{\mathrm{LUMO}}(C_{22}H_{14}$
LDA	0.1018 eV	0.0634 eV
GGA-PBE	0.1141 eV	0.0750 eV
GGA-PW91	0.1117 eV	0.0750 eV

$$\epsilon > 0.8t$$

Scientific Reports 2, 922 (2012).

Magnetic Phase Diagram



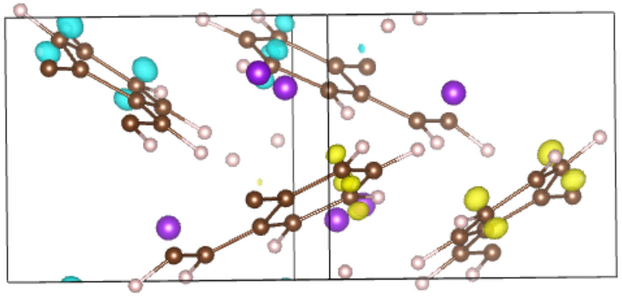
(1) For two electron doped cases, the total spin *S* switches from 0 to 1.

(2) For $C_{30}H_{18}$ with four electrons doped, there is *S*=1 to 0 transition; with three electrons doped, *S*=1/2 to 3/2.

Spin Density

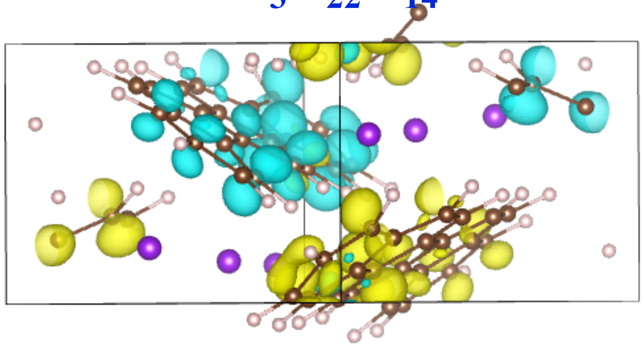
(PBE results)

$K_3C_{14}H_{10}$



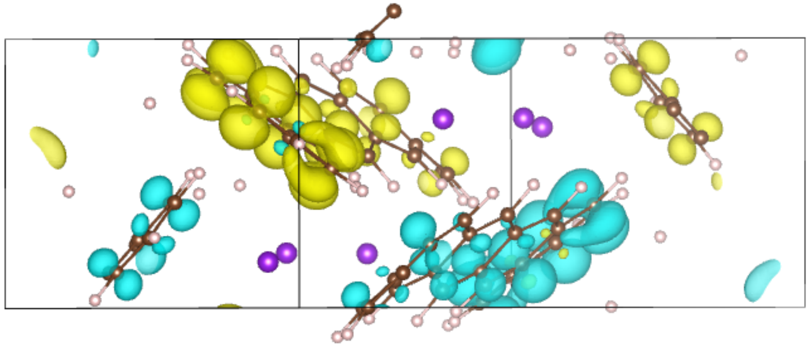
Local magnetic moment ~ 0. 09 μ_B/f.u.

$K_3C_{22}H_{14}$



Local magnetic moment ~ 0. 25 μ_B/f.u.

$K_3C_{30}H_{18}$



Local magnetic moment ~ 0. 45 μ_B/f.u.

Pair Binding Energy:

$$\Delta_i = 2(E_{i+1} - E_i) - (E_{i+2} - E_i) = 2E_{i+1} - E_i - E_{i+2}$$

i=0, 1, 2

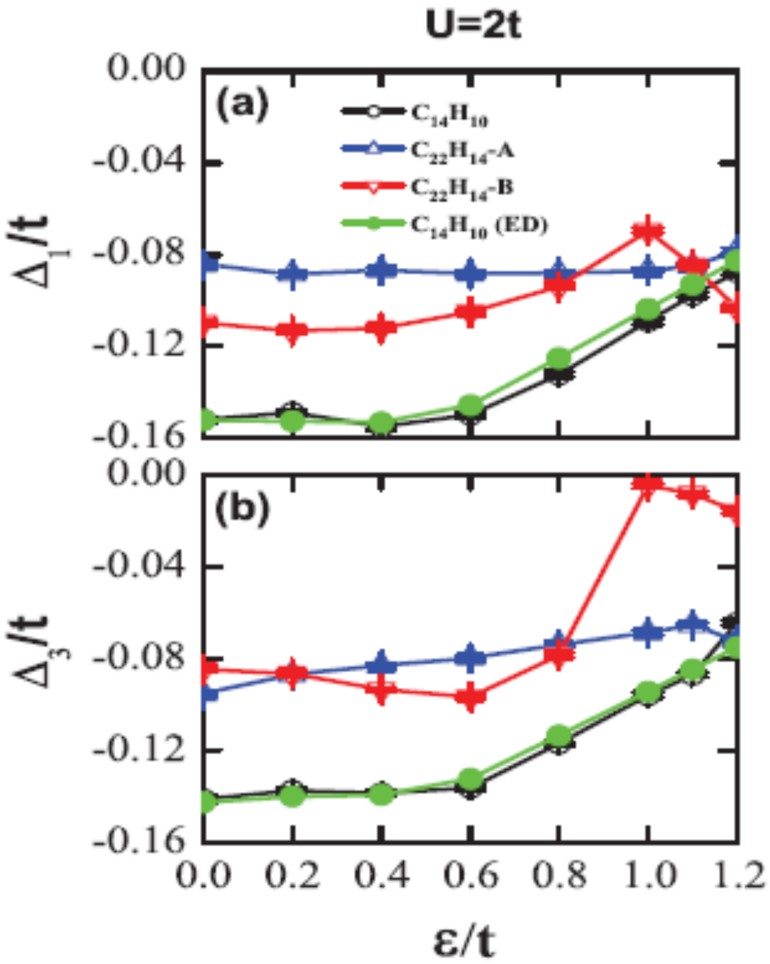
$\Delta_i > 0$: attractive interaction for added electrons

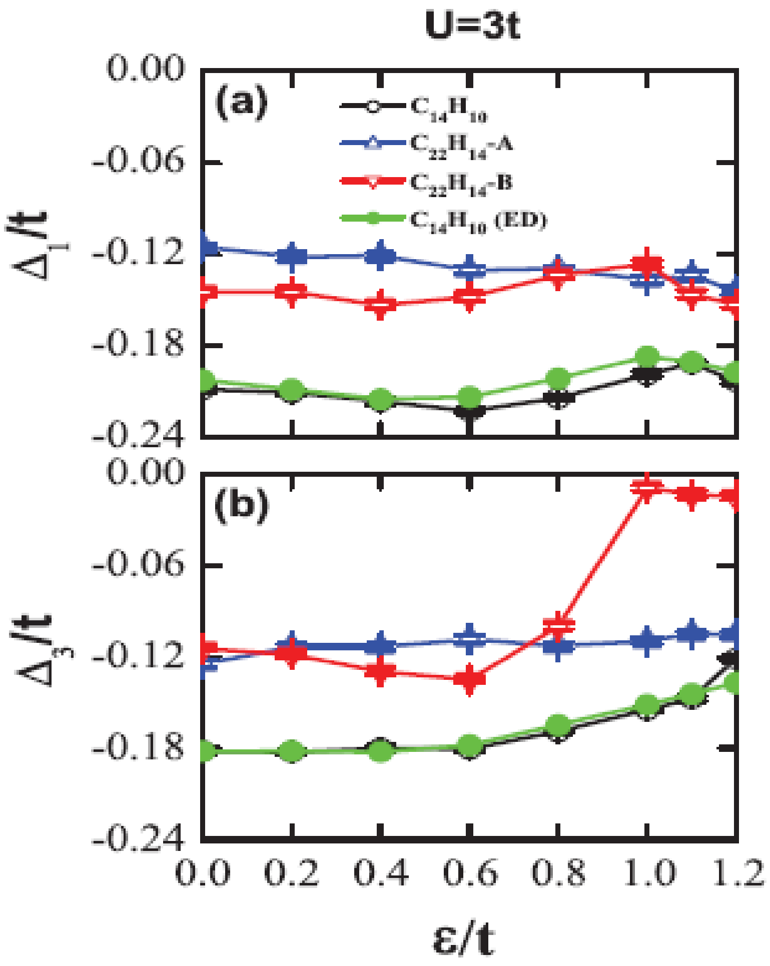
$\Delta_i < 0$: repulsive interaction for added electrons

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

(2) Applied for high-Tc superconductors and C_{60}.

Pair Binding Energy Δ_i for $C_{14}H_{10}$ & $C_{22}H_{14}$



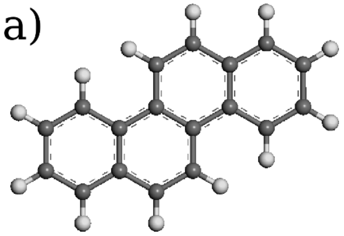


Δ_i is always negative => hardly to form Cooper pairs.

Δ_i for longer ring is less negative than shorter one.

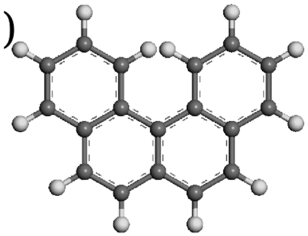
Other Aromatic Molecules

(a)



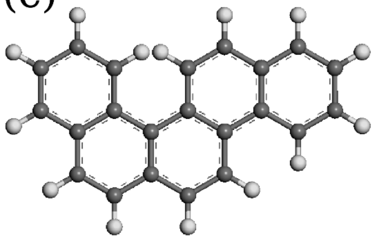
C18-A

(b)



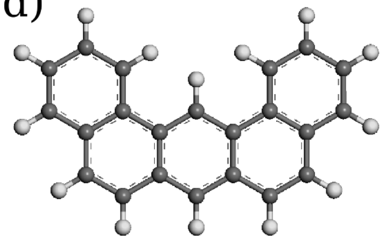
C18-B

(c)



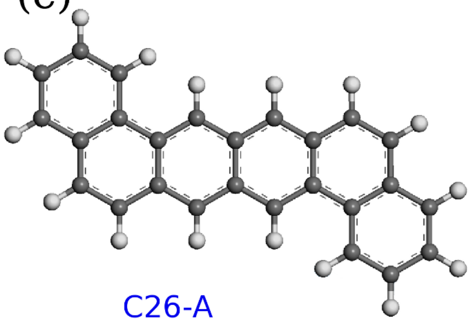
C22-A

(d)



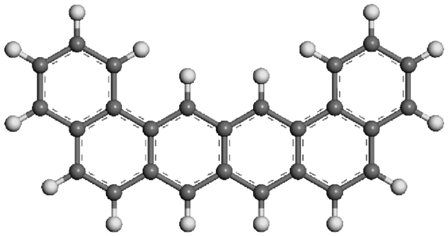
C22-B

(e)



C26-A

(f)



C26-B

Summary

- The spin polarized state is realized in the charge aromatic molecules of PAHs, especially for even number of added electrons.
- Electron correlations might contribute to superconductivity. Larger molecules with a similar structure to $C_{30}H_{18}$ may exhibit higher superconducting transition temperature.
- New PAH superconductors are possible.

Zhong GH, Yan XW, Chen XJ

Pressure Effects

1. Taking pressure as a probe and tool of manipulation
2. Searching optimal structure under pressure

Triphenylene: ($C_{18}H_{12}$)

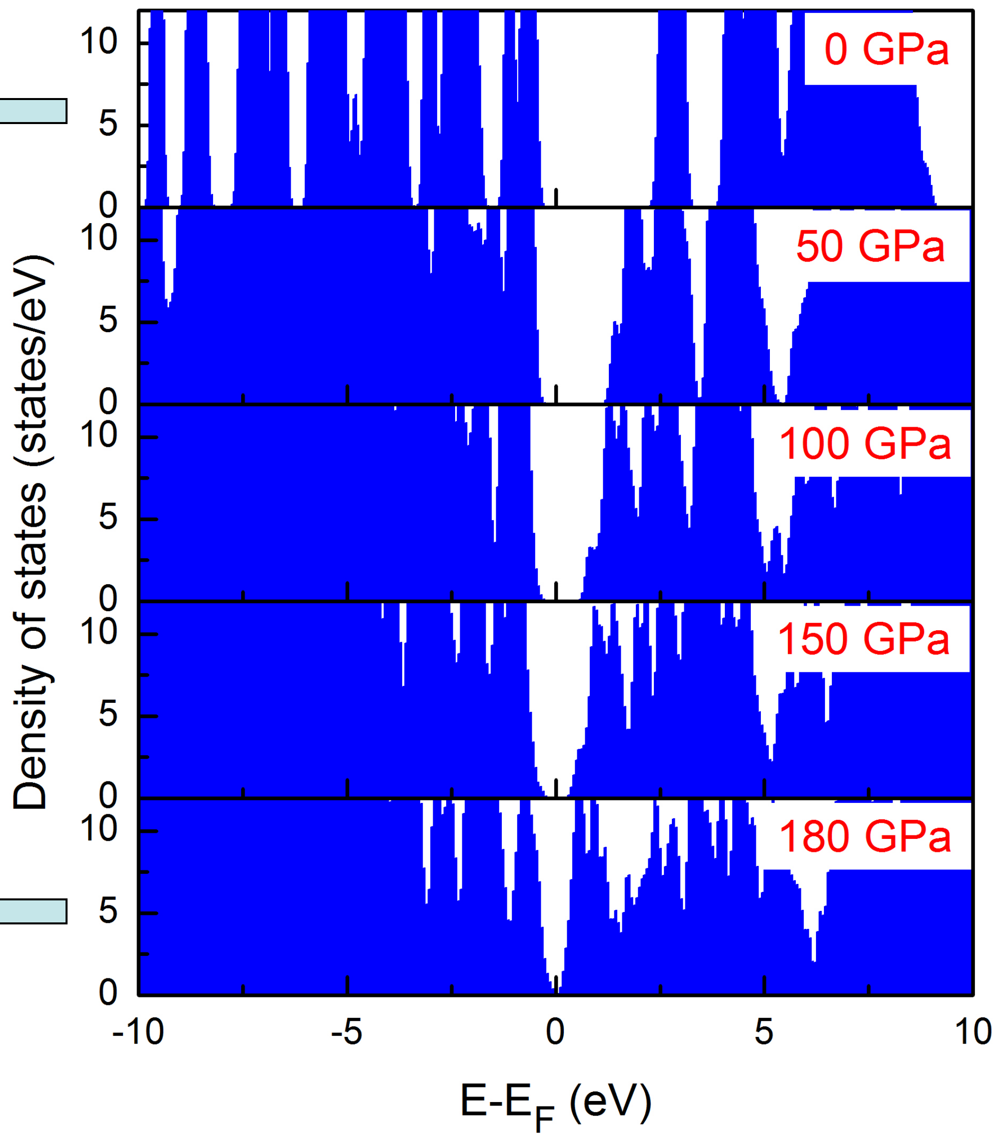
No doping!

Semiconductor

Eg = 2.5 eV

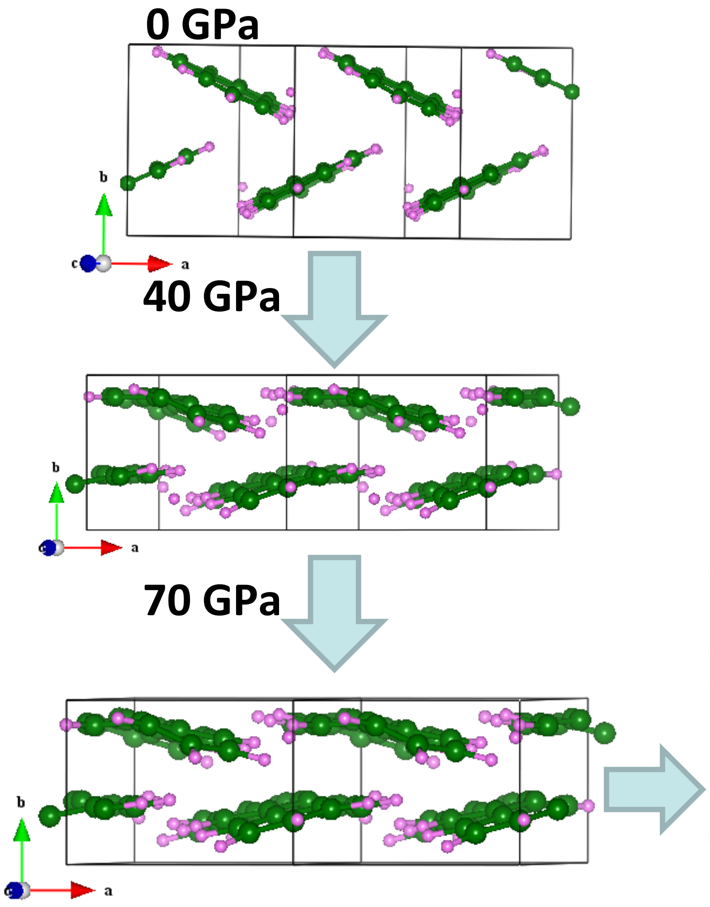
Pressurization

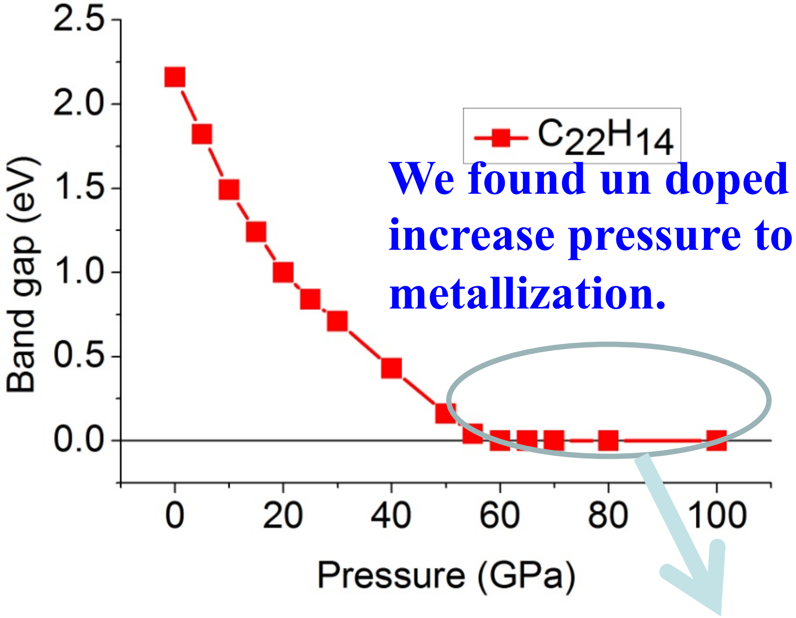
Metal



Picene $C_{22}H_{14}$ under pressure

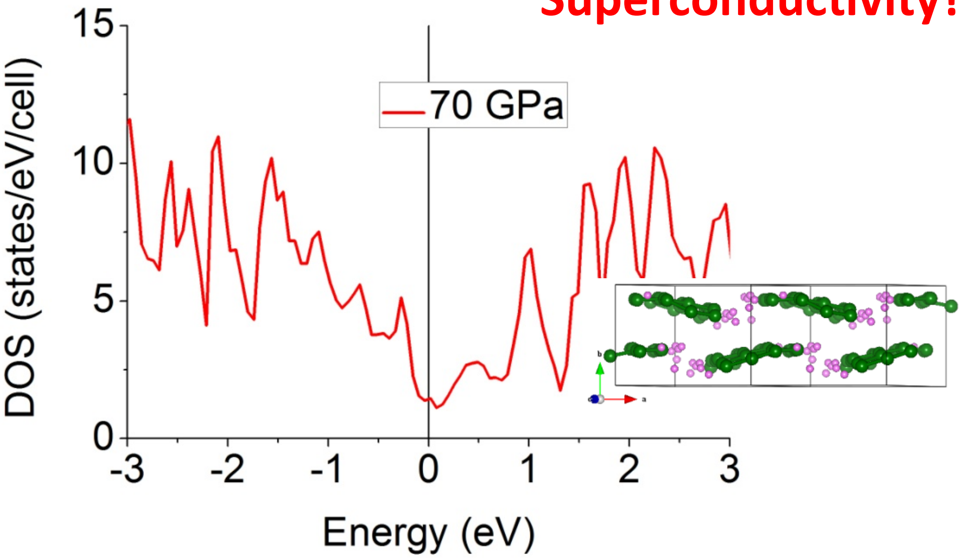
No doping!





We found un doped $C_{22}H_{14}$, increase pressure to 60 GPa metallization.

Superconductivity?



Summary and Discussions

- We searched for possible structures of Polycyclic Aromatic Hydrocarbon and obtained many interesting results. However, more systematic works are needed, including pressure effects. Different structure searching algorithm should be tested.
- For doped picene, based on its XRD data, we gave explanation for observed two SC phases.
- We proposed an unique SC phase in benzene rings.
- Systematic study on pressure effects would be very exciting, more to come.

Summary and Discussions

- We found that there exists strong correlation and it increases with the size of benzene rings.
- We proposed a model to address magnetic and superconducting properties. Our results showed that there exist local moment and pairing instability. Both of them increase with the size of benzene rings. Such behavior is very different from other systems.
- We found that doping simply provides charge carriers so different doping, such as co-doping, could have higher Tc.

CSRC

Thank You !