# Theoretical Studies on Recent Discovered Organic Superconductors

## H. Q. Lin

*Beijing Computational Science Research Center*
*The Chinese University of Hong Kong*

**Collaborators:**

**Dr. C. Zhang (CSRC), Dr. G.H. Zhong (SIAT)**

**Prof. Z.B. Huang (Hubei Univ. & CSRC)**

**Dr. X. J. Chen (Carnegie Institute of Washington)**

# Theoretical Studies on Recent Discovered Organic Superconductors

Abstract: In this talk, I report our recent study on the magnetic and pair binding properties in newly discovered polycyclic aromatic hydrocarbon (PAH) superconductors including alkali-metal-doped picene, coronene, phenanthrene, and dibenzopentacene. To gain a better understanding on magnetism and electron correlation in PAH, we have performed a systematic numerical investigation on the correlation effects and model the $\pi$-electrons on the carbon atoms of a single molecule by a one-orbital Hubbard model, in which the energy difference $\epsilon$ between carbon atoms with and without hydrogen bonds is taking into account. We demonstrate that the spin polarized ground state is realized for charged molecules in the physical parameter regions, which provides a reasonable explanation of local spins observed in PAHs. In alkali-metal-doped dibenzopentacene, our results show that electron correlation may produce an effective attraction between electrons for the charged molecule with one or three added electrons. We also propose a different doping pattern which may lead to higher transition temperature. Some results on the possible structure of PAH as functions of pressure and doing will be discussed.

# **Outline**

- Introduction: superconductivity and recent discoveries

- Possible structures

- Correlation effect

- Magnetic and Superconducting Instabilities

- Co-doped phenanthrene, new superconductor?

- Summary and discussions

# What is a Superconductor?

- Zero resistant Perfect conductor. $\rho = 0$ for $T < T_c$. No energy loss.

- Zero Magnetic Flux: The Meissner Effect Perfect Diamagnet.

- Critical Temperature $T_c$ is the key factor.



$\rho(T)$

$(H = 0)$

$T_c$

$T$

13
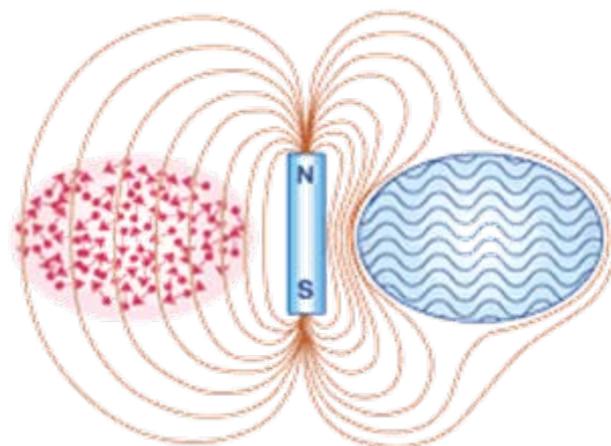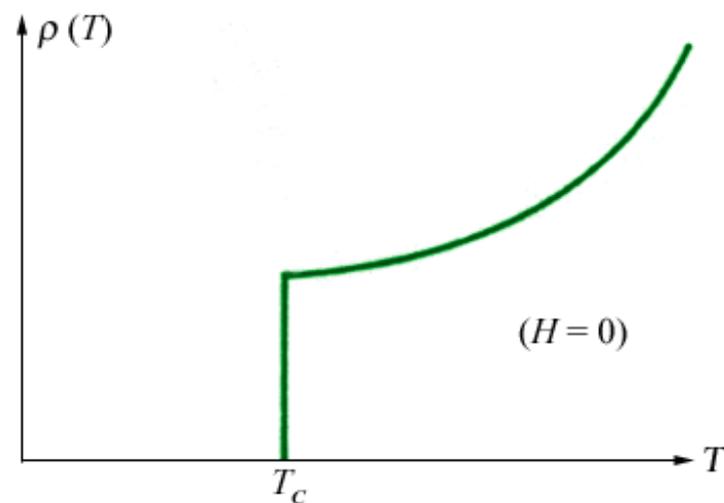
# **Existing Superconductors**

- **Metallic:** normal metals when $T > T_c$.
  Conventional, low $T_c \leq 23.3K$ (39K).

- **Organic:** semiconductors when $T > T_c$.
  New, low $T_c \leq 17K$ (before 2005); 2011, **33K?**

- **Ceramic:** complicated behavior when $T > T_c$.
  Novel, high $T_c \approx 165K$, under pressure.

- **Fullerenes:** insulating/semiconducting when $T > T_c$.
  Novel, intermediate $T_c \approx 35K$.

- **Mg-B:** metallic, $T_c \approx 39K$

- **Fe-based:** more complicated behavior, high $T_c \approx 55K$

- Others?
  Room temperature?

**Organic Superconductors**
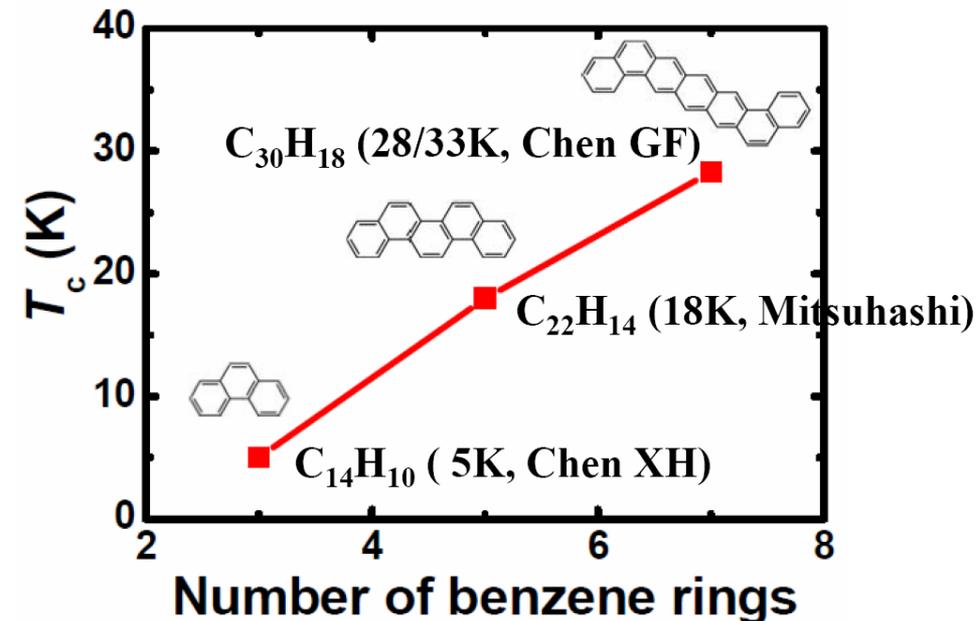


scoveries

**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**

15

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

## 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]
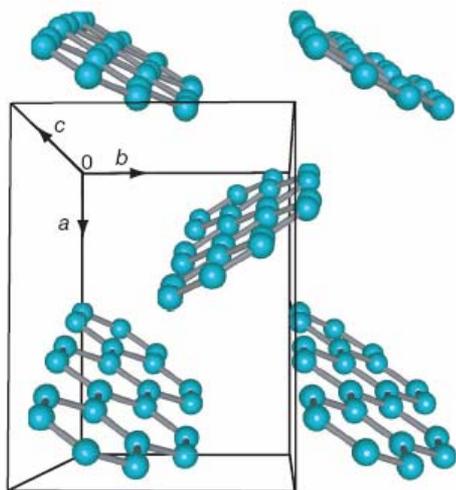


$T_C \sim$ 7--18K

**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) | $\ll 0.1\%$ |
| **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) | $\ll 0.1\%$ |
| **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) | $\ll 0.1\%$ |
| ***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) | $\ll 0.1\%$ |
| **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 |

# 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

18
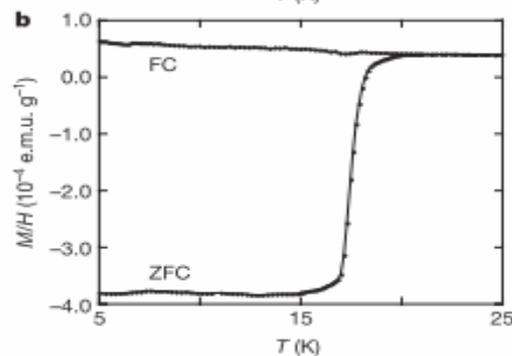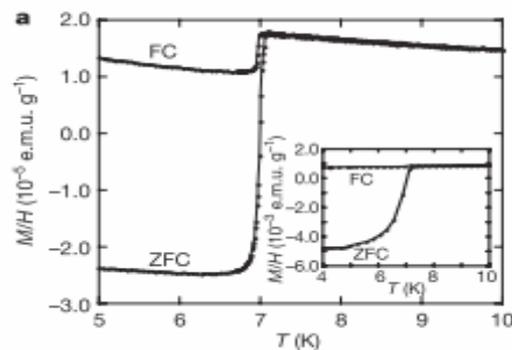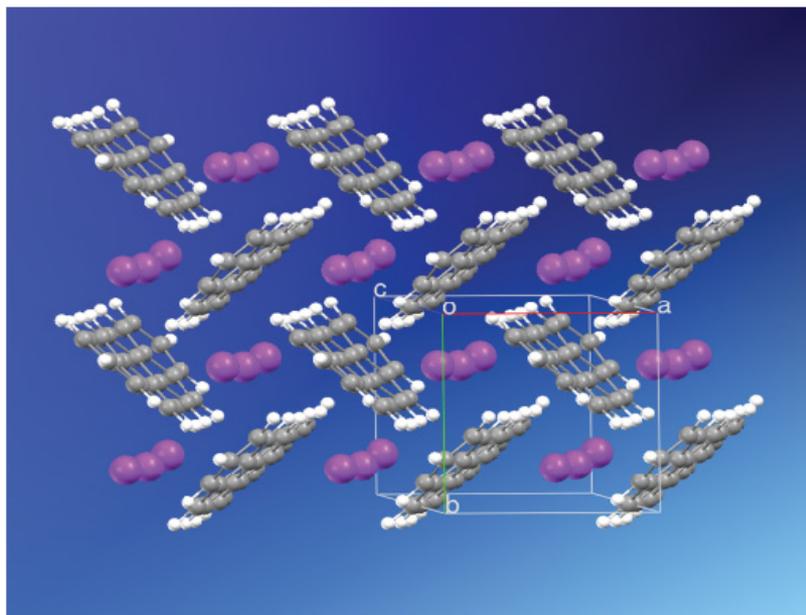
# Phenanthrene ($C_{14}H_{10}$) (2011-07-13, 09-21)

## 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

(Submitted on 20 Feb 2011)
arXiv:1102.4075v1



$C_{14}H_{10}$
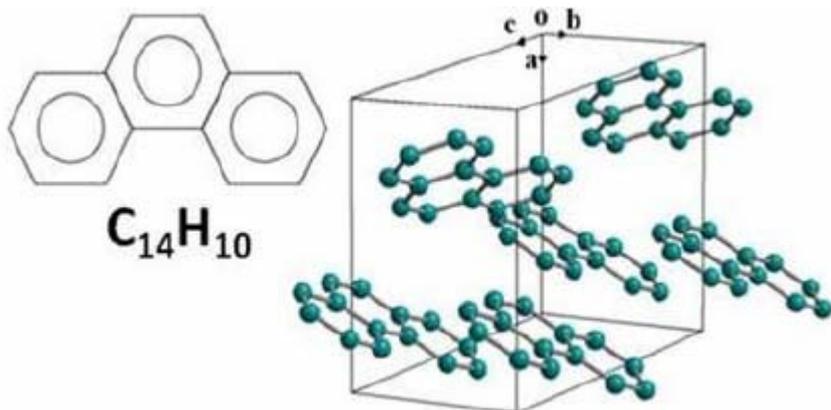
| N.O. | Nominal composition | Annealing temperature | Annealing time | Onset SC transition | Shielding fraction |
|---|---|---|---|---|---|
| Sample A | $K_3Ph$ | 200°C | 20 hours | 4.7 K | 1.9% |
| Sample B | $K_3Ph$ | 200°C | 20 hours | 4.9 K | 1.1% |
| Sample C | $K_3Ph$ | 200°C | 20 hours | 4.7 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)
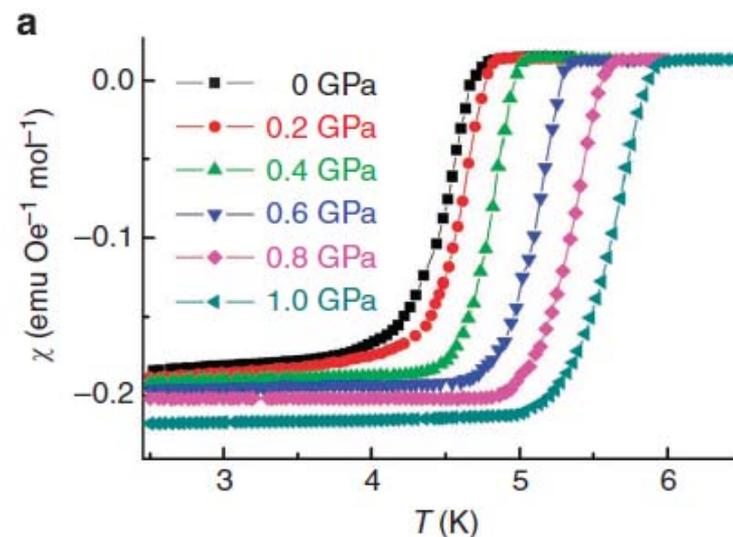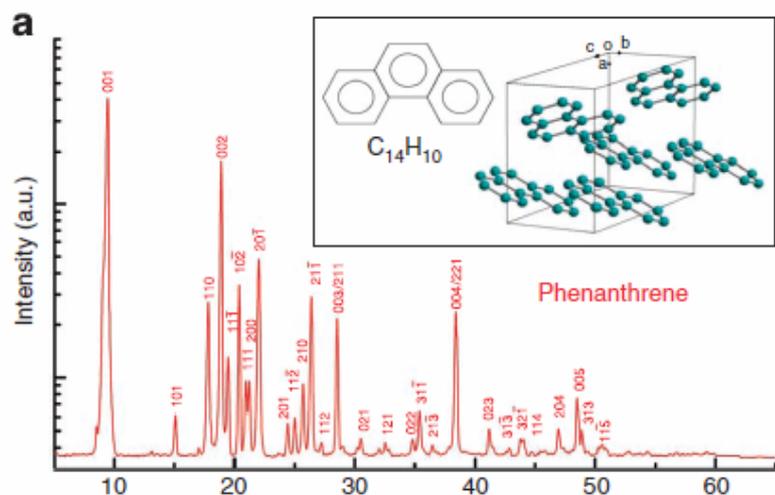


$T_c \sim 5$ K

At 1 GPa, 20% increase of $T_c$
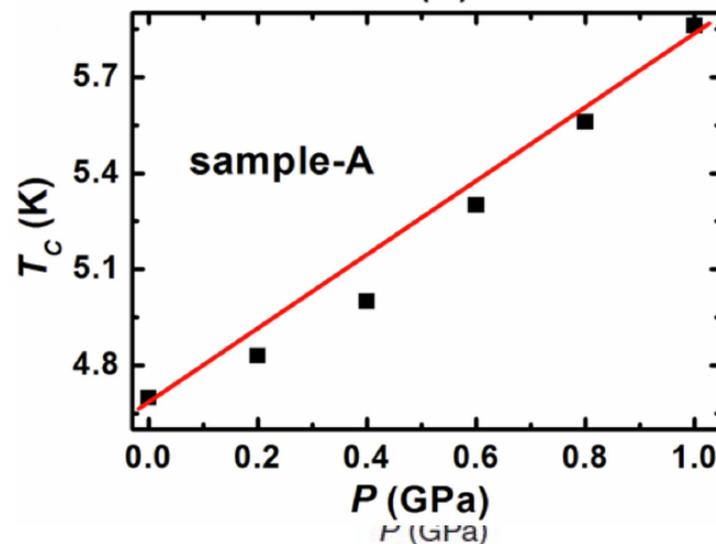
**OPEN**

# 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
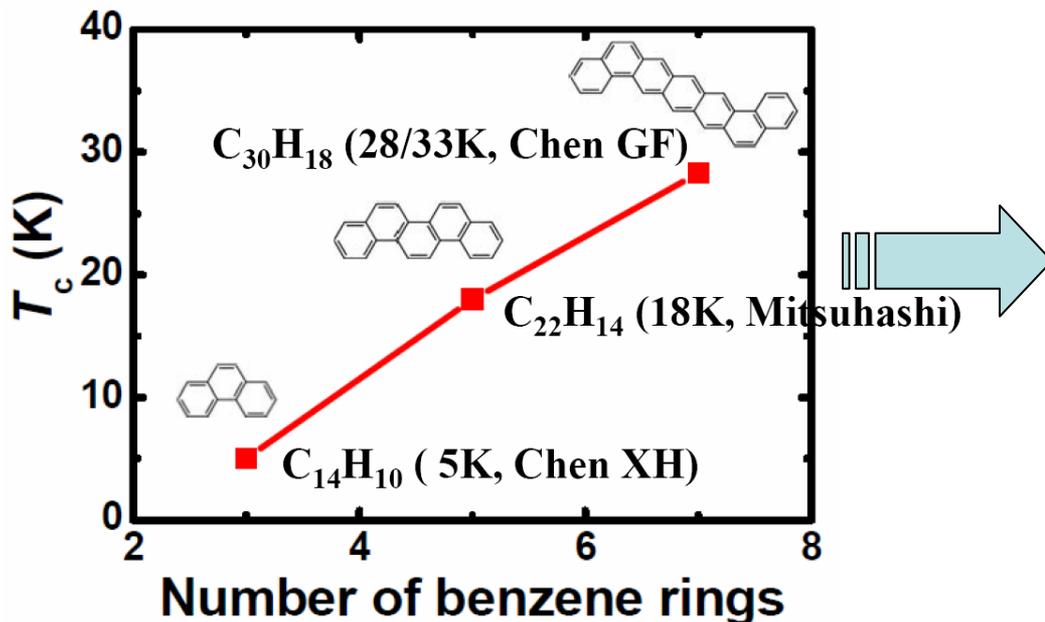


*After Copper- and Iron-base superconductivity, a new superconductor family is discovered.*

(Submitted on 3 Nov 2011)
arXiv:1111.0820v1

21

# 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]
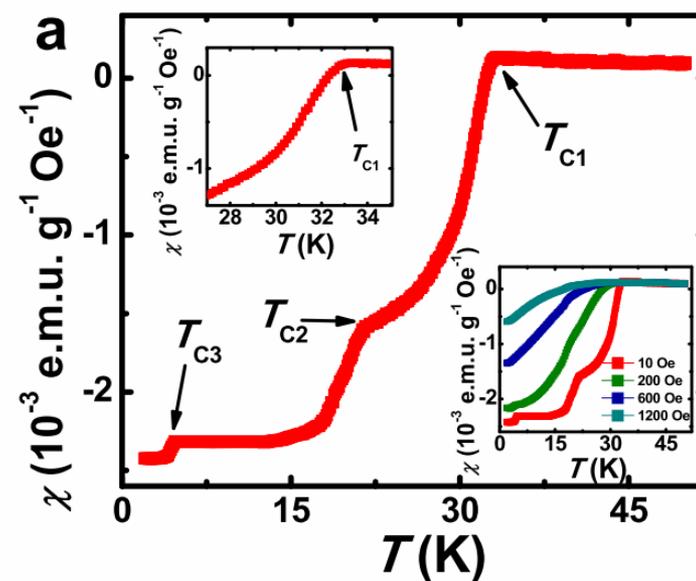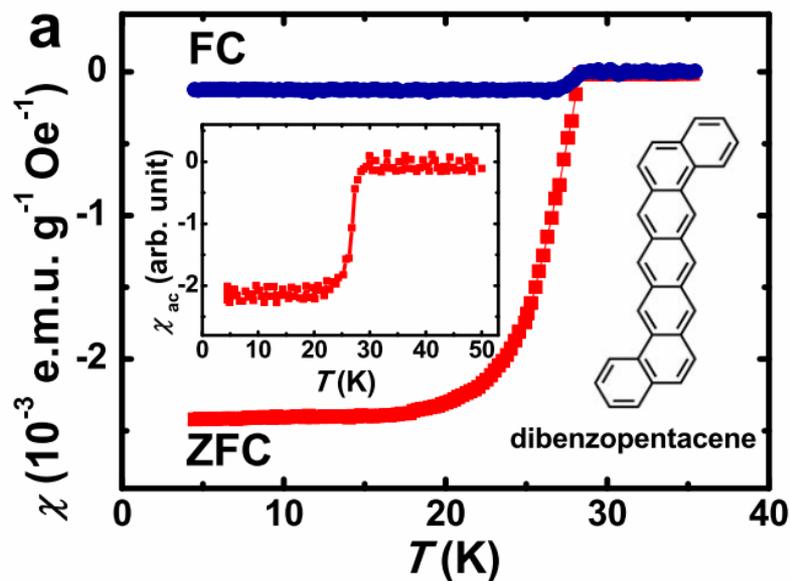


Tc ~ 28-33 K

# Possible Structures

Searching for optimal structure

1. Undoped, P = 1 atm, most are known;

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. Few results as functions of pressure.

# Computational Approach

**Structural,** **Electronic,** **and Dynamical properties**

Enthalpy (FP+DFT)

Band, DOS, $N(E_F)$

Phonon(DFPT)

**Stable phase**

Low enthalpy structure

**Metallization**

$T_C$
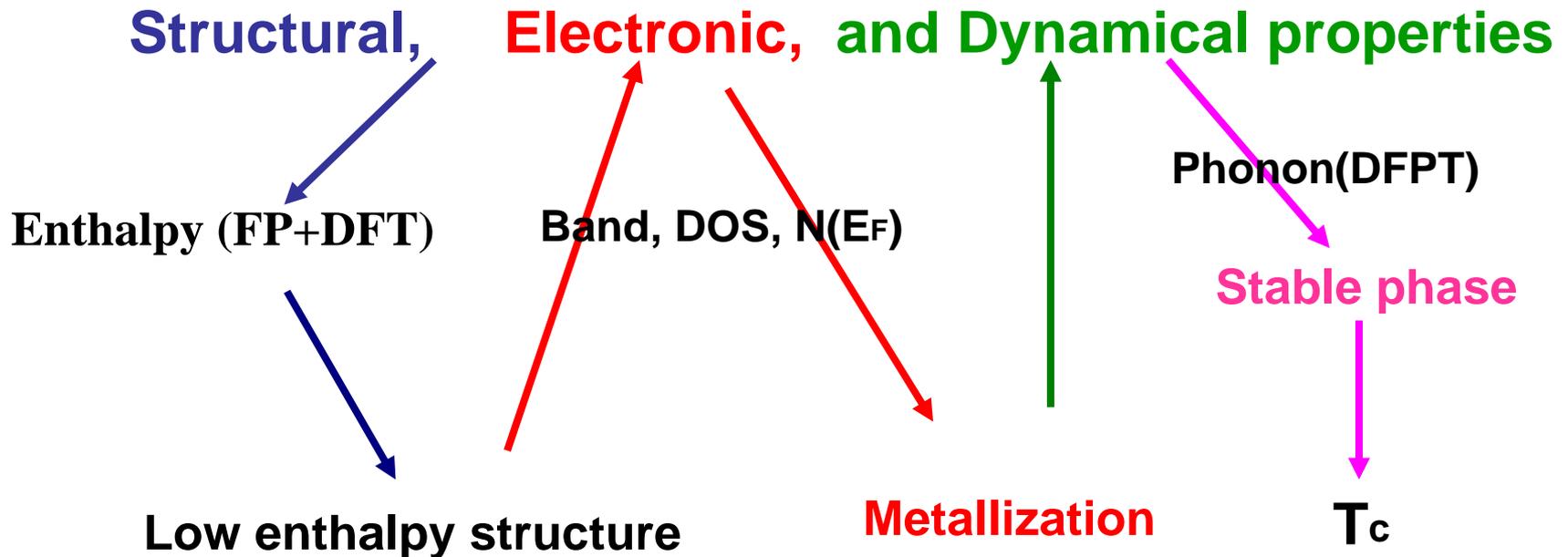
- **Issues: Structure phase transition; Metallization pressure; Electronic and Dynamic properties; Superconductivity.**

- **Codes: CASTEP, Quantum Espresso, etc.**

- **When determining stable structure, zero point energy included.**

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



Picene

Picene crystals
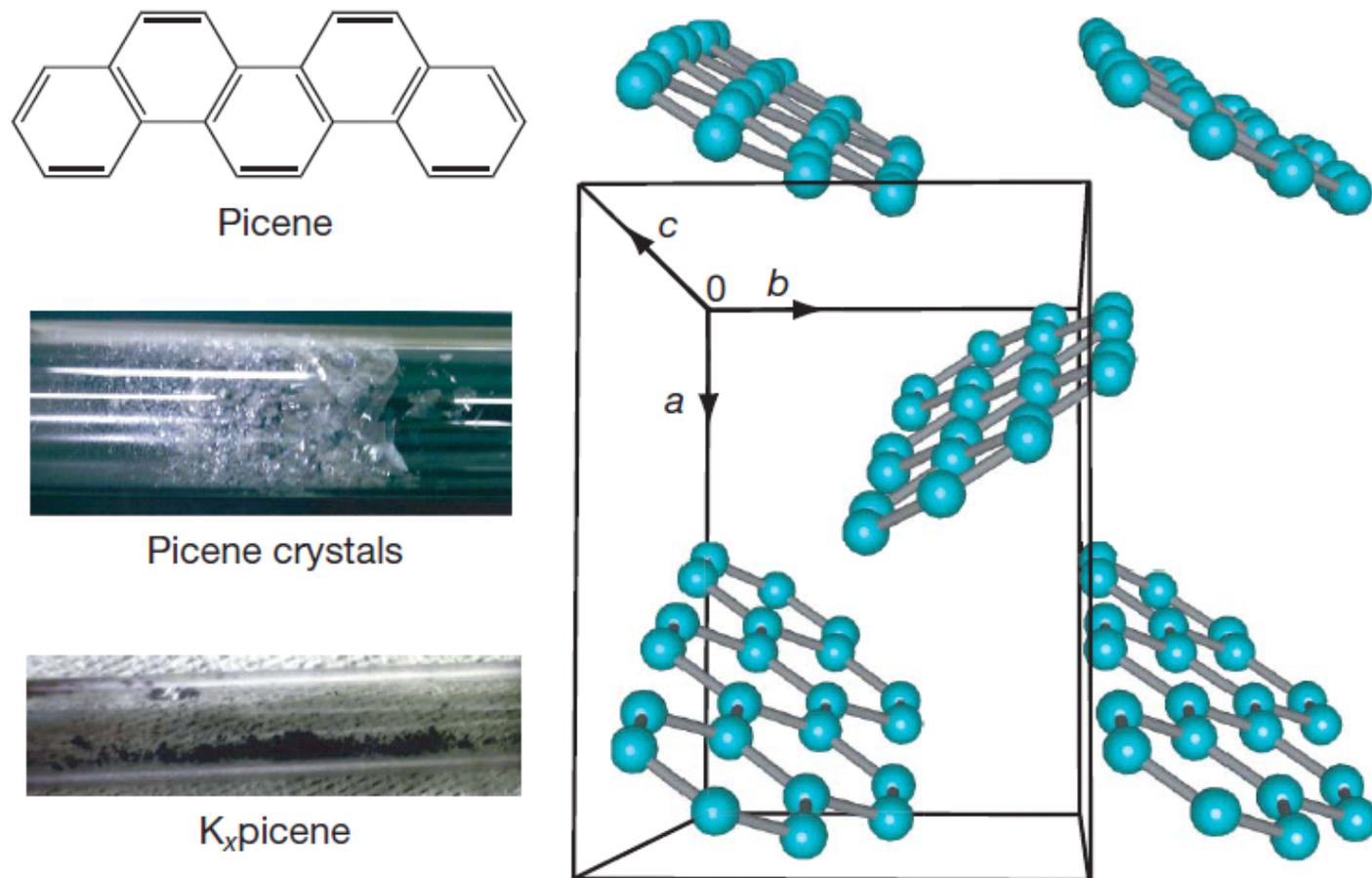
$K_x$picene

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

# C$_{22}$H$_{14}$ (theory)

## 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]

[1]*Department of Physics, University of Tokyo, Bunkyo, Tokyo 113-0033*
[2]*Research Institute for Computational Sciences (RICS), AIST, Tsukuba, Ibaraki 305-8568*
[3]*Department of Applied Physics, University of Tokyo, Bunkyo, Tokyo 113-8656*
[4]*Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 332-0012*
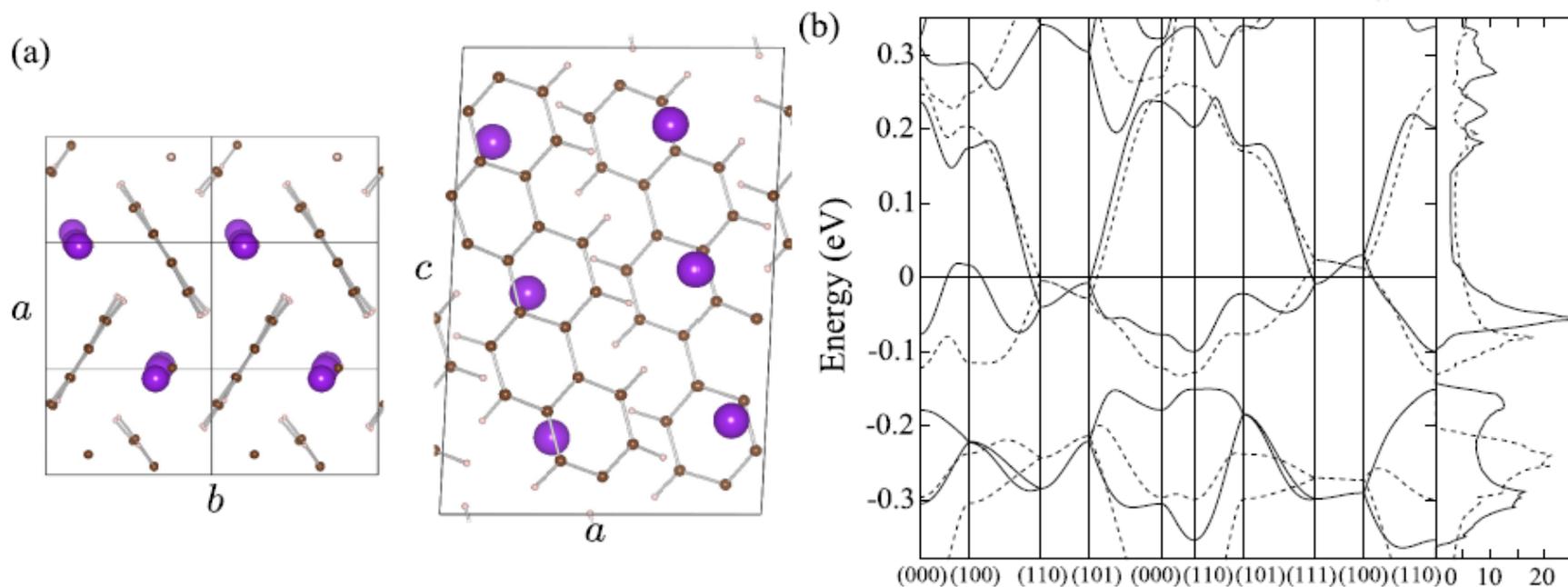
# $C_{22}H_{14}$ (theory)

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*
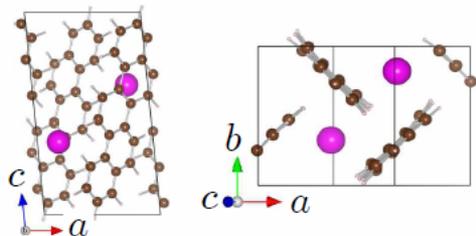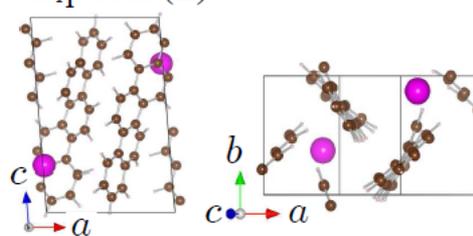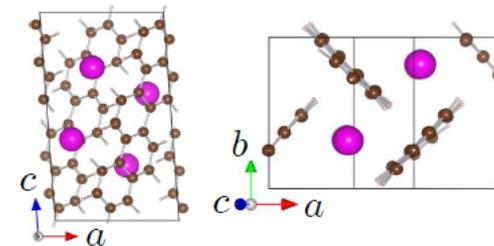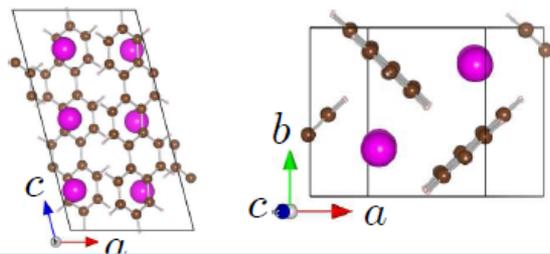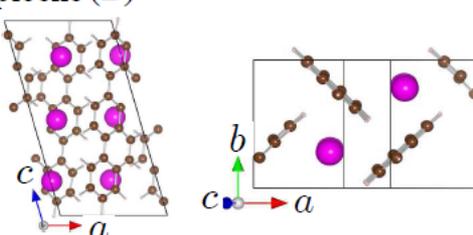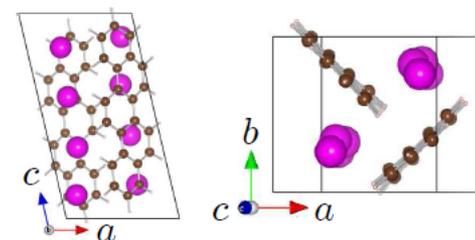
**Searching Optimal Structure is Undergoing**

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

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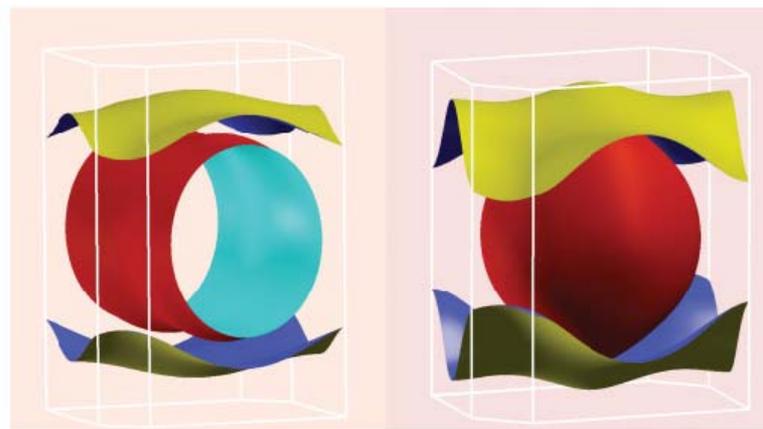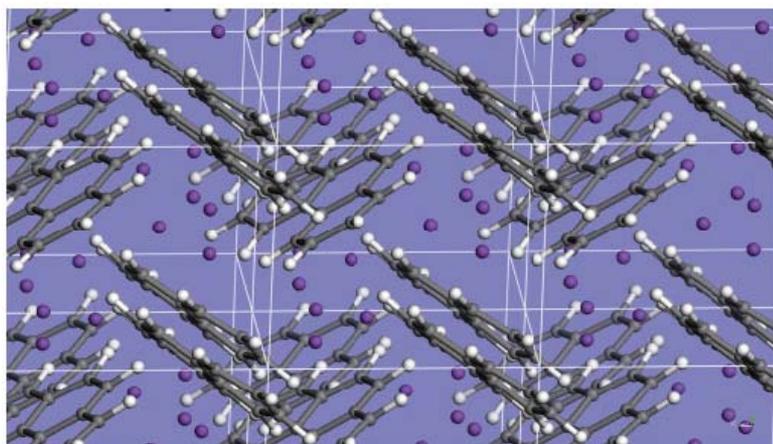
**Two sheets Fermi surface -> 1D & 2D Characters**

# $K_3C_{14}H_{10}$ (our results)



LDA
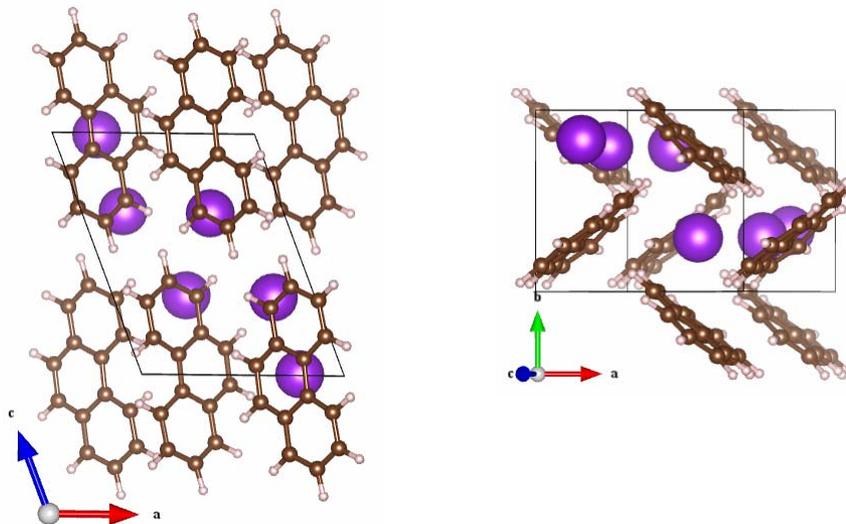
a=7.758Å,
b=6.852Å,
c=10.039Å;
$\beta$=110.6$^0$,
V=499.36 Å$^3$

GGA-PBE

a=8.358Å,
b=7.169Å,
c=10.687Å;
$\beta$=115.1$^0$,
V=580.13 Å$^3$

29
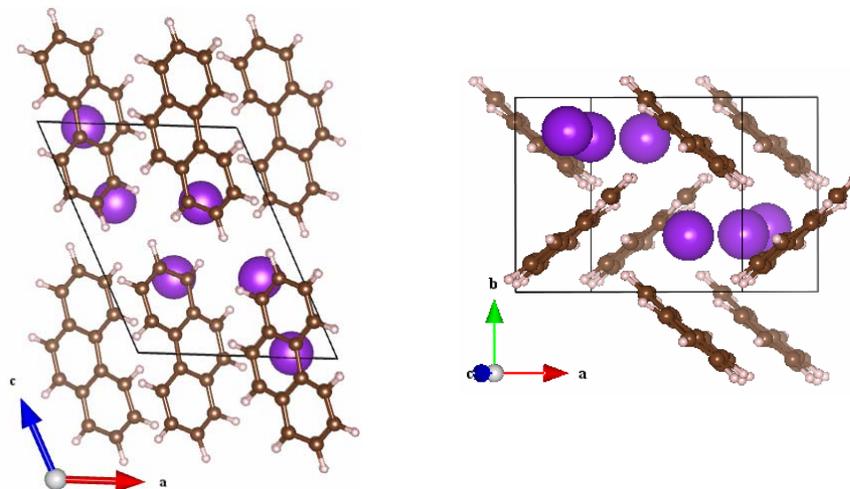
# $K_3C_{22}H_{14}$ (our results)

LDA



a=7.316Å,
b=7.366Å,
c=14.209Å;
$\beta$=106.8⁰
V=732.9 Å³

GGA-PBE



a=7.719Å,
b=7.725Å,
c=14.974Å;
$\beta$=107.6⁰
V=851.11 Å³

30
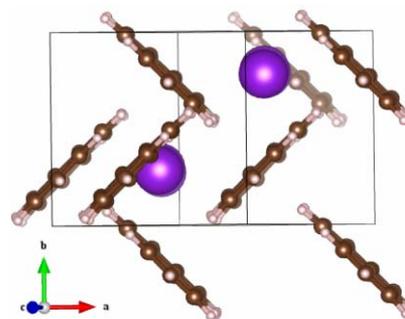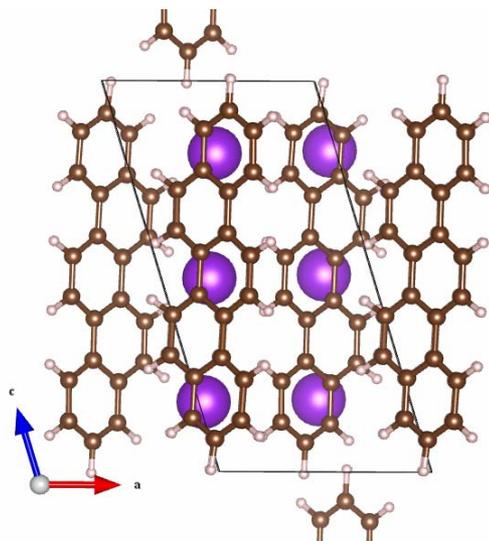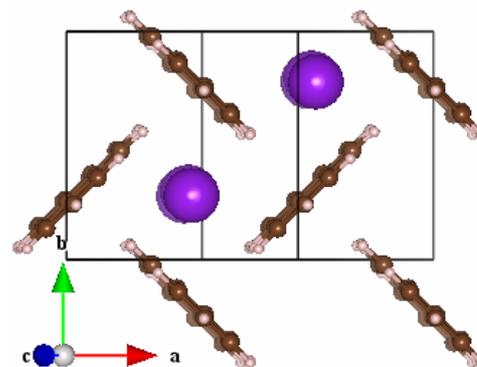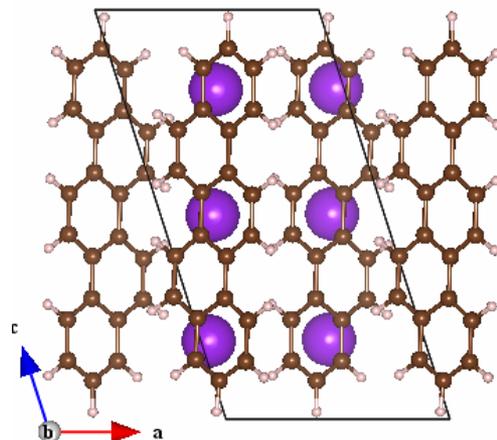
# $K_3C_{30}H_{18}$ (our results)

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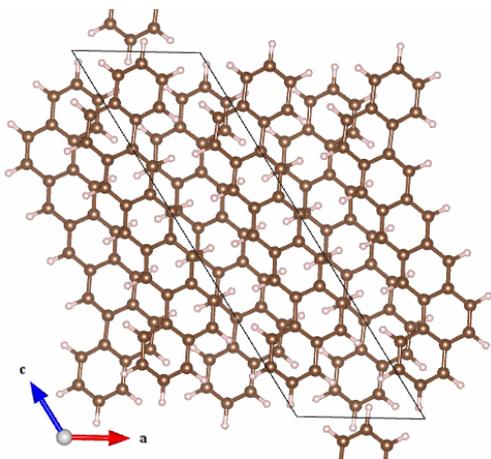


Hypothetical structure
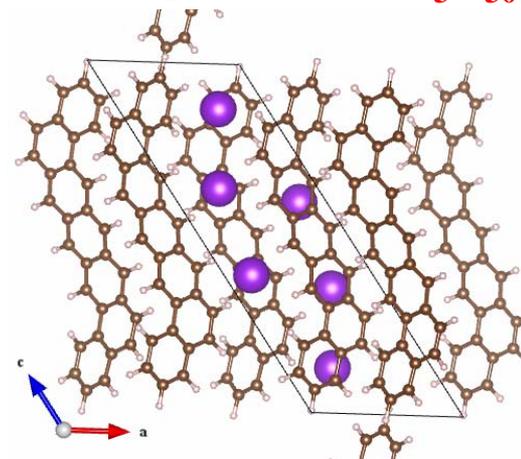
**Tri-potassium**

No experimental data
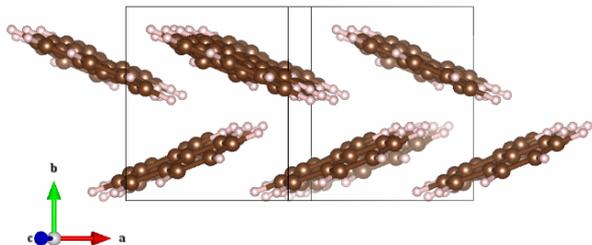
V=831.00 Å$^3$

a=6.279Å, b=7.381Å, c=21.225Å; $\beta$ =122.35$^0$

V=962.09 Å$^3$

a=7.711Å, b=7.041Å, c=21.357Å; $\beta$ =123.93$^0$

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



**0 GPa**

**40 GPa**

**70 GPa**

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

**Superconductivity?**

32
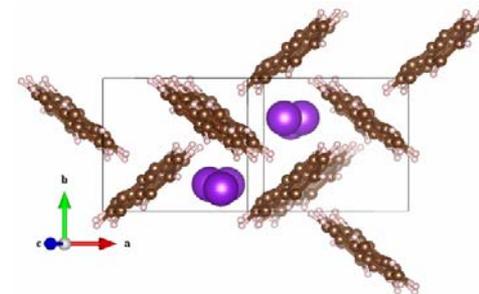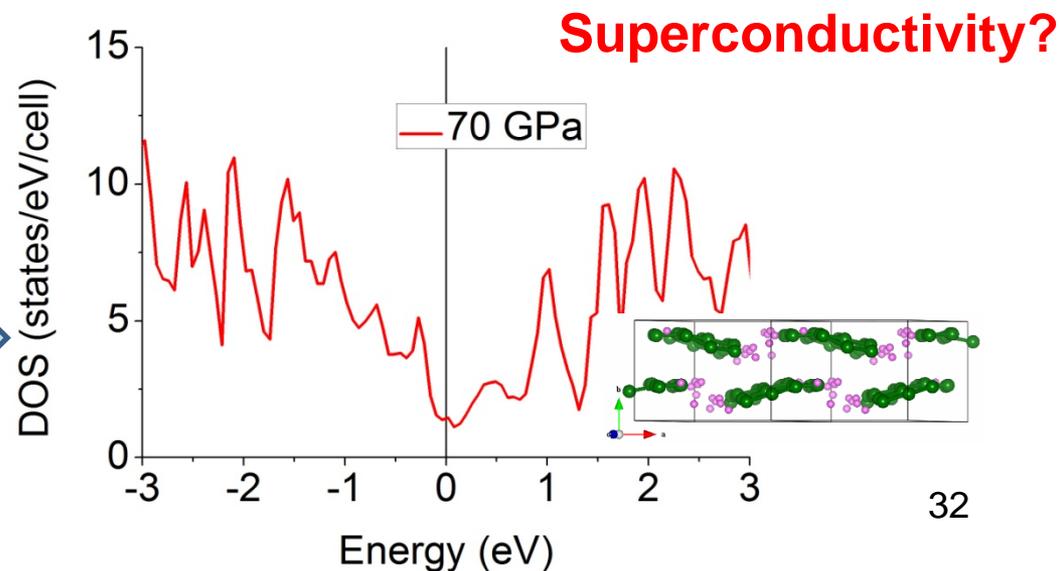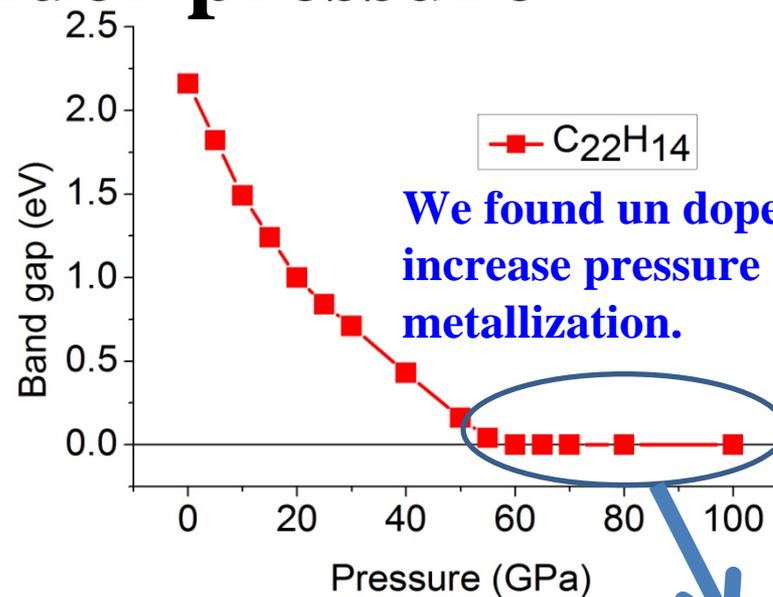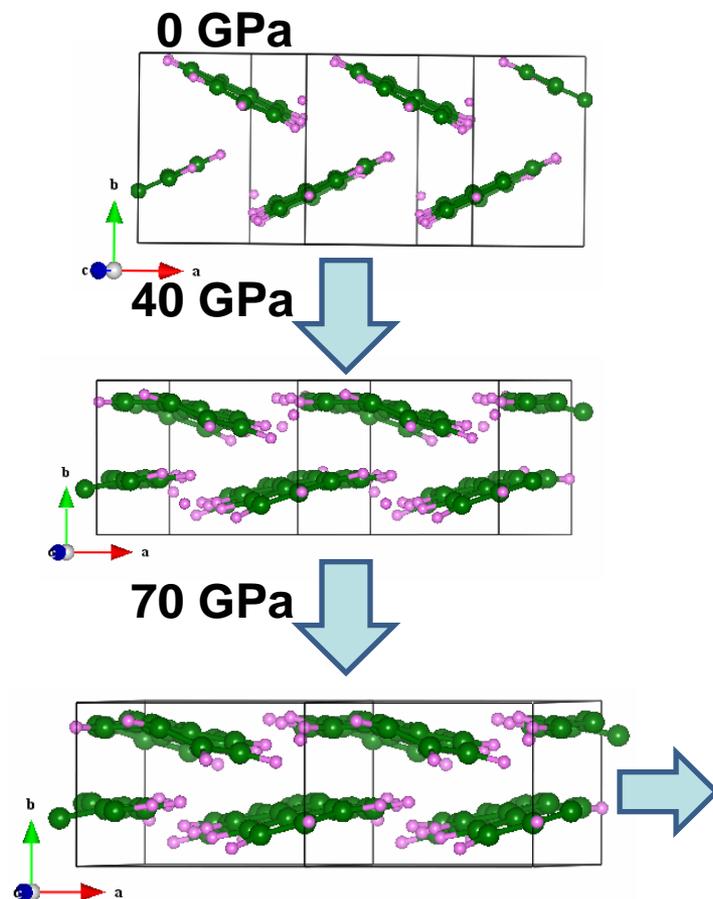
# Superconductivity of Metallic SiH$_4$ with Layered Structure

**X.J. Chen, J. L. Wang, V.V. Struzhkin, H.K. Mao, R.J. Hemley, and H.Q Lin, (PRL 101, 077002 (2008); Jun 19, 2007)**

The electronic and lattice dynamical properties of compressed solid **SiH$_4$** have been calculated in the pressure range up to 300 GPa with density functional theory. We find two energetically preferred insulating phases with ***P2$_1$/c*** and ***Fdd$_2$*** symmetries at low pressures. We demonstrate that the ***Cmca*** structure having layered network is the most likely candidate of the metallic phase of **SiH$_4$** over a wide pressure range above **60 GPa**. The superconducting transition temperature in this layered metallic phase is found to be in the range of **20** and **75** K.

# Brief Summary

- For undoped hydrocarbon compounds, crystal structures of $C_{14}H_{10}$ and $C_{22}H_{14}$ are experimentally known, but not $C_{30}H_{18}$ and other longer rings.

- For K-doped cases, few structures are known. Searching optimal structures are non-trivial.

- Studies on crystal structure as functions of pressure are called for, especially for doped cases. Usual DFT optimization does not provide results agree well with experiments. Different searching algorithms will find their values here.

# Correlation Effect

Electron-Electron Correlation (EC)?

Measure of correlation?

Magnetism?

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

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

Gianluca Giovannetti[1,2] and Massimo Capone[1,3]

[1]*ISC-CNR and Dipartimento di Fisica, Università di Roma "La Sapienza," Piazzale A. Moro 5, I-00185 Rome, Italy*
[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*

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.

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

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

## Density functional calculations of electronic structure and magnetic properties of the hydrocarbon $K_3$picene 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*

We have investigated the electronic structures and magnetic properties of a newly discovered hydrocarbon superconductor, $K_3$picene, having $T_c = 18$ K. We have shown that the metal-insulator transition is driven in $K_3$picene 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 $K_3$picene 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 $K_3$picene is located in the vicinity of the Mott transition. Our findings suggest that $K_3$picene is a strongly correlated electron system.

$U/W = 2.83 > 1.73$ (Mott Insulator); $CuO_2$, $U \sim W = 8t$ 38

$K_3C_{22}H_{14}$ **is a strongly correlated electron system.**
**Then how about** $K_3C_{14}H_{10}$ **and** $K_3C_{30}H_{18}$**?**
**Other similar systems ?**

**Organic Superconductors**



$C_{30}H_{18}$ (28/33K, Chen GF)

$C_{22}H_{14}$ (18K, Mitsuhashi)

$C_{14}H_{10}$ ( 5K, Chen XH)

$T_c$ (K)

Number of benzene rings
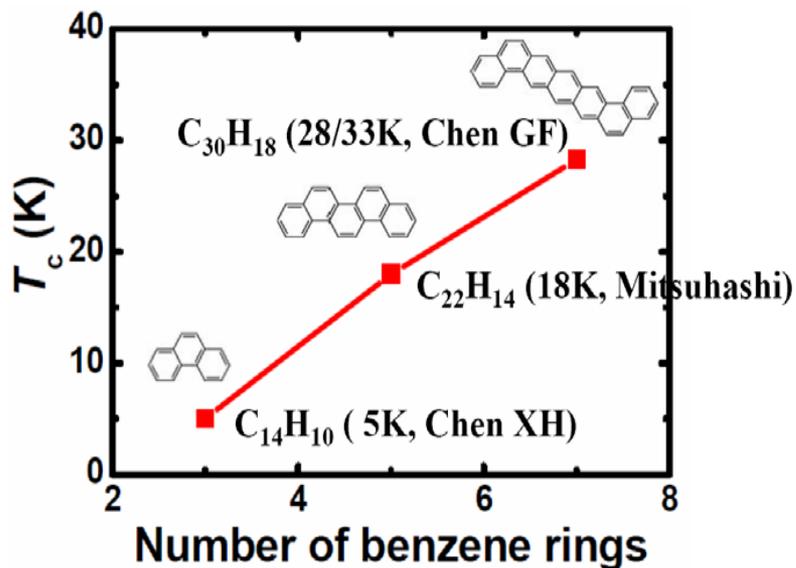
**How about the relation between EC and Tc (or structure)?**

39

# Our Studies

- Comparisons of electronic correlation effects for <span style="color:red">undoped</span> hydrocarbon compounds

- Comparisons of electronic correlation effects and electronic structures for <span style="color:red">doped</span> hydrocarbon compounds

# 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

# 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, and 2.0 a.u. for C, H , and 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

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

# Estimating Correlation

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

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 $\nu$ represents the amount of the HF exchange interaction and reflects the intensity of electronic correlation (EC).

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

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

Coulomb screen $\mu$ was adjusted from the 0.1 Å to 0.2 Å.
$\nu$ was adjusted from 0 to 1, $\nu = 0$ corresponds to PBE.

44

# Pure phenanthrene ($C_{14}H_{10}$):                    Fixing    $\mu = 0.2$

Based on
experimental
lattice
constants



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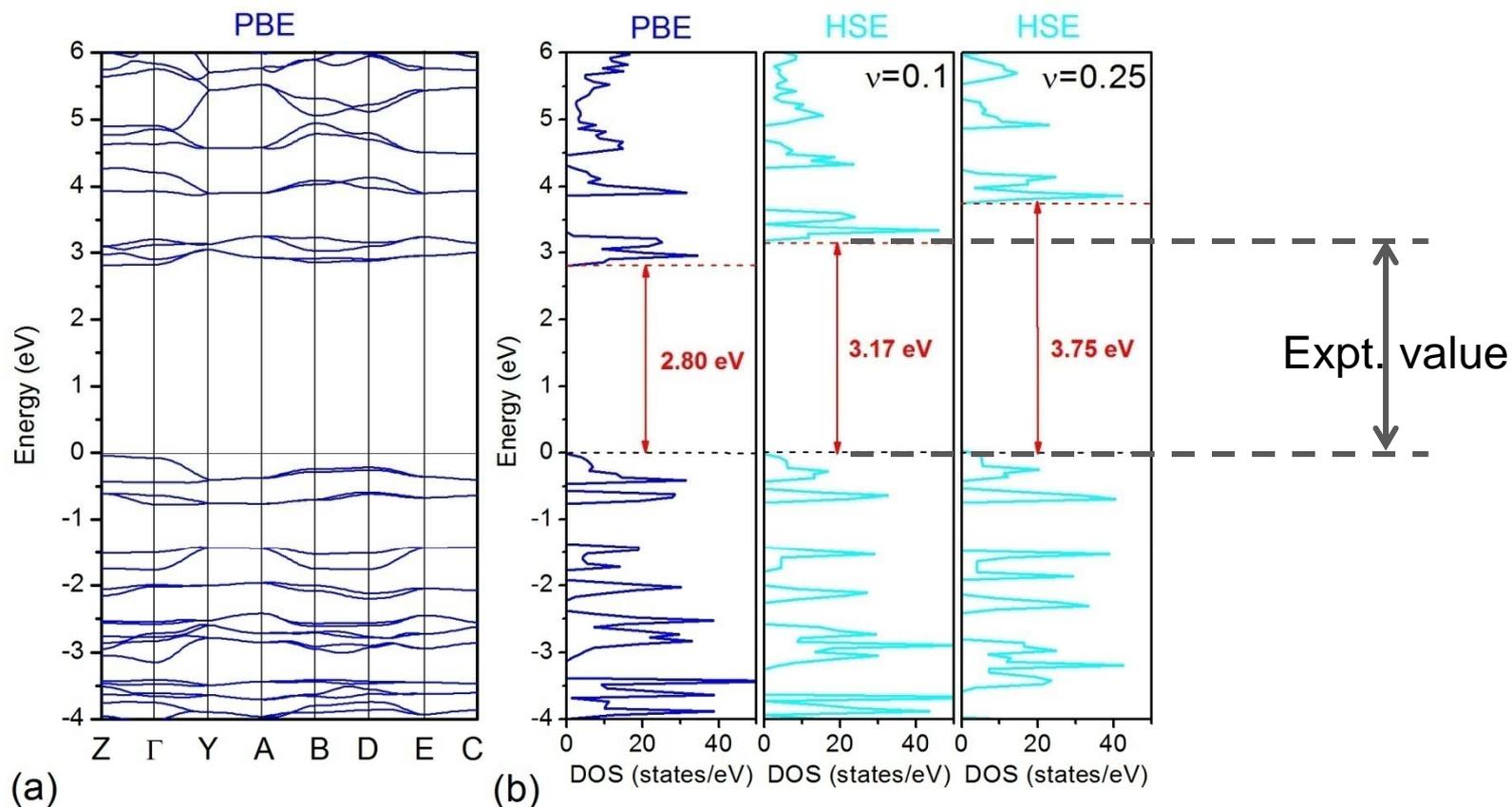
For phenanthrene, the Band-gap obtained from PBE is 2.80 eV, which is less than the experimental value. Small account ($\nu > 0.1$) of exact exchange (HSE calculation) is added to correct the error. However, normal HSE calculation (adopted default $\nu > 0.25$) will overestimate the gap.

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

Experimental Band-gap: 3.16 eV;                    LDA result: 2.75 eV    47

M. T. Bhatti et al., Turk. J. Phys. **24**, 673 (2000).                    P. L. de Andres et al.  PRB **84**, 144501 (2011)

**Pure picene (C$_{22}$H$_{14}$):**    **Fixing** $\mu$ =0.2



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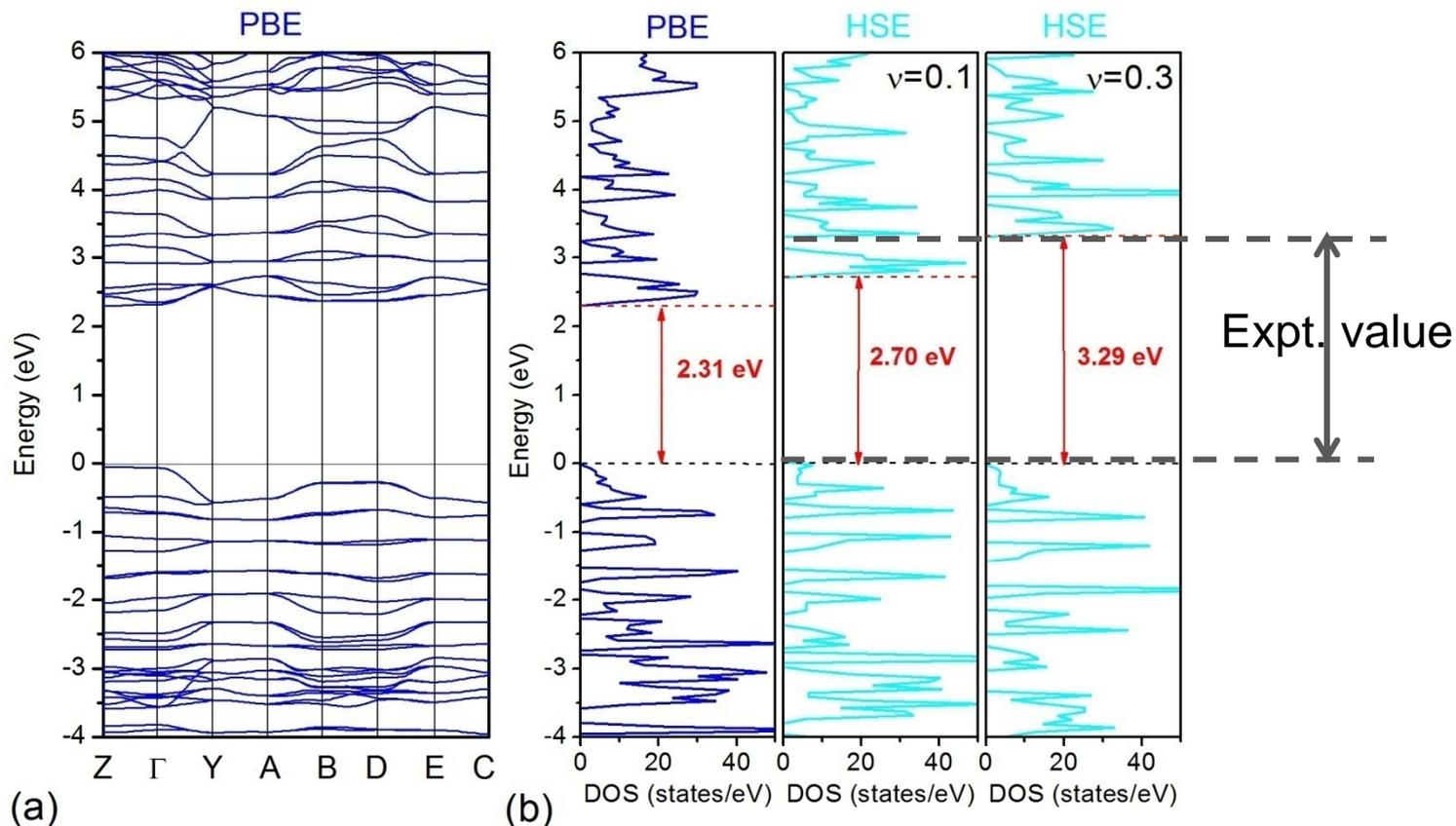
For picene, the Band-gap obtained from PBE is only 2.31 eV, the gap is intensively underestimated by PBE. HSE functional induces the increase of gap and furthers with increasing the ratio $v$ of exact/DFT exchange. When $v$ is increased to ~ 0.3, the obtained gap is equal to the experimental value.

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;    LDA result: 2.36 eV    48

H Okamoto et al., JACS 130, 10470 (2008)    T. KOSUGI et al., JPSJ 78, 113704 (2009)

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



Based on optimized lattice constants

(a)   (b)
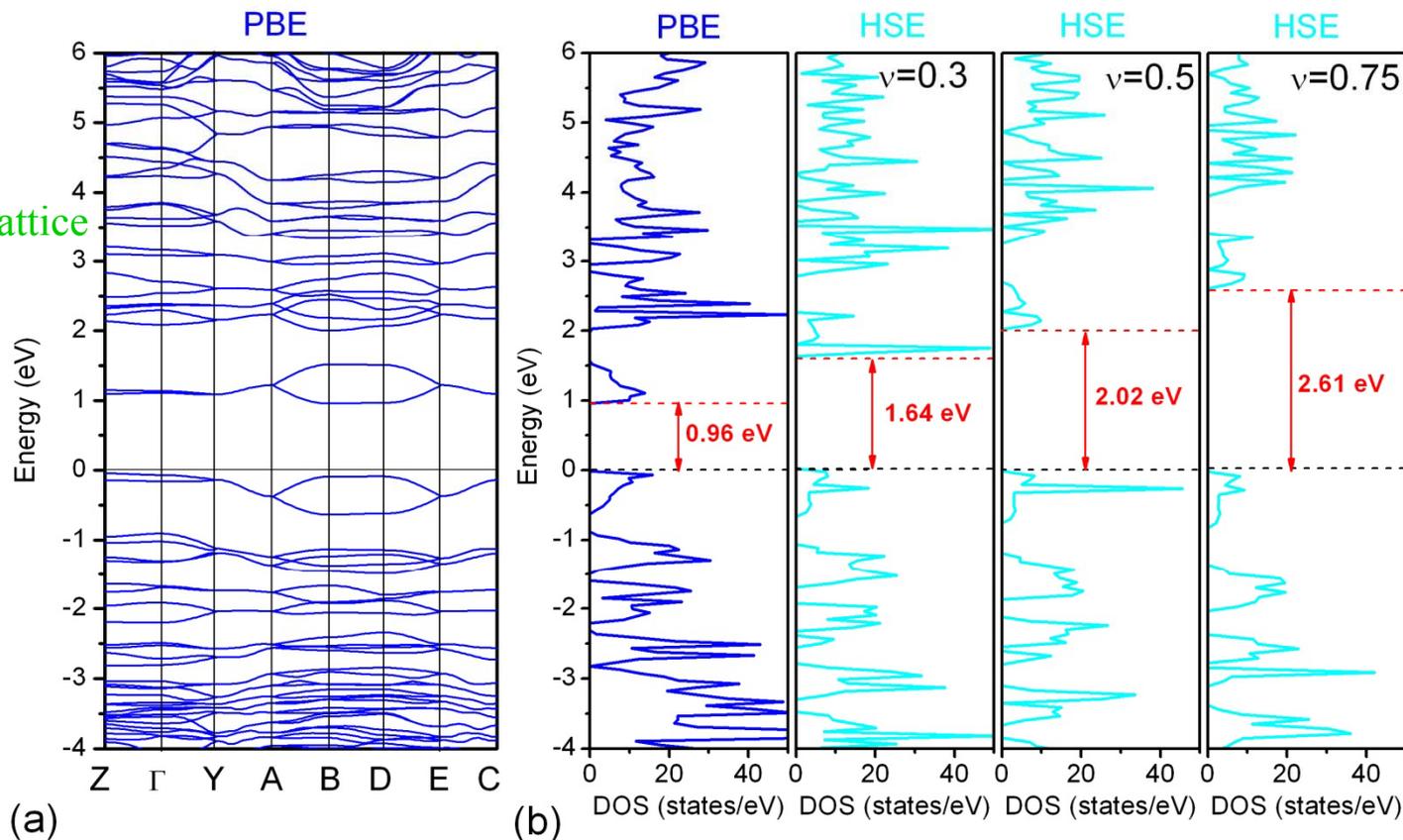
For $C_{30}H_{18}$, the Band-gap obtained from PBE is only 0.96 eV, the gap is intensively underestimated by PBE. HSE functional induces the increase of gap and furthers with increasing the ratio $\nu$ of exact/DFT exchange. When $\nu$ reaches $> 0.5$, the obtained gap is consistant with the experimental 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. König, B. Mahns, B. Büchner, and M. Knupfer, arXiv:1206.0526v1

# Correlation Measure

Reproducing the experimental band gap, the values of $\nu$ and $\mu$ parameters are

|  | $C_{14}H_{10}$ | $C_{22}H_{14}$ | $C_{30}H_{18}$ | $C_{30}H_{18}$ |
|---|---|---|---|---|
| $E_g$ (Expt.) | 3.16 | 3.3 | $\sim 2.0$ | ~3.5 |
| $\nu$ (fix $\mu$=0.1) | 0.05 | 0.2 | $\sim 0.35$ | ~0.75 |
| $\nu$ (fix $\mu$=0.2) | 0.1 | 0.3 | $\sim 0.5$ | > 0.75 |

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 suggest the electronic structures of $K_3C_{14}H_{10}$, $K_3C_{22}H_{14}$, and $K_3C_{30}H_{18}$ in the following slides:

# Electronic structures of $K_3C_{14}H_{10}$

**(a) The band structures based on PBE and HSE levels.**

**(b) The density of states (DOS) based on PBE and HSE levels.**

**(c) The Fermi surface sheets based on PBE and HSE levels.**



(a)    (b)    (c)
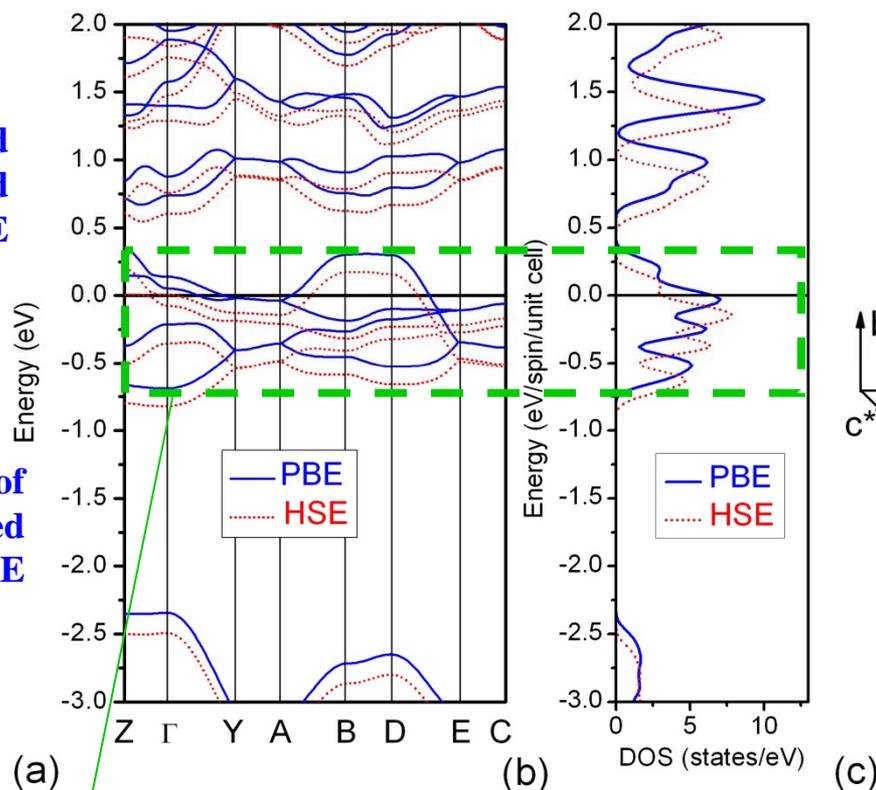
Based on the HSE method, bands shift toward to the lower energy level, results in the decrease of the DOS at Fermi level and variations of Fermi surface. **No clear magnetic ground state, metallic behavior**.

The wide band dispersion implies the **weak correlation** in $K_3C_{14}H_{10}$.

55

# Electronic structures of $K_3C_{22}H_{14}$

(a) The band structures based on PBE and HSE levels.

(b) The density of states (DOS) based on PBE and HSE levels.
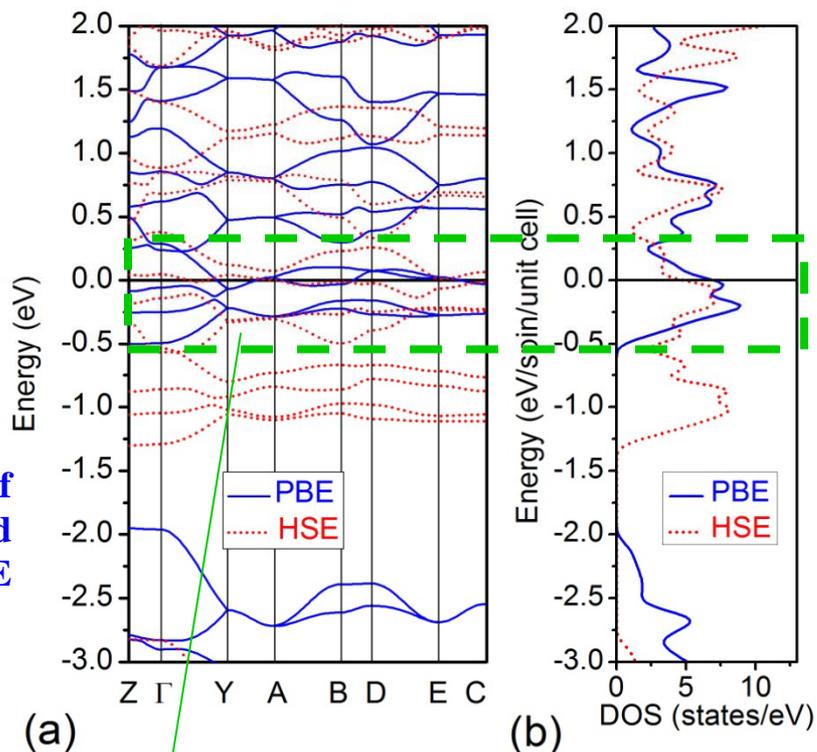
(c) The Fermi surface sheets based on PBE and HSE levels.



The HSE method results in the decrease of the DOS at Fermi level and variations of Fermi surface.

The feature of **flat bands** indicates that the correlation effect in $K_3C_{22}H_{14}$ is stronger than that in $K_3C_{14}H_{10}$.

57

# Electronic structures of $K_3C_{30}H_{18}$

(a) The band structures based on PBE and HSE levels.

(b) The density of states (DOS) based on PBE and HSE levels.
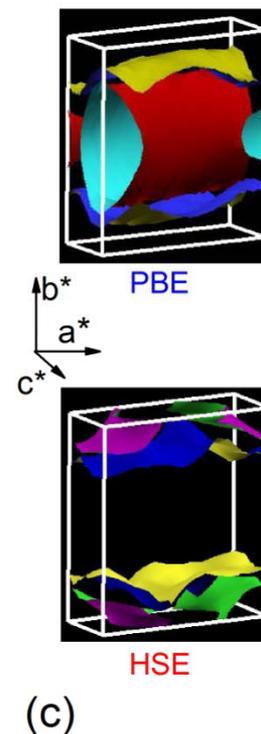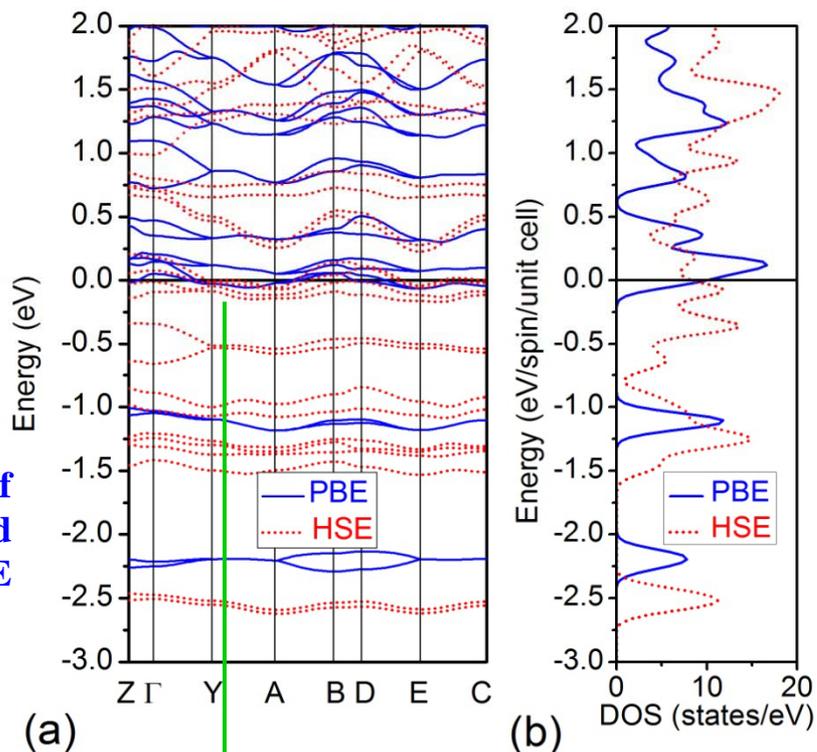
(c) The Fermi surface sheets based on PBE and HSE levels.



The HSE method results in the big variation of bands and DOS near Fermi level. **Metal, trends to AFM ground-state**.

In $K_3C_{30}H_{18}$, bands become **narrow and more flat**, showing that the **correlation is more stronger**, comparing with $K_3C_{22}H_{14}$.

59

# Magnetism

> **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 rings.

# $U_{eff}, W, t = U_{eff}/W$

- We compute $U_{bare}$ for a single molecule with three electrons from the energies of the molecule charged with 2, 3, and 4 electrons as $U_{bare} = E(4) - 2E(3) + E(2)$, where $E(M)$ is the total energy of a molecule charged with $M$ extra electrons.

- Such an estimate for an isolated molecule needs to be corrected ($E_{pol}(M)$) in order to include the screening effects in the solid. A first estimate can be obtained by considering the effect of the polarization of a charged molecule placed inside a cavity of a homogeneous dielectric medium characterized by a dielectric constant $\varepsilon$ .

- Thus, we estimate, $U_{eff} = U_{bare} - E_{pol}$
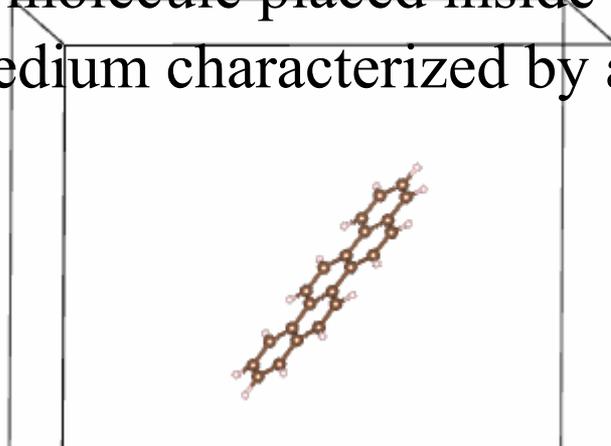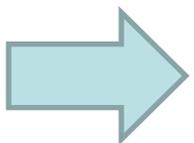
# $U_{eff}$ *for undoped systems*

| | $\varepsilon$ | $U_{eff}$ (eV) |
|---|---|---|
| | 3.0 | -5.14 |
| | 3.5 | -5.23 |
| $C_{14}H_{10}$ | 4.0 | -5.29 |
| | 4.5 | -5.34 |
| | 5.0 | -5.38 |
| | 3.0 | -4.29 |
| | 3.5 | -4.37 |
| $C_{22}H_{14}$ | 4.0 | -4.43 |
| | 4.5 | -4.48 |
| | 5.0 | -4.52 |
| | 3.0 | -2.41 |
| | 3.5 | -2.50 |
| $C_{30}H_{18}$ | 4.0 | -2.56 |
| | 4.5 | -2.61 |
| | 5.0 | -2.65 |



**For each hydrocarbon compound, the $U_{eff}$ dependence on dielectric constant $\varepsilon$.**

# $U_{eff}$, $W$, $t = U_{eff}/W$

| | $\varepsilon$ | $U_{eff}$ (eV) | $W$ (eV) | $t = U_{eff}/W$ |
|---|---|---|---|---|
| | 3.0 | 0.66 | 0.52 | 1.27 |
| | 3.5 | 0.57 | 0.52 | 1.10 |
| $K_3C_{14}H_{10}$ | 4.0 | 0.51 | 0.52 | 0.98 |
| | 4.5 | 0.46 | 0.52 | 0.88 |
| | 5.0 | 0.42 | 0.52 | 0.81 |
| | 3.0 | 0.72 | 0.39 | 1.85 |
| | 3.5 | 0.64 | 0.39 | 1.64 |
| $K_3C_{22}H_{14}$ | 4.0 | 0.58 | 0.39 | 1.49 |
| | 4.5 | 0.53 | 0.39 | 1.36 |
| | 5.0 | 0.49 | 0.39 | 1.26 |
| | 3.0 | 0.67 | 0.21 | 3.19 |
| | 3.5 | 0.58 | 0.21 | 2.76 |
| $K_3C_{30}H_{18}$ | 4.0 | 0.52 | 0.21 | 2.48 |
| | 4.5 | 0.47 | 0.21 | 2.24 |
| | 5.0 | 0.43 | 0.21 | 2.05 |

66
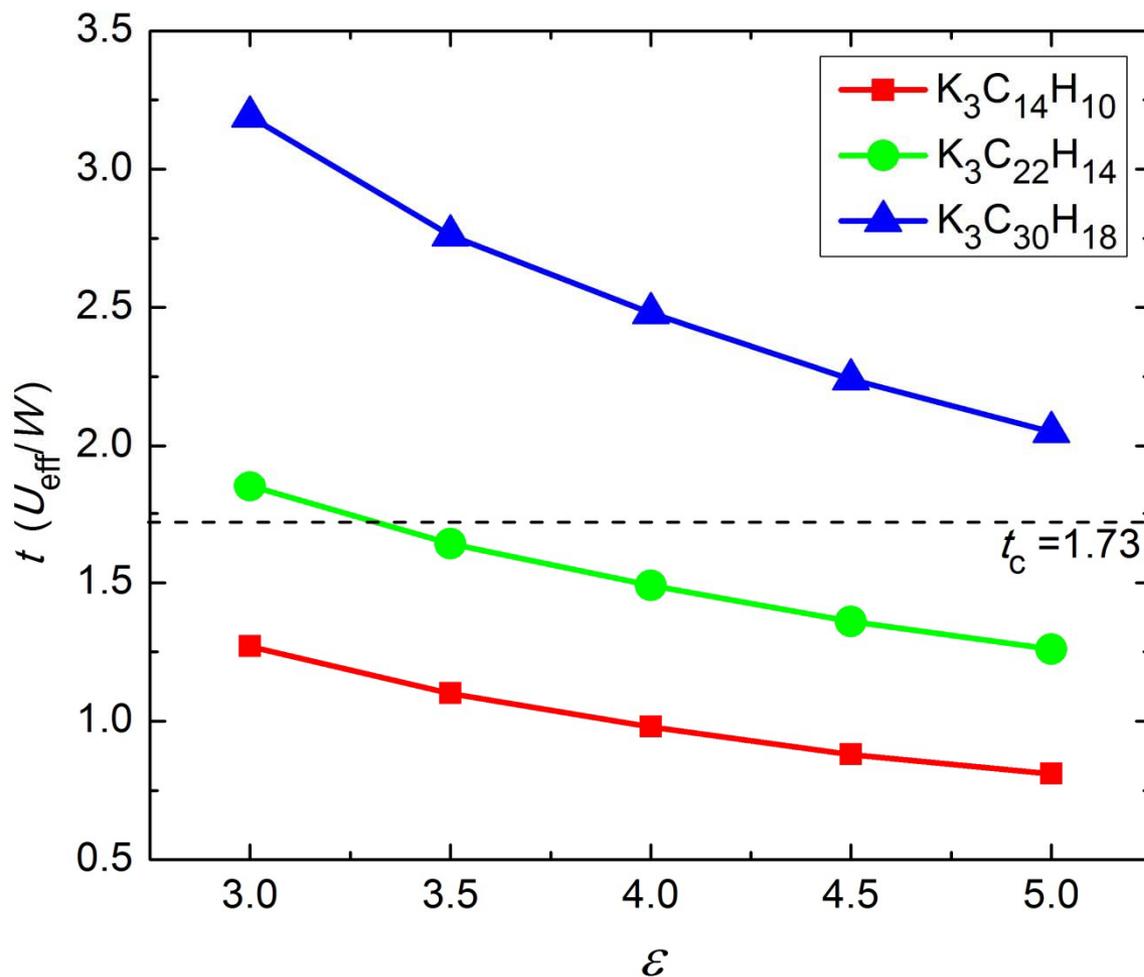
# $U_{eff}$, $W$, $t = U_{eff}/W$



**The $t$ ($U_{eff}/W$) dependence on dielectric constant $\varepsilon$.**

# Brief Summary

- For undoped hydrocarbon compounds, the electronic correlation effect (EC) increases from $C_{14}H_{10}$ to $C_{22}H_{14}$ to $C_{30}H_{18}$.

- 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)

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

H. Okazaki,[1,2] T. Wakita,[1,2] T. Muro,[3] Y. Kaji,[1] X. Lee,[1] H. Mitamura,[1] N. Kawasaki,[1] Y. Kubozono,[1] Y. Yamanari,[1] T. Kambe,[1] T. Kato,[4] M. Hirai,[1] Y. Muraoka,[1,2] and T. Yokoya[1,2]

[1]*The Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan*
[2]*CREST, Japan Science and Technology Corporation (JST), 3-1-1 Tsushima-naka, Okayama 700-8530, Japan*
[3]*Japan Synchrotron Radiation Research Institute (JASRI)/SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan*
[4]*Institute for Innovative Science and Technology, Graduate School of Engineering, Nagasaki Institute of Applied Science, 3-1, Shuku-machi, Nagasaki 851-0121, Japan*
(Received 27 August 2010; revised manuscript received 14 October 2010; published 10 November 2010)

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)

## Vibrational spectrum and electron-phonon coupling of doped solid picene from first principles

Alaska Subedi and Lilia Boeri

*Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
(Received 21 March 2011; revised manuscript received 5 July 2011; published 25 July 2011)

We study superconductivity in doped solid picene ($C_{22}H_{14}$) with linear response calculations of the phonon spectrum and electron-phonon (*ep*) interaction. We show that the coupling of the high-energy C bond-stretching phonons to the $\pi$ molecular orbitals for a doping of ~3 electrons per picene molecule is sufficiently strong to reproduce the experimental $T_c$ of 18 K within Migdal-Eliashberg theory. For hole doping, we predict a similar coupling leading to a maximum $T_c$ of 6 K. However, we argue that, due to its molecular nature, picene may belong to the same class of strongly correlated *ep* superconductors as fullerides. We propose several experimental tests for this hypothesis and suggest that intercalated hydrocarbons with different arrangements and numbers of benzene rings may be used to study the interplay between *ep* interaction and strong electronic correlations in the highly nonadiabatic limit.

**Found a large coupling of bond-stretching phonons at 1400 and 1600 cm$^{-1}$ both to electrons in the four lowest conduction bands and holes in the two highest valance bands, …, sufficiently strong to explain T$_c$=18K in Migdal-Eliashberg theory.**

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

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

Takashi Kato,[1,*] Takashi Kambe,[2] and Yoshihiro Kubozono[3,4]

[1]*Institute for Innovative Science and Technology, Graduate School of Engineering, Nagasaki Institute of Applied Science,
3-1, Shuku-machi, Nagasaki 851-0121, Japan*
[2]*Department of Physics, Okayama University, 3-1-1, Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*
[3]*Research Laboratory for Surface Science, Okayama University, 3-1-1, Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*
[4]*Research Centre of New Functional Materials for Energy Production, Storage and Transport, Okayama University,
3-1-1, Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*
(Received 7 April 2011; published 9 August 2011)

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)

## Intercalant and Intermolecular Phonon Assisted Superconductivity in K-Doped Picene

Michele Casula,[1] Matteo Calandra,[1] Gianni Profeta,[2] and Francesco Mauri[1]

[1]*CNRS and Institut de Minéralogie et de Physique des Milieux condensés,
Université Paris 6, case 115, 4 place Jussieu, 75252, Paris cedex 05, France*
[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 $\lambda$ as also shown by the **isotope exponents** of potassium (0.19) and carbon (0.31).

Other calculations: $\lambda = 0.88/1.41$, $\omega_{log} = 207/240$ cm$^{-1}$
(Note that intramolecular phonons dominate in $C_{60}$)      73

# Electron-Phonon alone is not enough
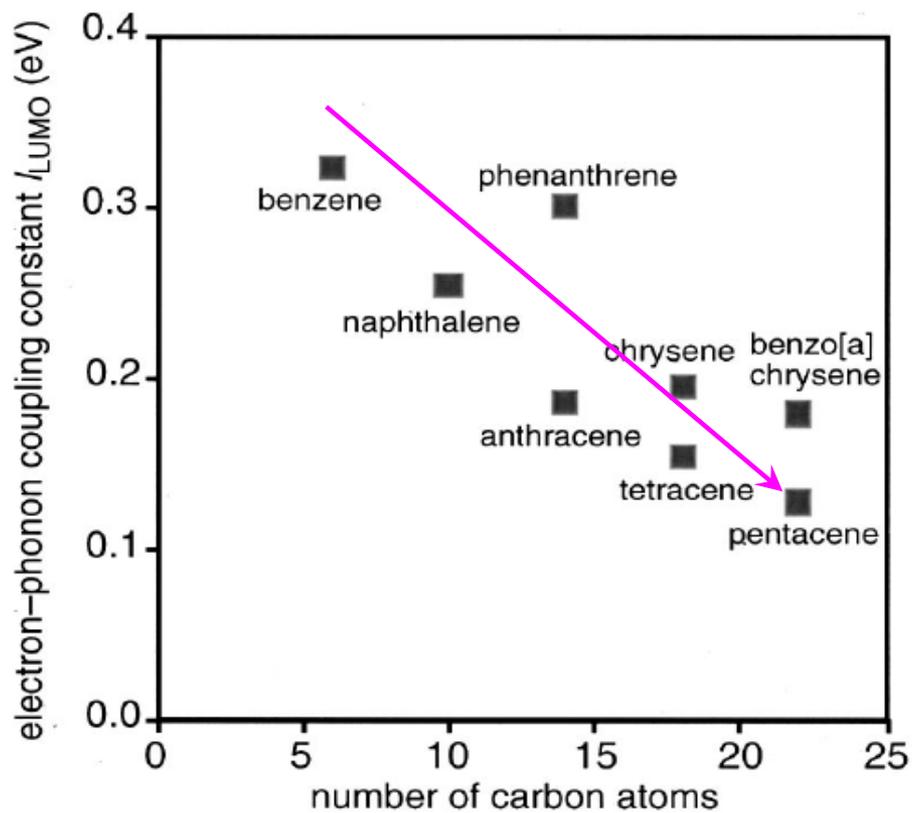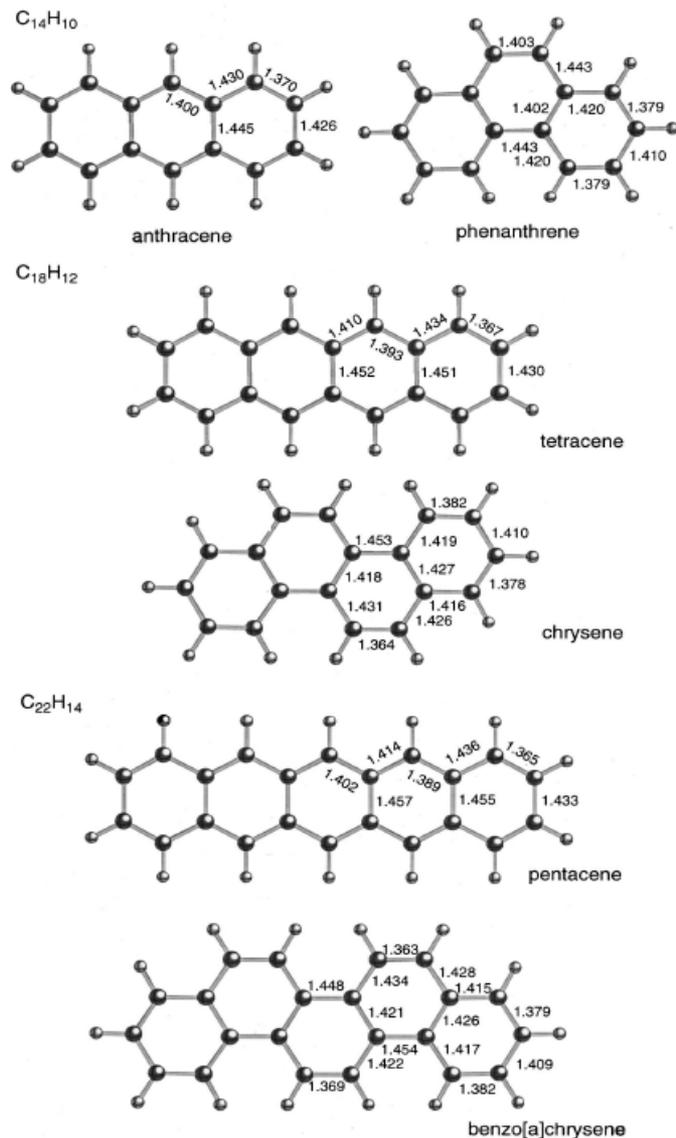


T. Kato et al., J. Chem. Phys. 116, 3420 (2002).

74

# Brief Summary

- Electron-phonon interaction does play role;

- 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

## High magnetic susceptibility
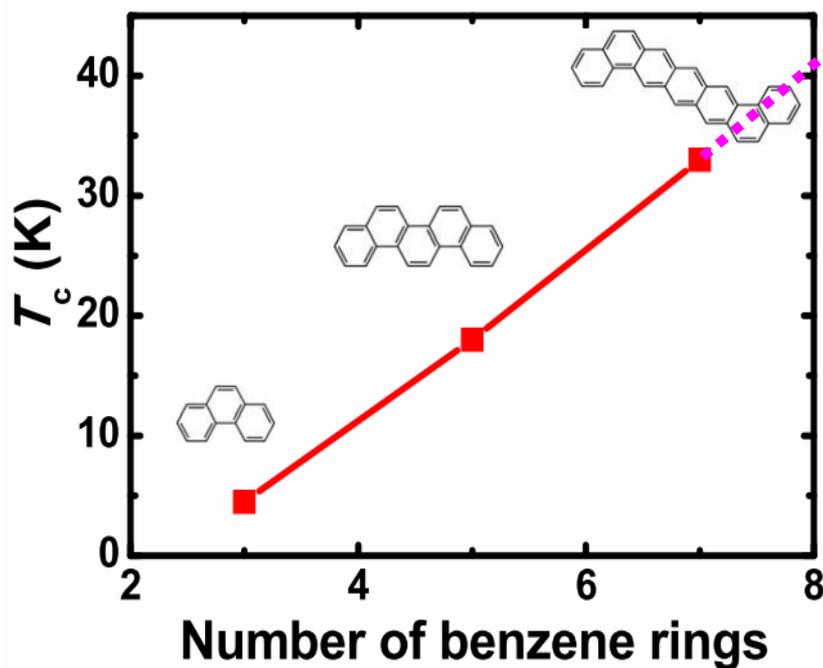


**$T_c$ increases with increasing the Number of benzene rings!**
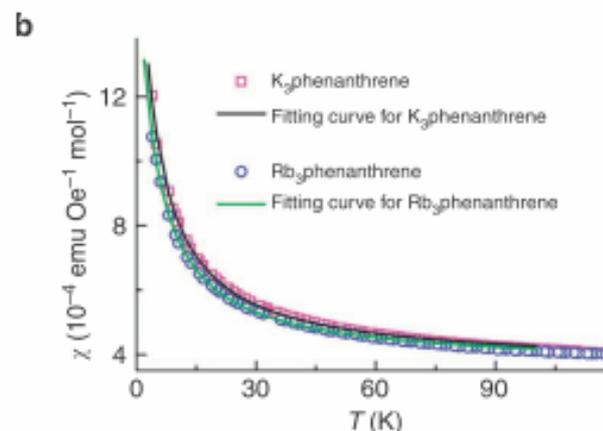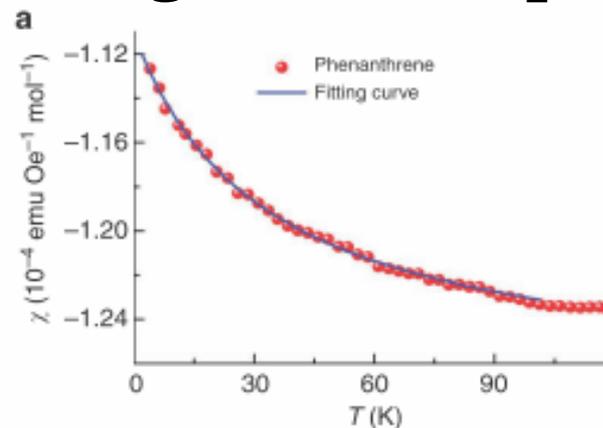
**Curie-Weiss magnetic behavior**
**⟶ local spin!**

76

# Magnetic Properties

## 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) | $\ll$ 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) | $\ll$ 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) | $\ll$ 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) | $\ll$ 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**

77

# 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

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



(a) C$_{14}$H$_{10}$

(b) C$_{30}$H$_{18}$
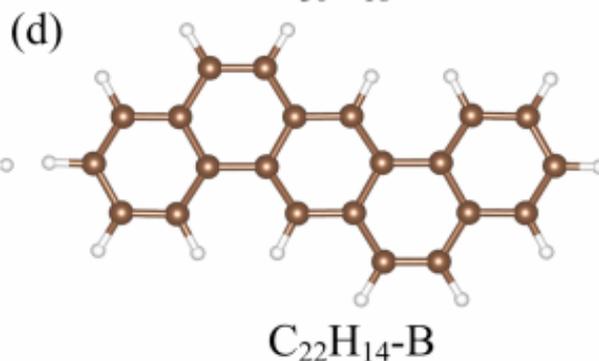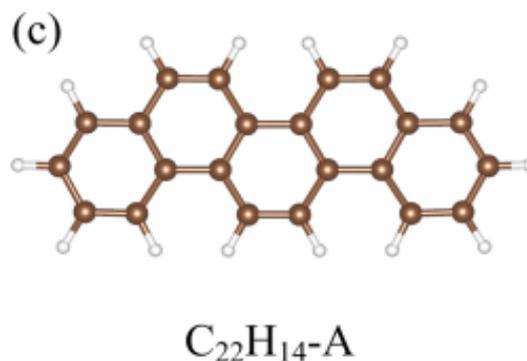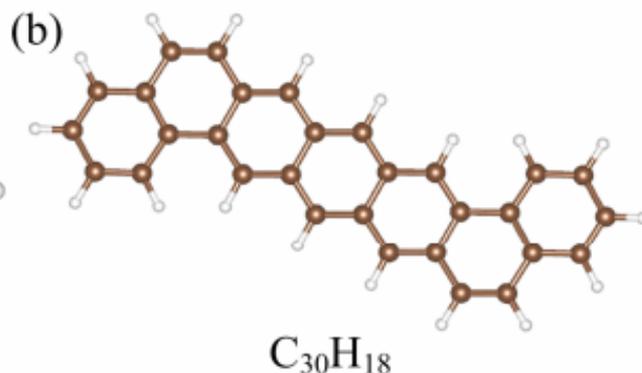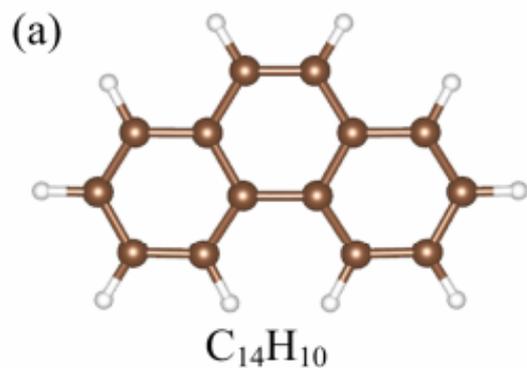
(c) C$_{22}$H$_{14}$-A

(d) C$_{22}$H$_{14}$-B

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

**$\varepsilon$ ? (~ t)**

Electron-phonon interaction could be accounted by $t\,(1 + \alpha x)$

79

# The Parameter $\varepsilon$
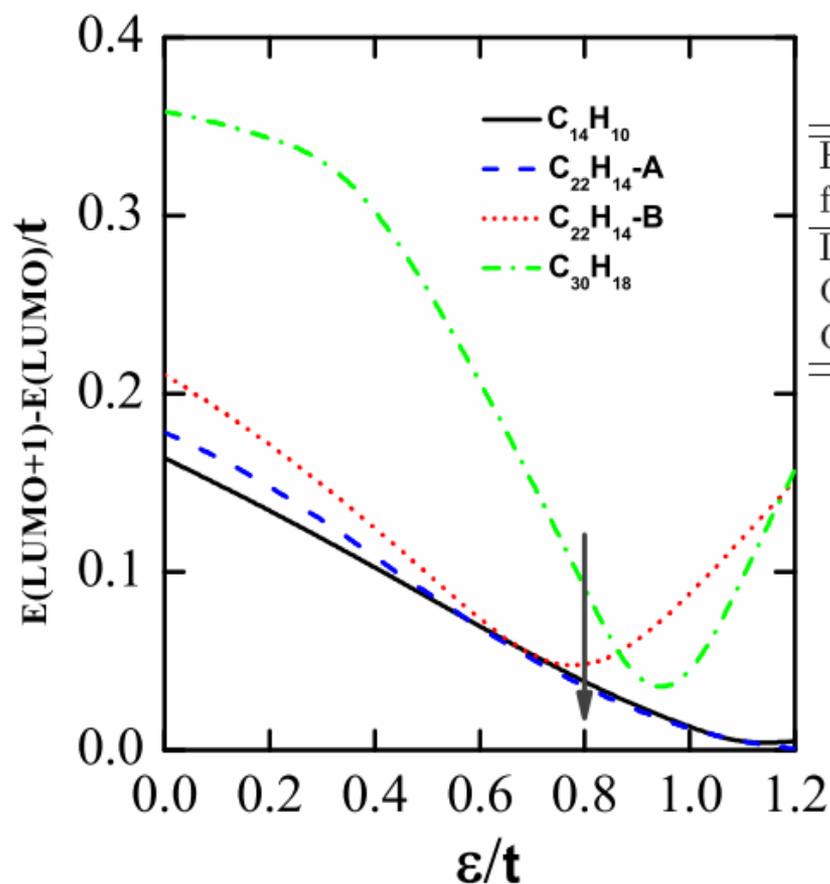


$$\Delta E_{LUMO} = E(LUMO + 1) - E(LUMO)$$

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

$$\epsilon > 0.8t$$

# Magnetic Phase Diagram
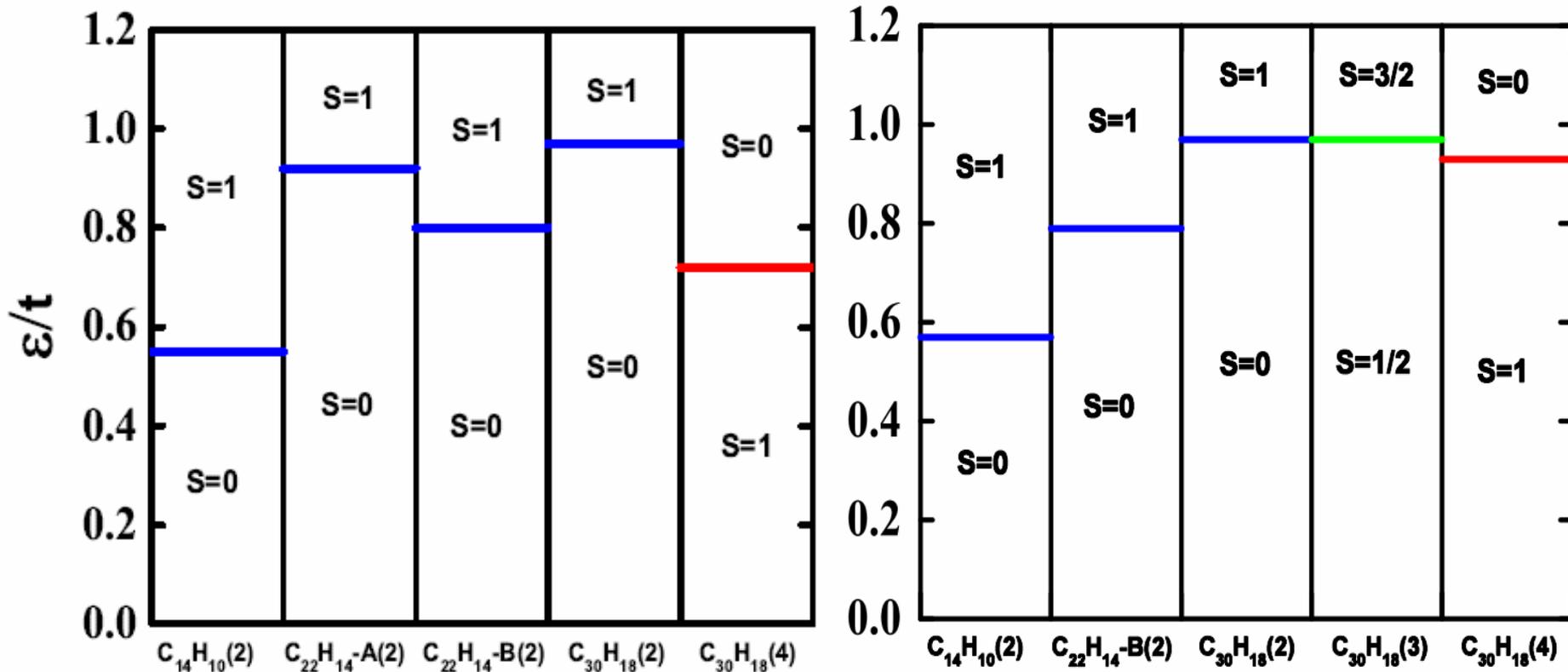


(1) For two electron doped cases, the total spin $S$ switches from 0 to 1.

(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.

85

# Spin Density

**(PBE results)**

**$K_3C_{14}H_{10}$**
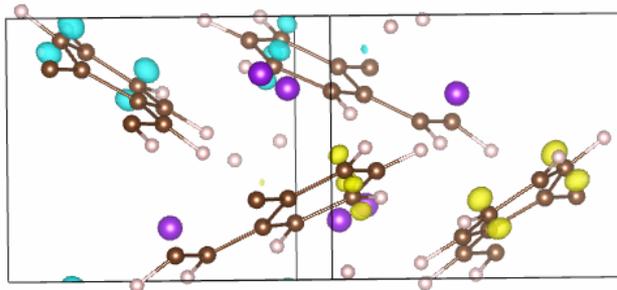


Local magnetic moment ~ 0. 09  $\mu_B$/f.u.

**$K_3C_{22}H_{14}$**
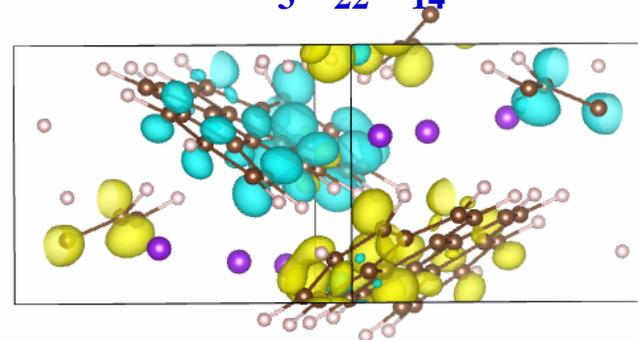


Local magnetic moment ~ 0. 25  $\mu_B$/f.u.

**$K_3C_{30}H_{18}$**
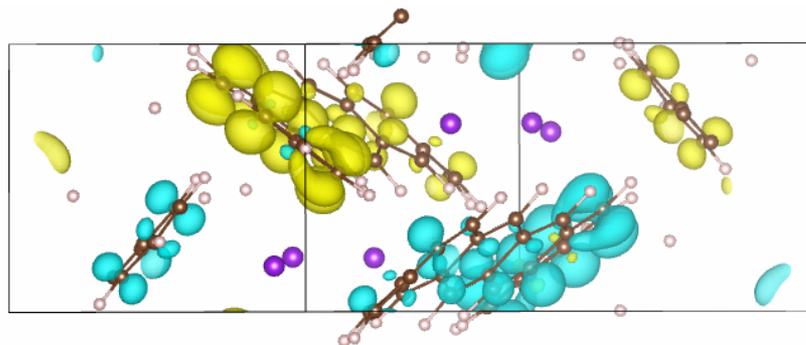


Local magnetic moment ~ 0. 45  $\mu_B$/f.u.

86

# 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 for large V.**

# Pair Binding Energy:

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

**i=1, 2, 3**

$\Delta_i >0$: **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 $\Delta_i$ for $C_{14}H_{10}$ & $C_{22}H_{14}$
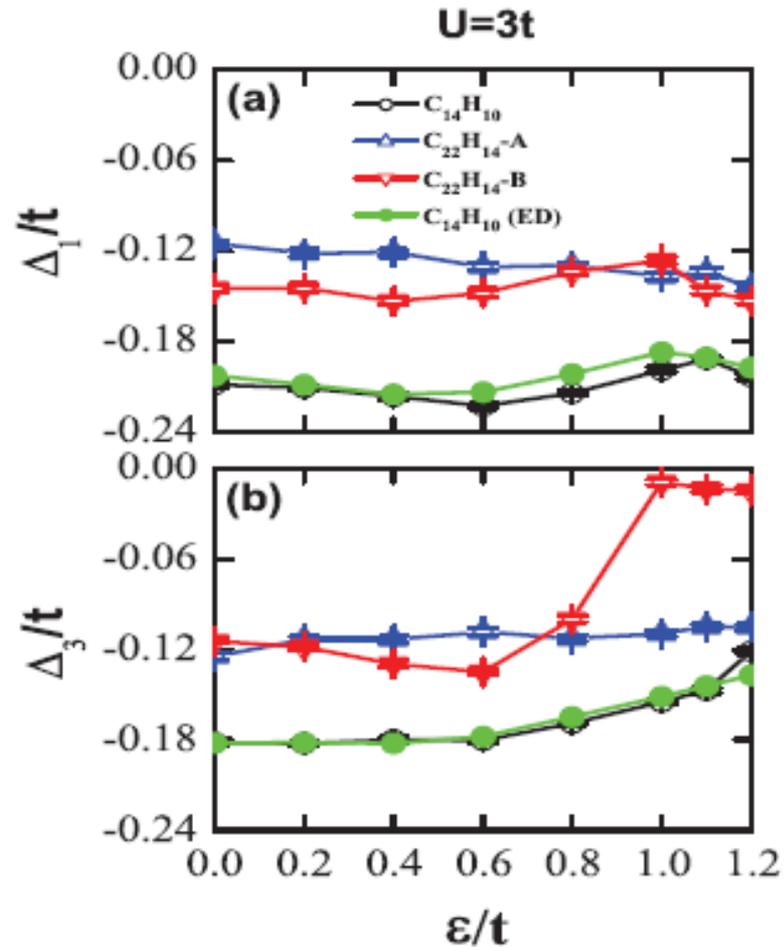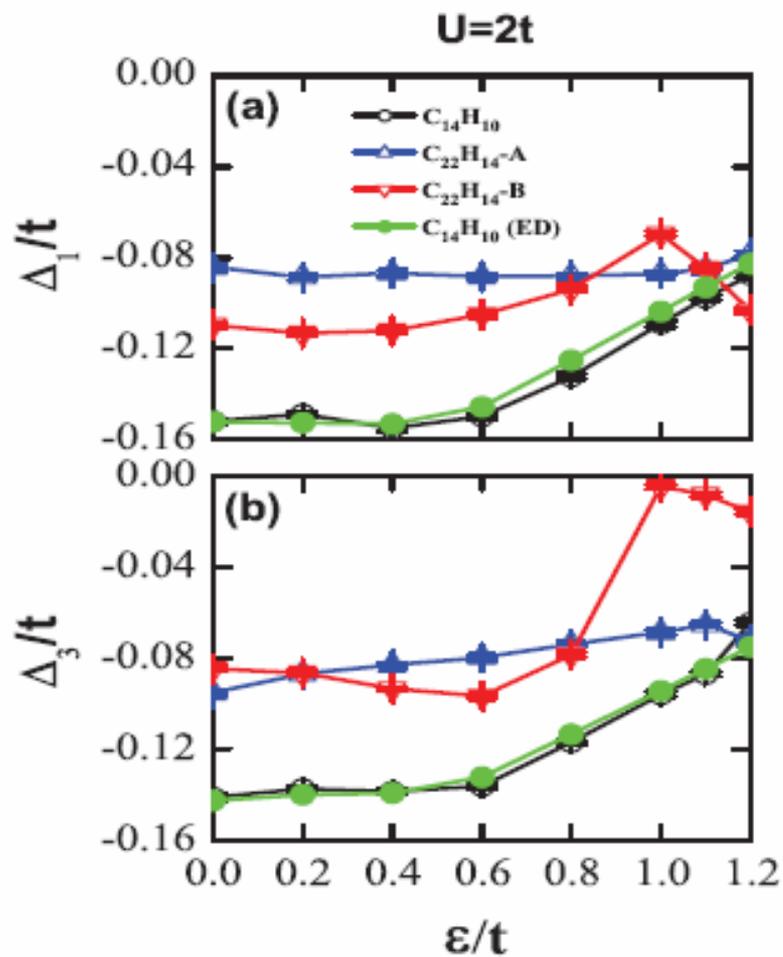


$\Delta_i$ is always negative => hardly to form Cooper pairs.

89

# Pair Binding Energy $\Delta_i$ for $C_{30}H_{18}$



Binding Energy ($C_{30}H_{18}$)

(a) $\Delta_1/t$, U=2t, U=3t

(b) $\Delta_3/t$

$\varepsilon/t$
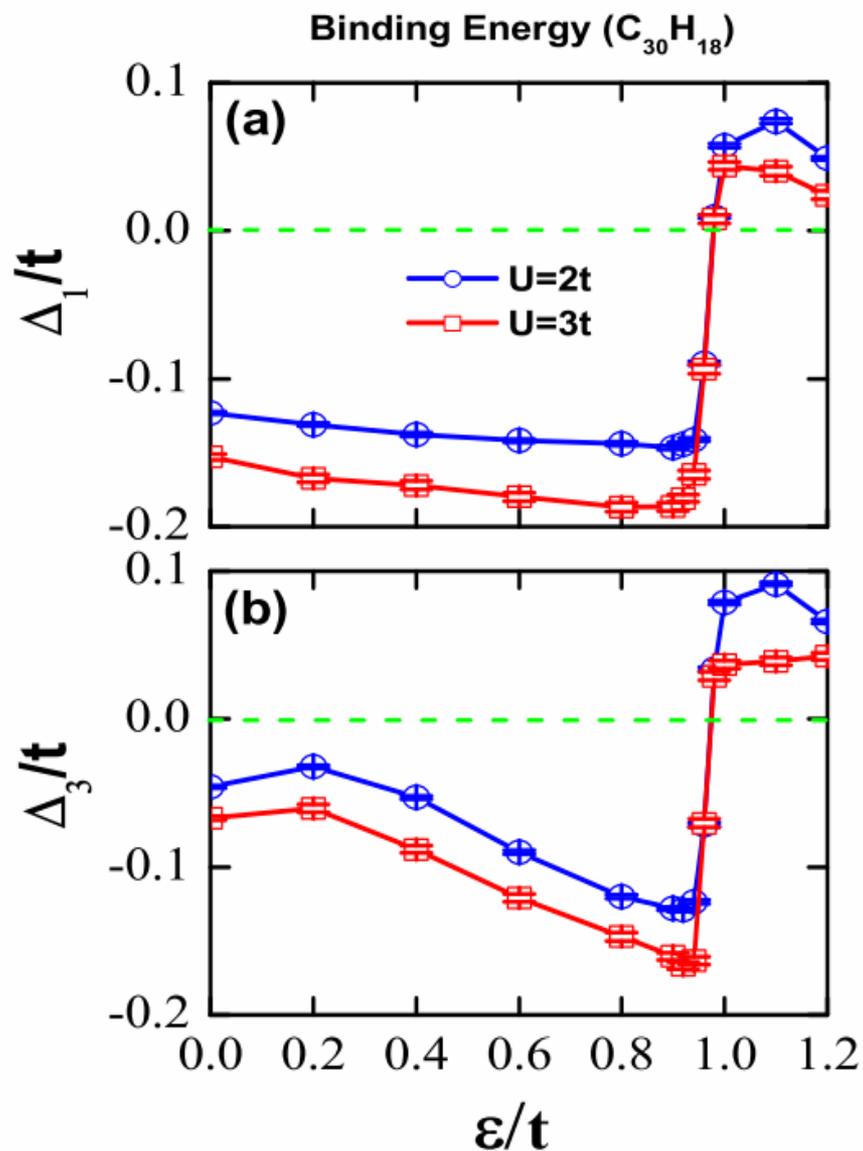
- **Pair binding energy is positive for $\varepsilon > 1.0t$.**

- **Electron attraction through charge disproportionation:**

$$1+1 \rightarrow 0+2 \text{ or } 3+3 \rightarrow 2+4$$



$E_L \quad > \quad E_R$

90
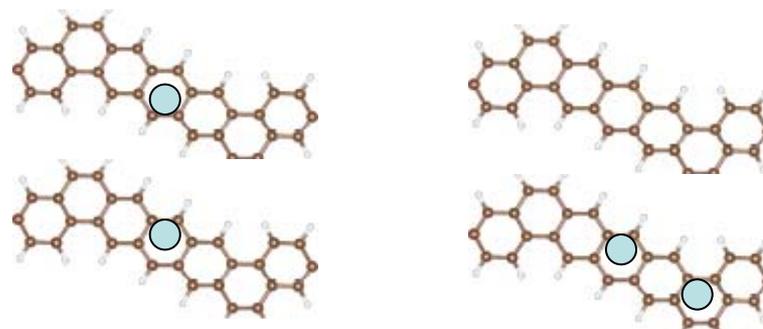
# Brief Summary

- 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.

- Parameters are consistent with DFT results.

# Summary and Discussions

- We searched for possible structures of Polycyclic Aromatic Hydrocarbon. More systematic works are needed, including pressure effects.

- 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.

# 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]