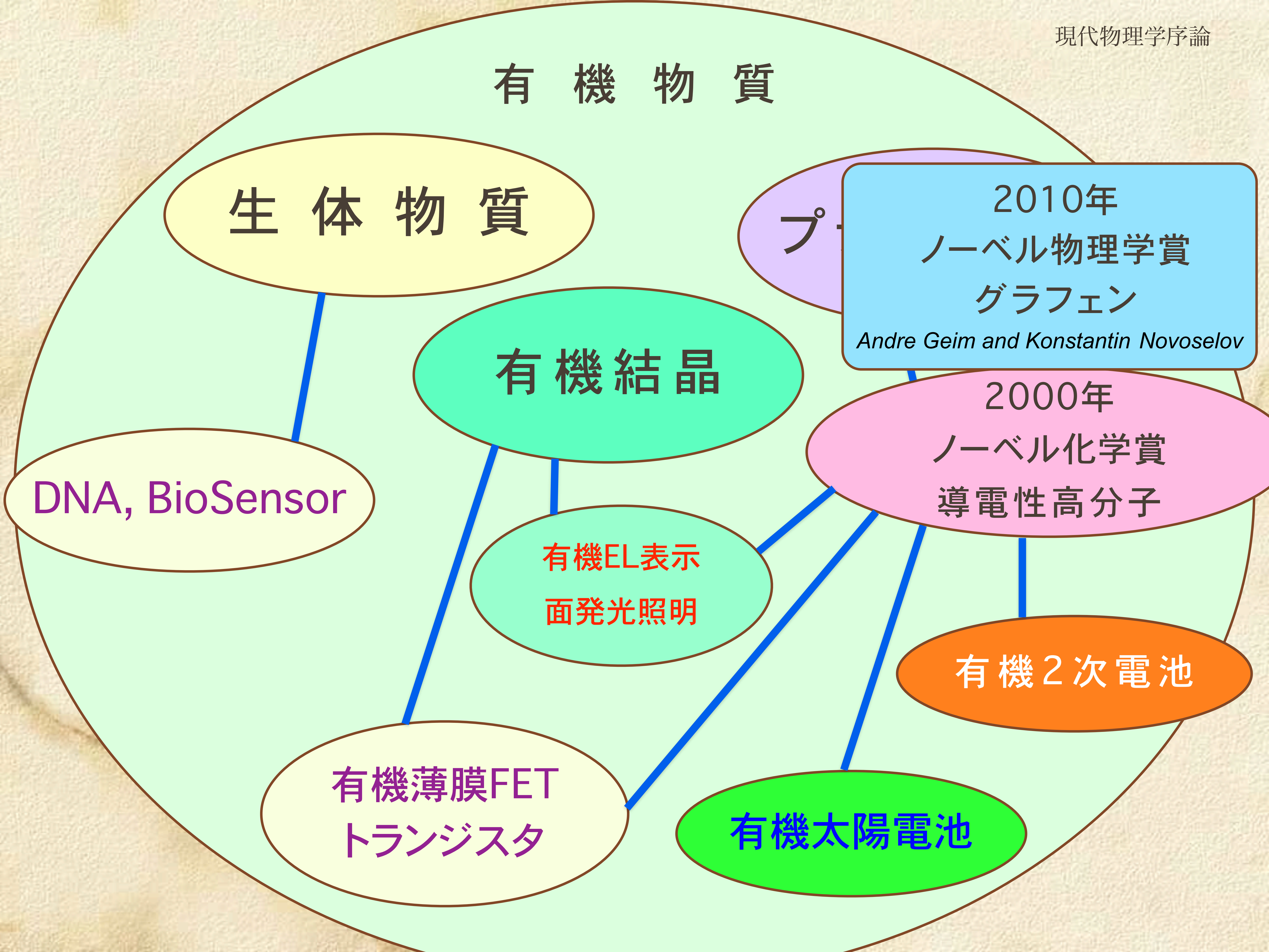
現代物理学序論

有機物質の基礎と応用

ESR物性：溝口憲治



有機物質

生体物質

DNA, BioSensor

有機結晶

プ

2010年
ノーベル物理学賞
グラフェン
Andre Geim and Konstantin Novoselov

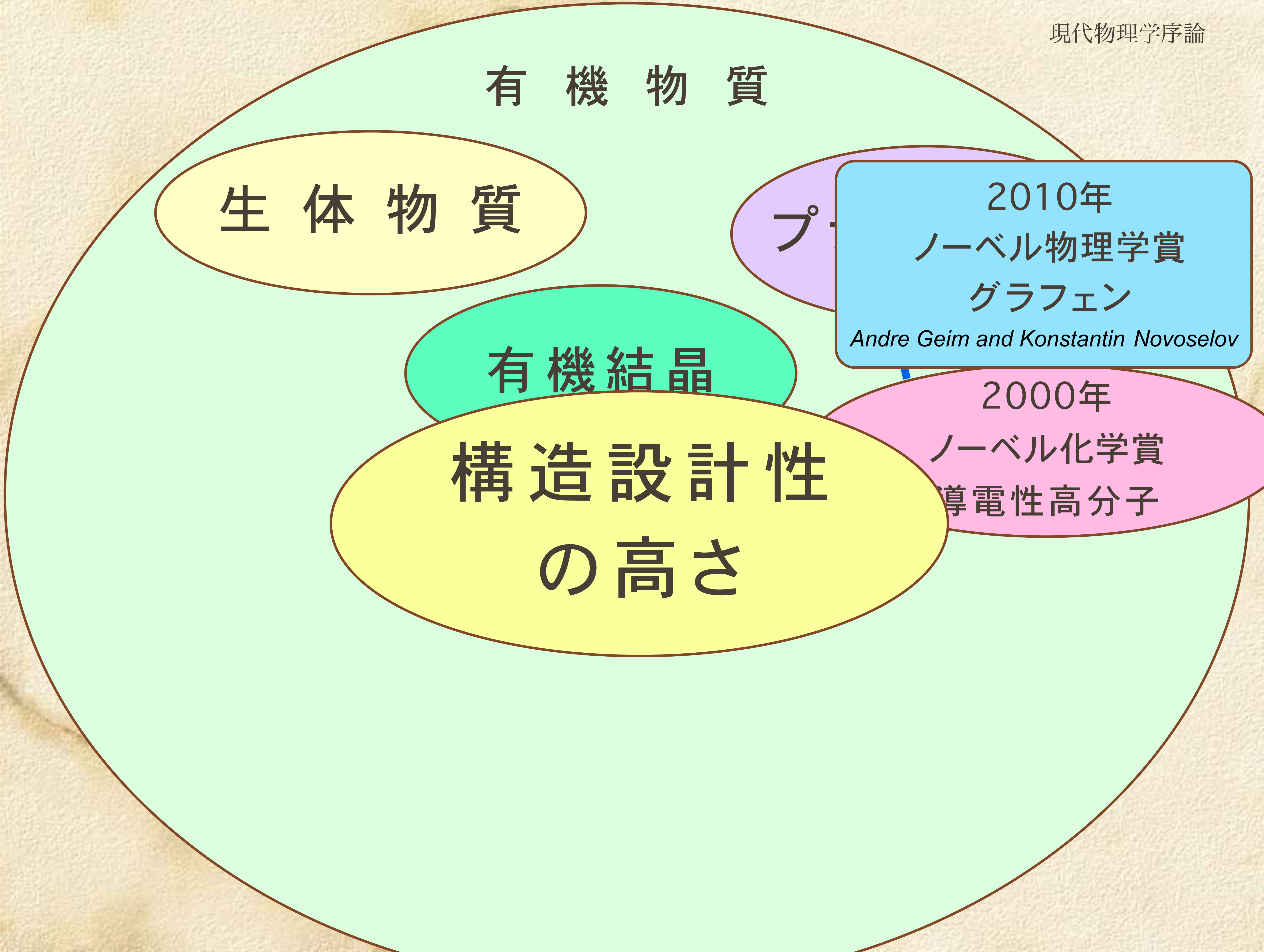
2000年
ノーベル化学賞
導電性高分子

有機EL表示
面発光照明

有機2次電池

有機薄膜FET
トランジスタ

有機太陽電池



有機物質

生体物質

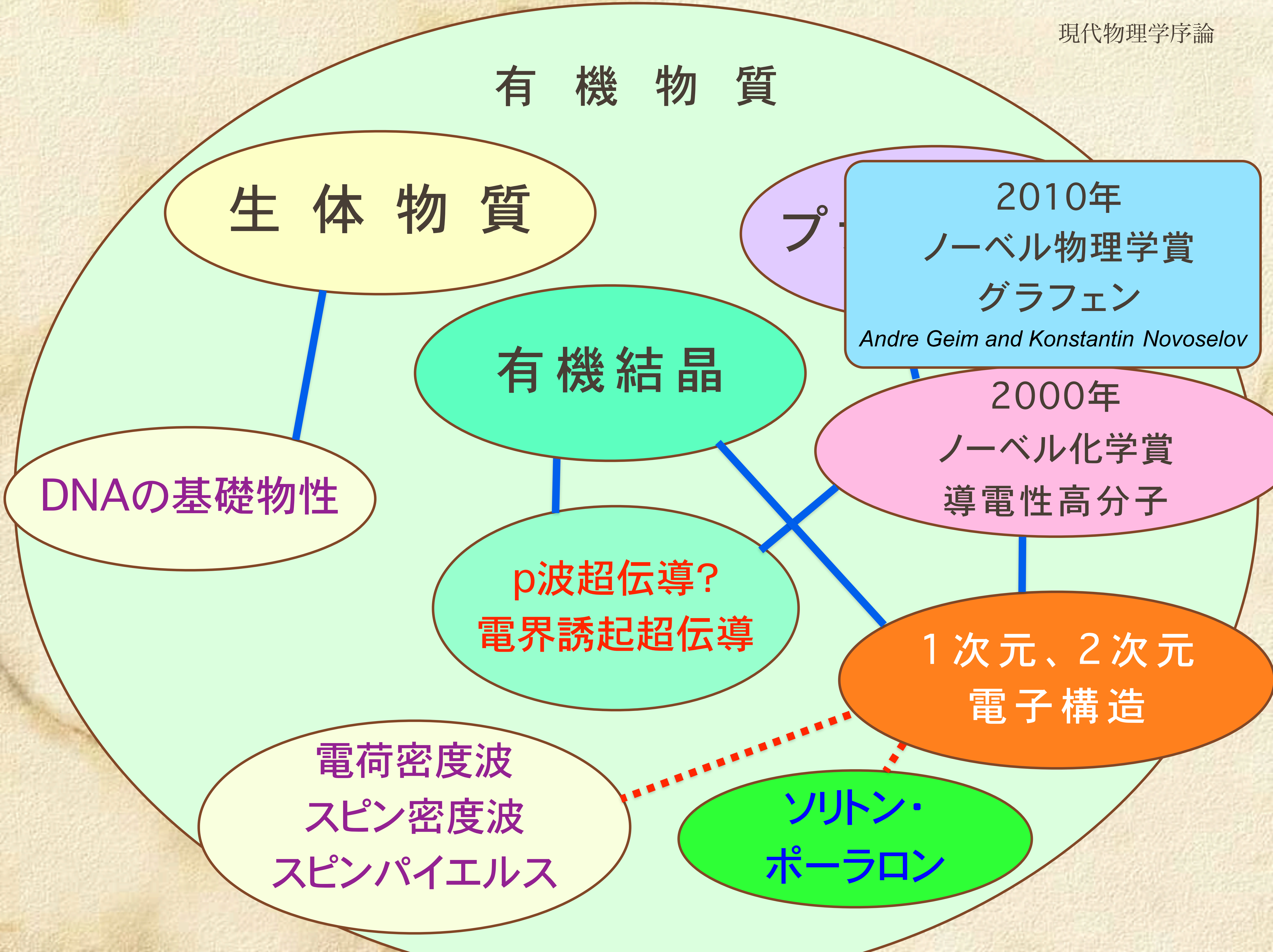
プ

2010年
ノーベル物理学賞
グラフェン
Andre Geim and Konstantin Novoselov

有機結晶

2000年
ノーベル化学賞
導電性高分子

構造設計性
の高さ



有 機 物 質

生 体 物 質

プ

2010年
ノーベル物理学賞
グラフェン
Andre Geim and Konstantin Novoselov

有 機 結 晶

DNAの基礎物性

2000年
ノーベル化学賞
導電性高分子

p波超伝導?
電界誘起超伝導

1 次 元、2 次 元
電 子 構 造

電荷密度波
スピン密度波
スピンパイエルス

ソリトン・
ポーラロン

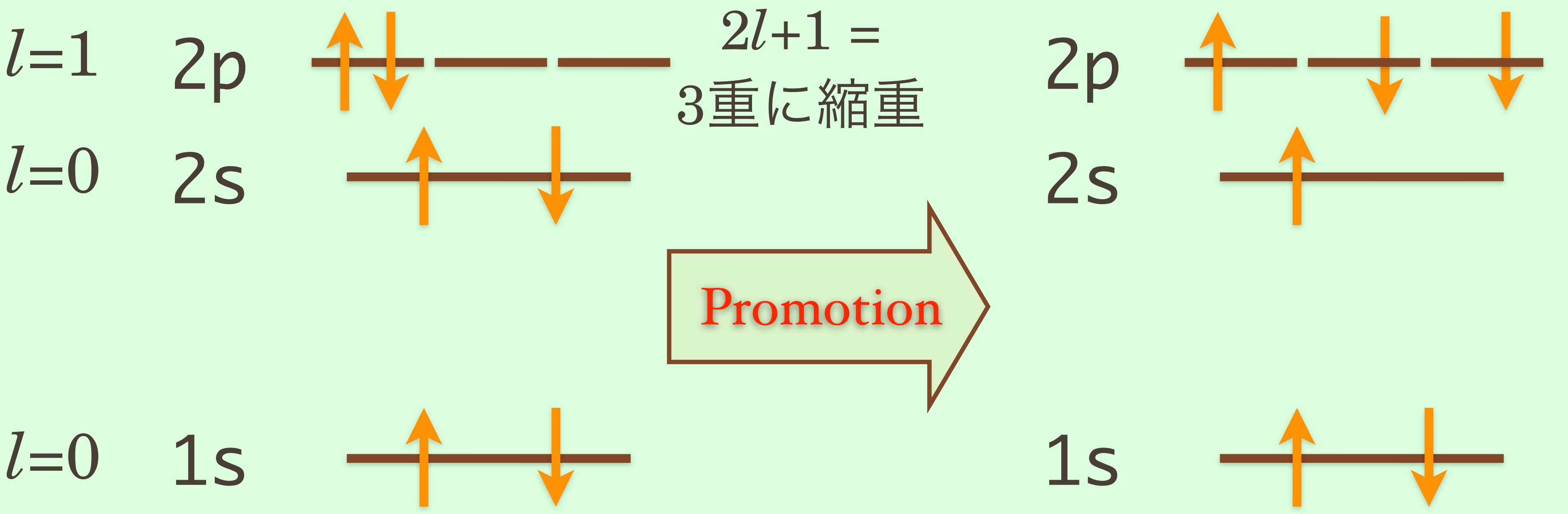
有機物質

炭素の世界

高い結合の自由度

atomic ^{12}C

bonding ^{12}C



$l=1$ 2p

$2l+1$ =
3重に縮重

2p

$l=0$ 2s

2s

Promotion

$l=0$ 1s

1s

$(1s)^2(2s)^2(2p)^2$

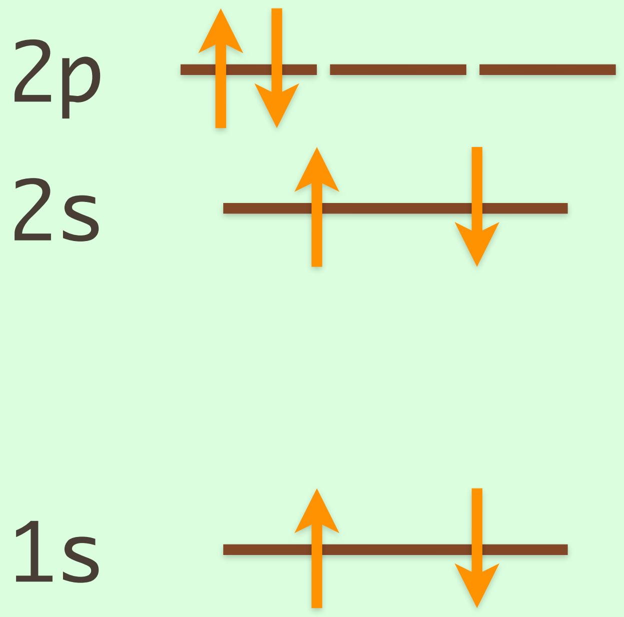
$(1s)^2(2s)^1(2p)^3$

有機物質

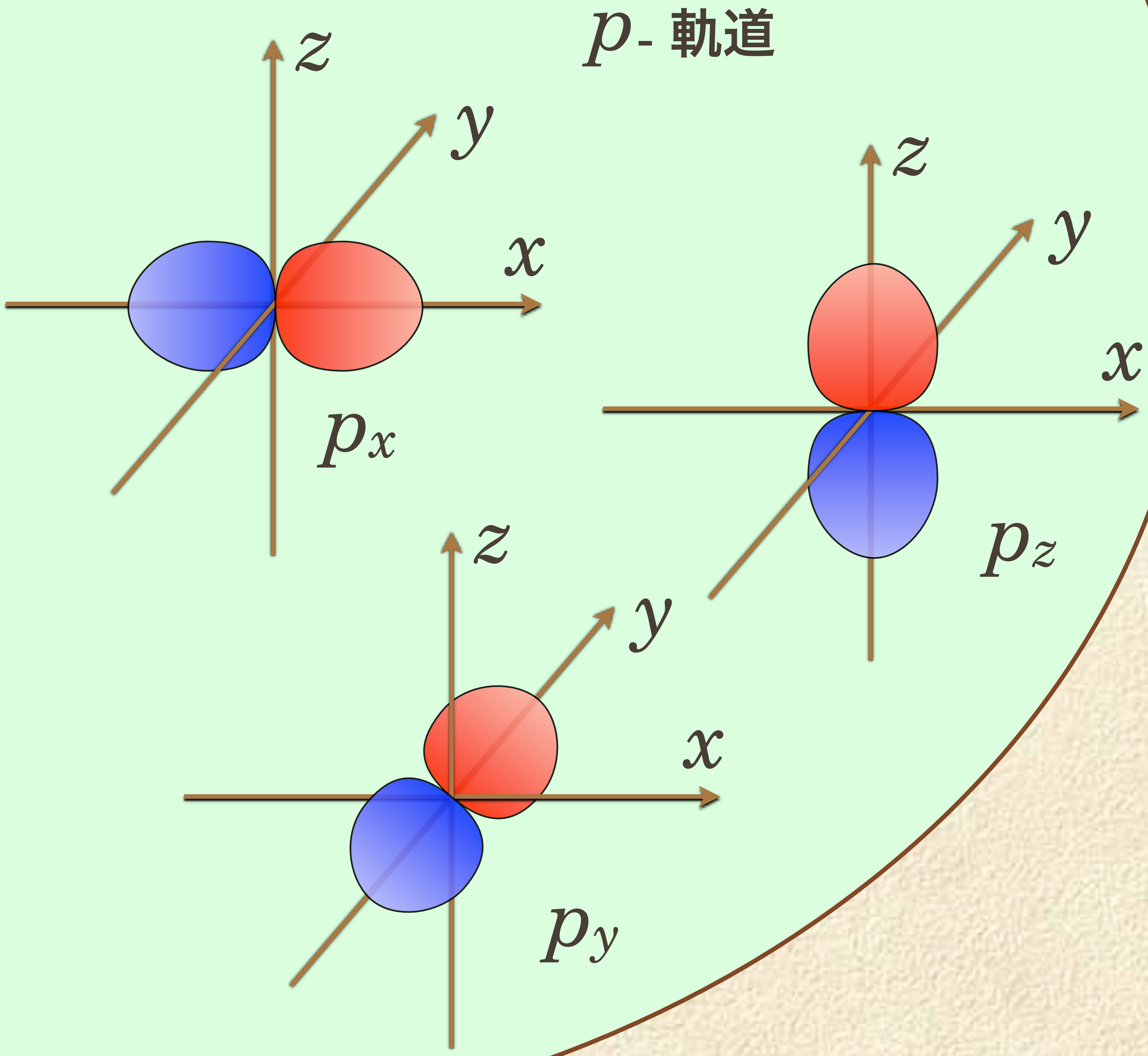
炭素の世界

高い結合の自由度

atomic $^{12}\mathrm{C}$



$(1s)^2(2s)^2(2p)^2$



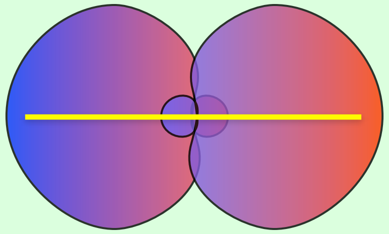
有機物質

炭素の世界

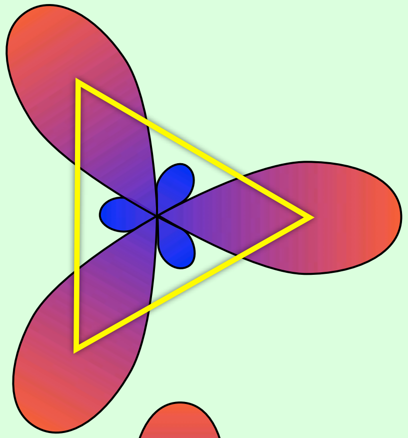
有機構造を形作る

混成 σ 軌道

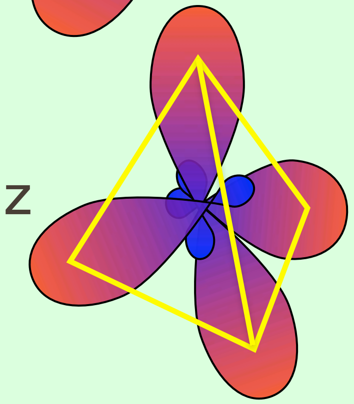
sp = $s \pm p_x$



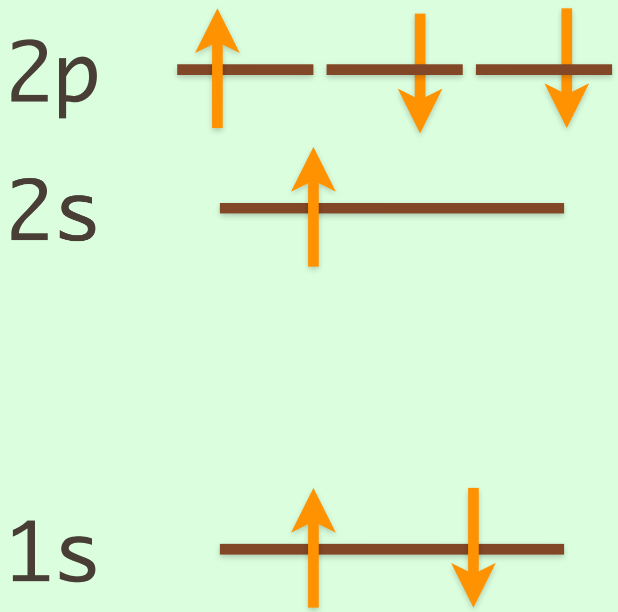
sp² = $s \pm p_x \pm p_y$



sp³ = $s \pm p_x \pm p_y \pm p_z$

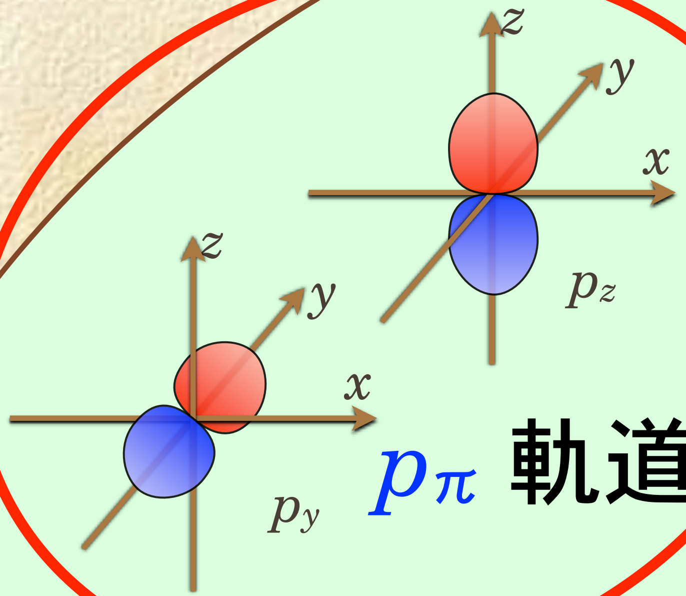


bonding ^{12}C



$(1s)^2(2s)^1(2p)^3$

有機物質



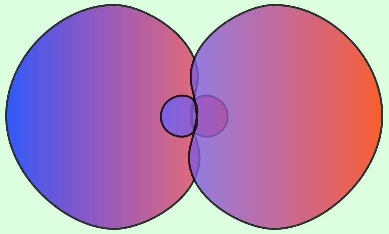
p_π 軌道

炭素の世界

有機構造を形作る

sp-混成 σ 軌道

= $s \pm p_x$

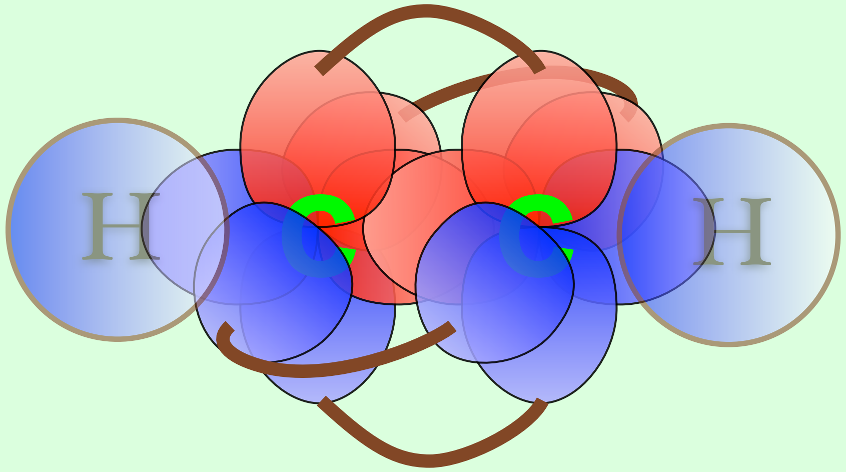


$$\phi(1) = \frac{1}{\sqrt{2}}(s + p_x)$$

$$\phi(2) = \frac{1}{\sqrt{2}}(s - p_x)$$

例: アセチレンガス

C_2H_2



$\sigma + \pi_z + \pi_x$

の3重結合

有機物質

炭素の世界

有機構造を形作る

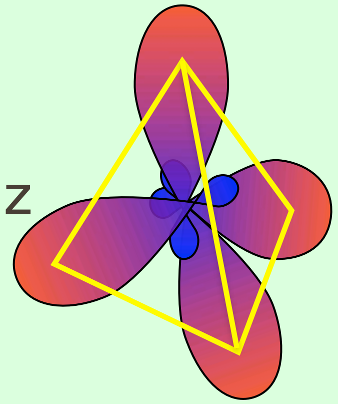
sp^3-混成軌道

-(3-4) eV/bond

lowering by **-(12-16) eV**
for 4 bonds

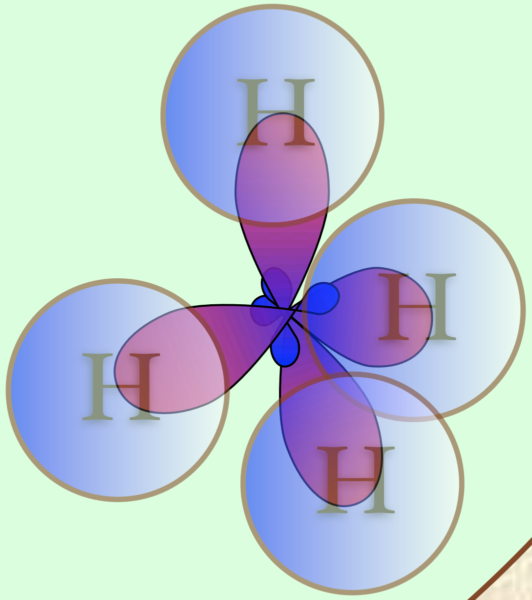
→ 強固な結合
高融点
高硬度

$= s \pm p_x \pm p_y \pm p_z$



$$\begin{aligned}
\phi(1,1,1) &= c_1 s + c_2(p_x + p_y + p_z) \\
\phi(1,-1,-1) &= c_1 s + c_2(p_x - p_y - p_z) \\
\phi(-1,1,-1) &= c_1 s + c_2(-p_x + p_y - p_z) \\
\phi(-1,-1,1) &= c_1 s + c_2(-p_x - p_y + p_z)
\end{aligned}$$

例: **メタン**



ダイアモンド
シリコン
ゲルマニウム
GaAs
等々

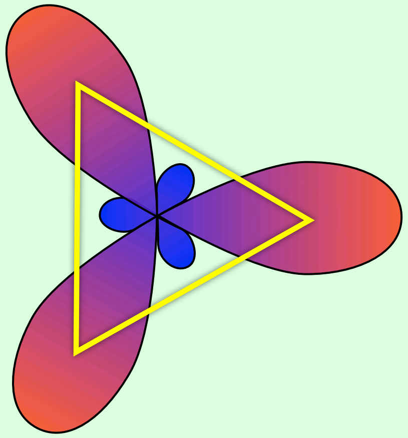
有機物質

炭素の世界

有機構造を形作る

sp^2-混成軌道

$= s \pm p_x \pm p_y$



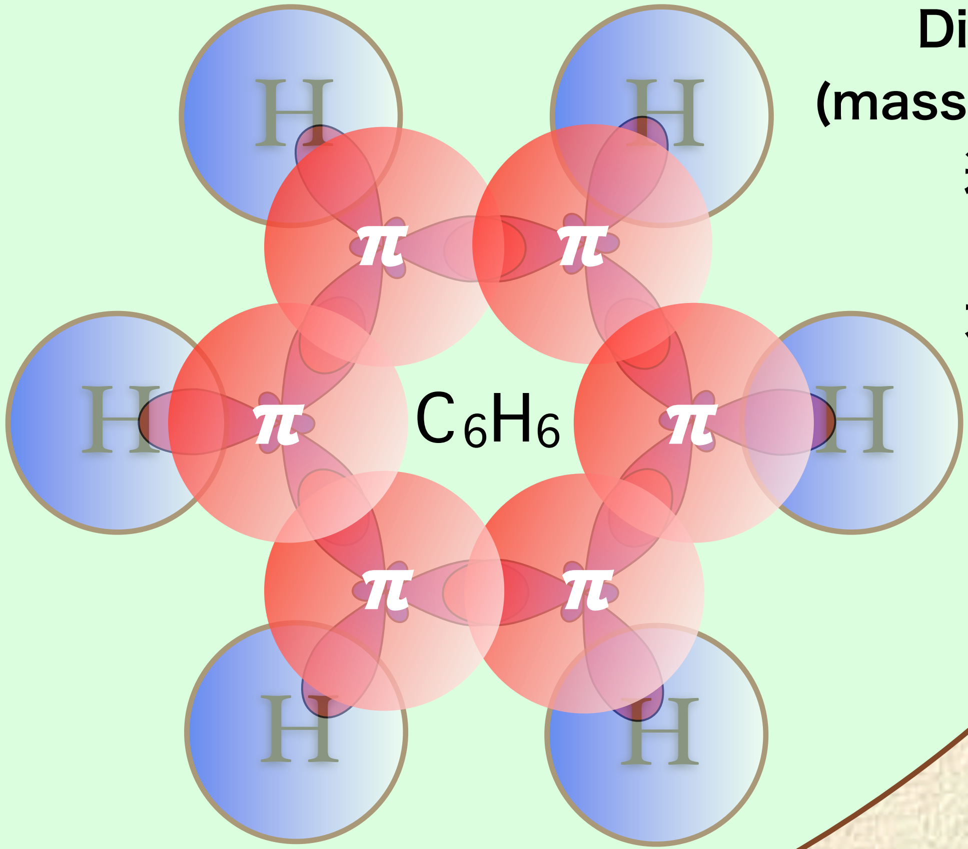
$$\phi(1) = \frac{1}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_x$$

$$\phi(2) = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$\phi(3) = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y$$

これを**2次元平面**で繋ぐと

=> **graphene**



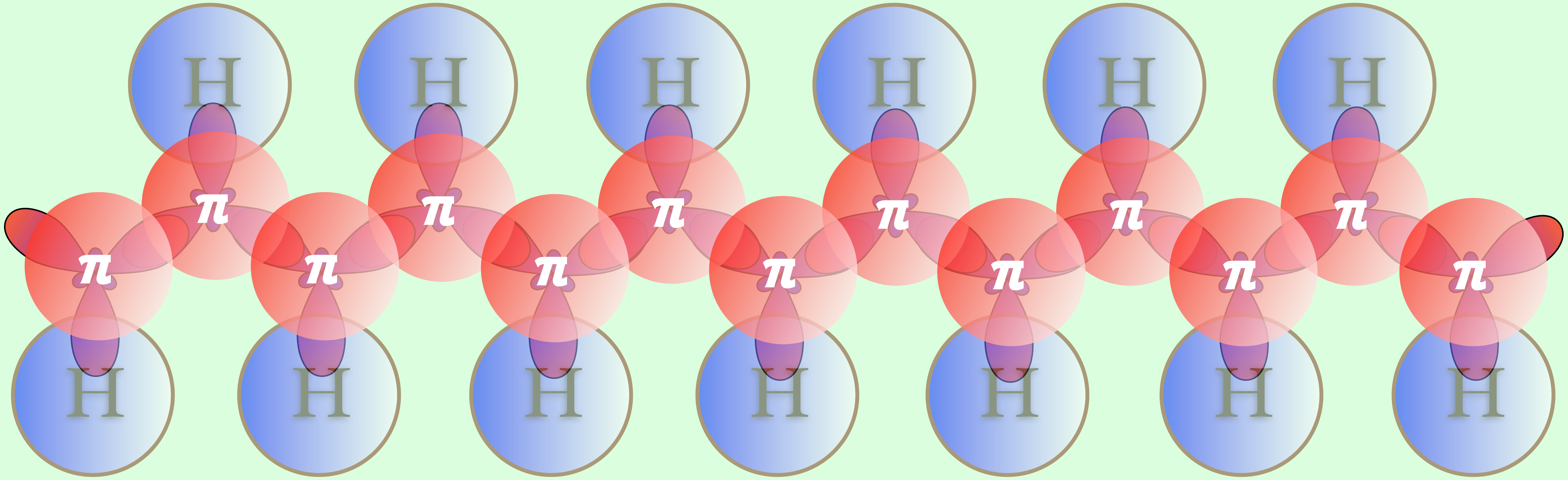
Dirac Cone
(massless fermion)
透明電極
FET
太陽電池

有機物質

導電性高分子

p_π-電子の活躍

→ 電気伝導性



ポリアセチレン

$(CH)_x$ + AsF_6^- → ノーベル賞

10月11日 白川英樹 筑波大学名誉教授
ノーベル化学賞受賞

「伝導性ポリマーの発見と開発」の業績

Dr. Heeger (Prof. of physics at the University of California, Santa Barbara), Dr. MacDiarmid (Prof. of chemistry at the University of Pennsylvania)

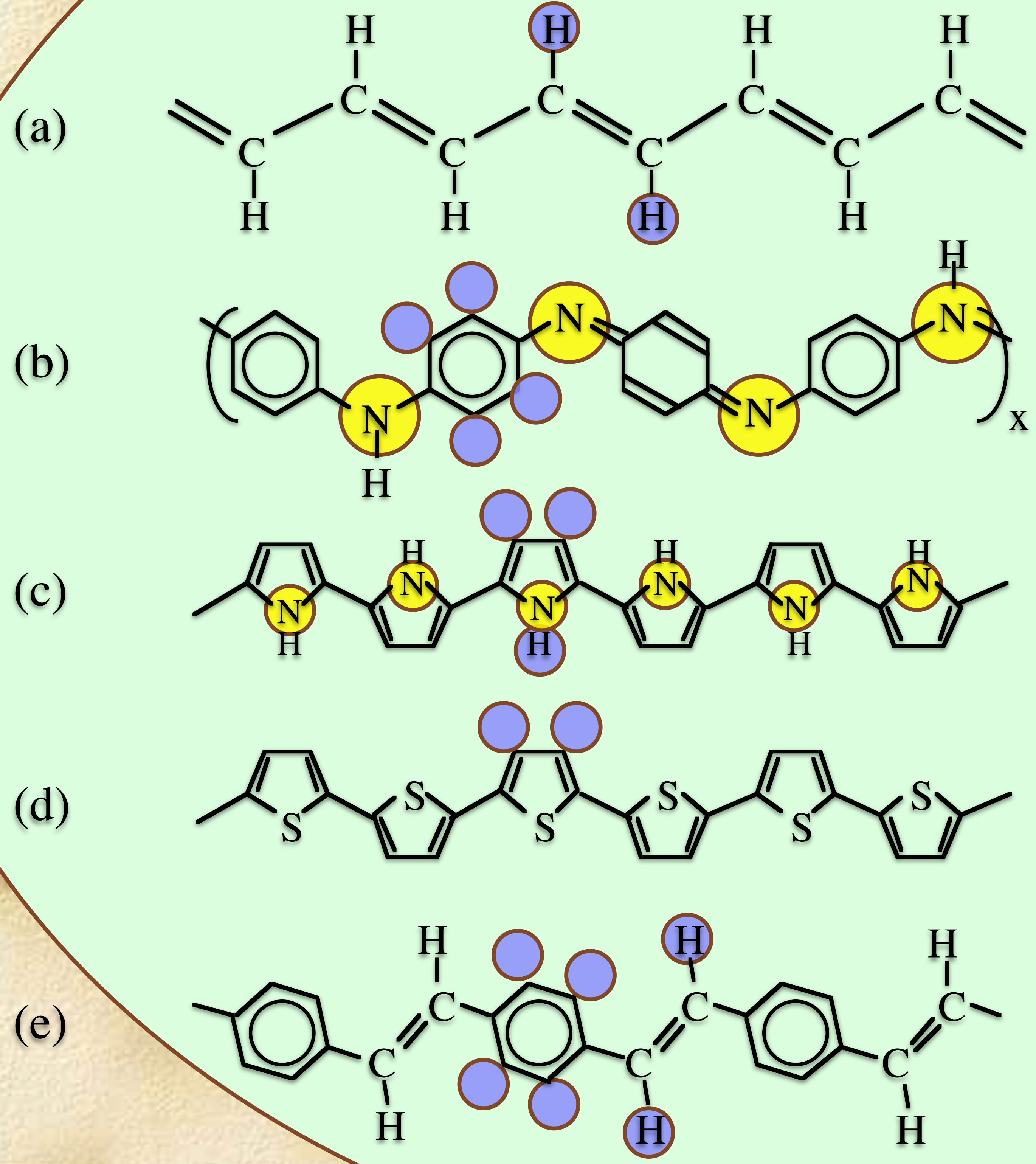
PHOTO: ROLAND S. LUNDSTROM

Alan G. MacDiarmid	Hideki Shirakawa	Alan J. Heeger
Professor at the University of Pennsylvania, Philadelphia, USA	Professor Emeritus, University of Tsukuba, Japan	Professor at the University of California at Santa Barbara, USA

有機物質

金属的な光沢：
小さなエネルギーギャップ

種々の導電性ポリマー



t-PA
trans-Polyacetylene

PANI
Polyaniline

PPY
Polypyrrole

PT
Polythiophene

PPV
Poly-p-phenylene-vinylene

生命体の材料

炭素 C

窒素 N

酸素 O

水素 H

有機物質

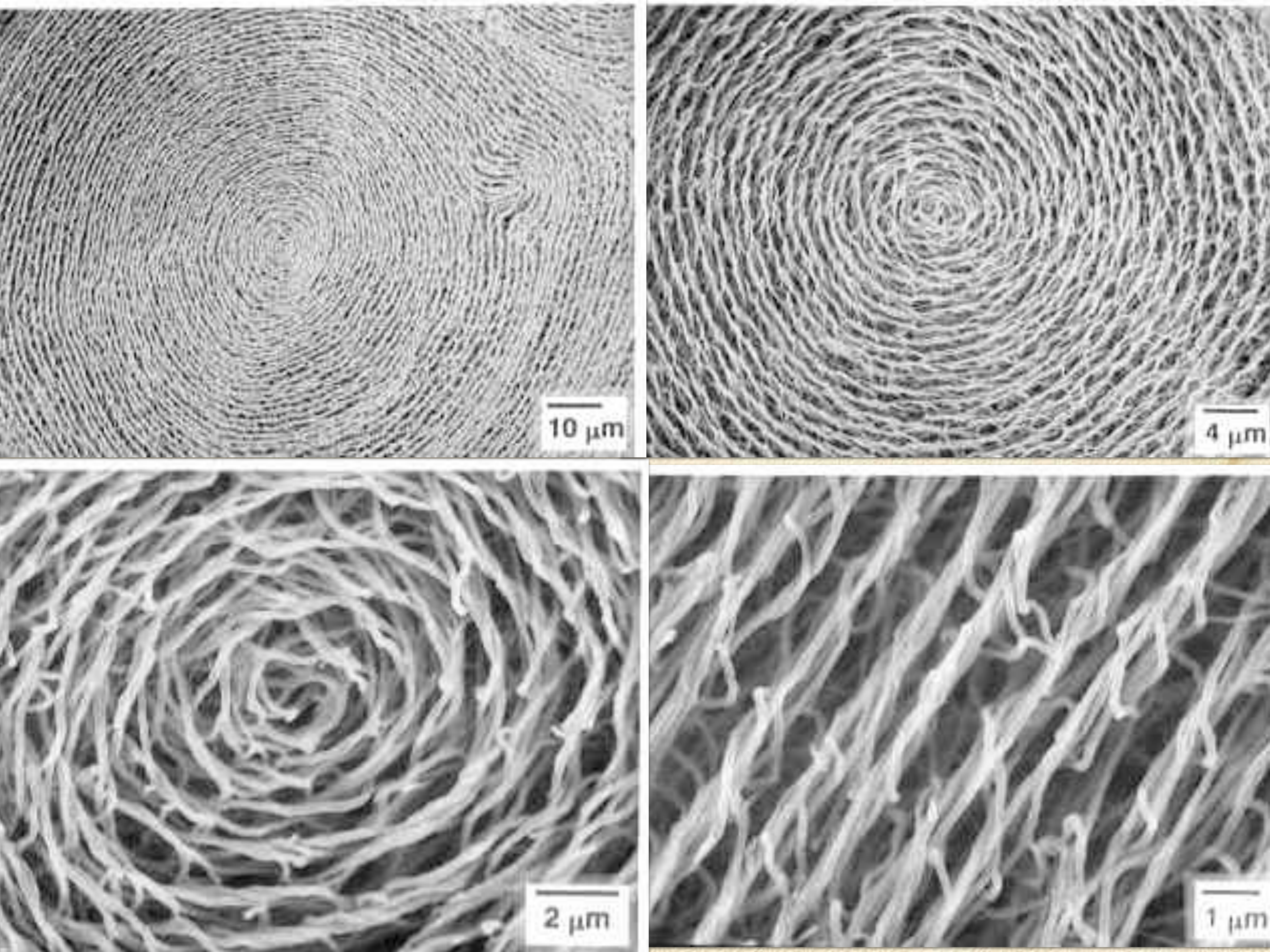
ねじれた導電性ポリマー

ヘリカルポリアセチレン

ナノコイル・分子コイル

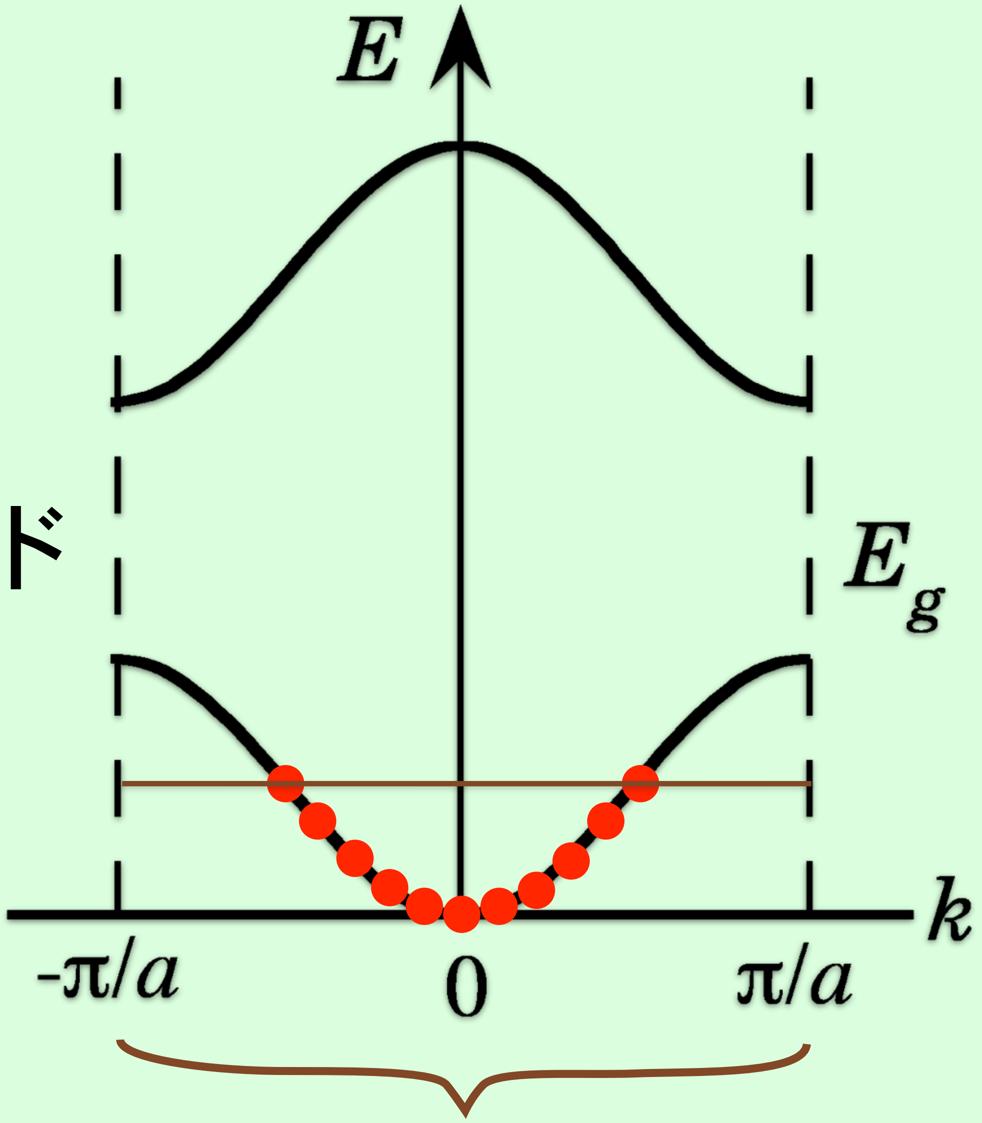
赤木和夫

（白川英樹先生の弟子）


10 μm
4 μm
2 μm
1 μm

有機物質

炭素原子 N 個に π電子が N 個



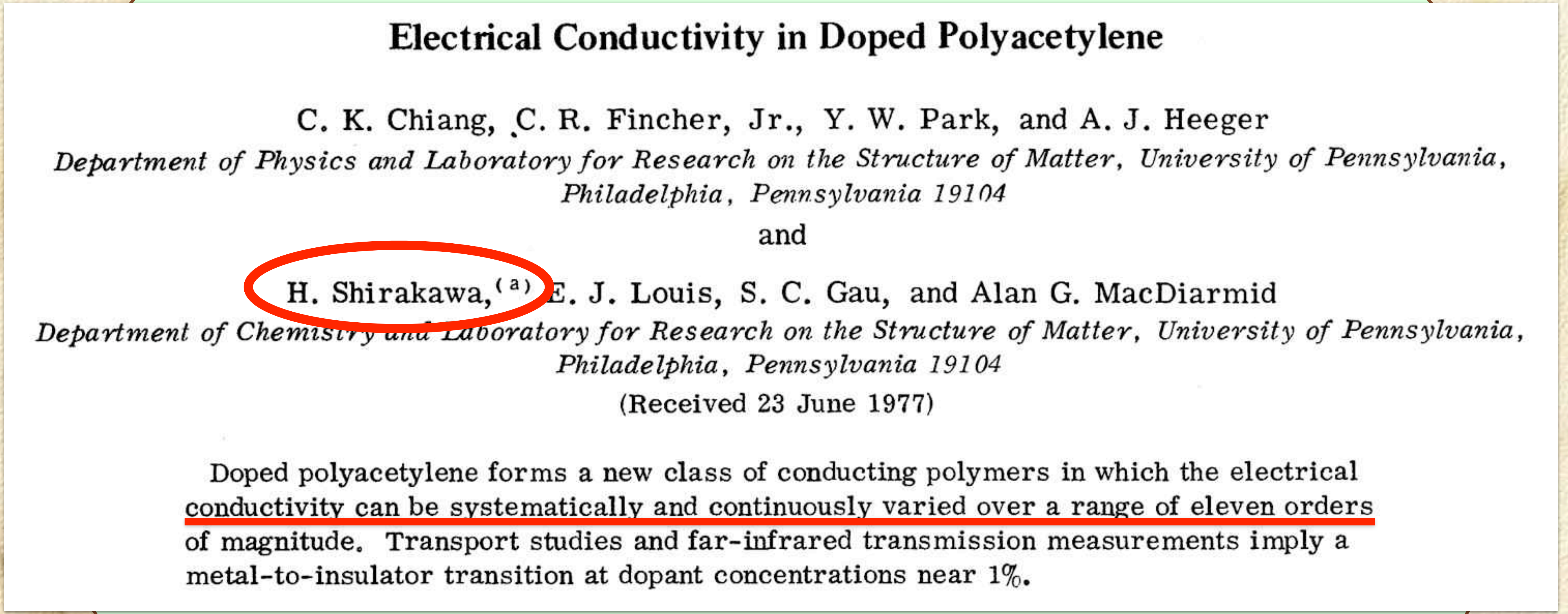
π電子バンド

金属!?

N 個の電子を収容可能

スピンの↑↓で $2N$ 個

有機物質



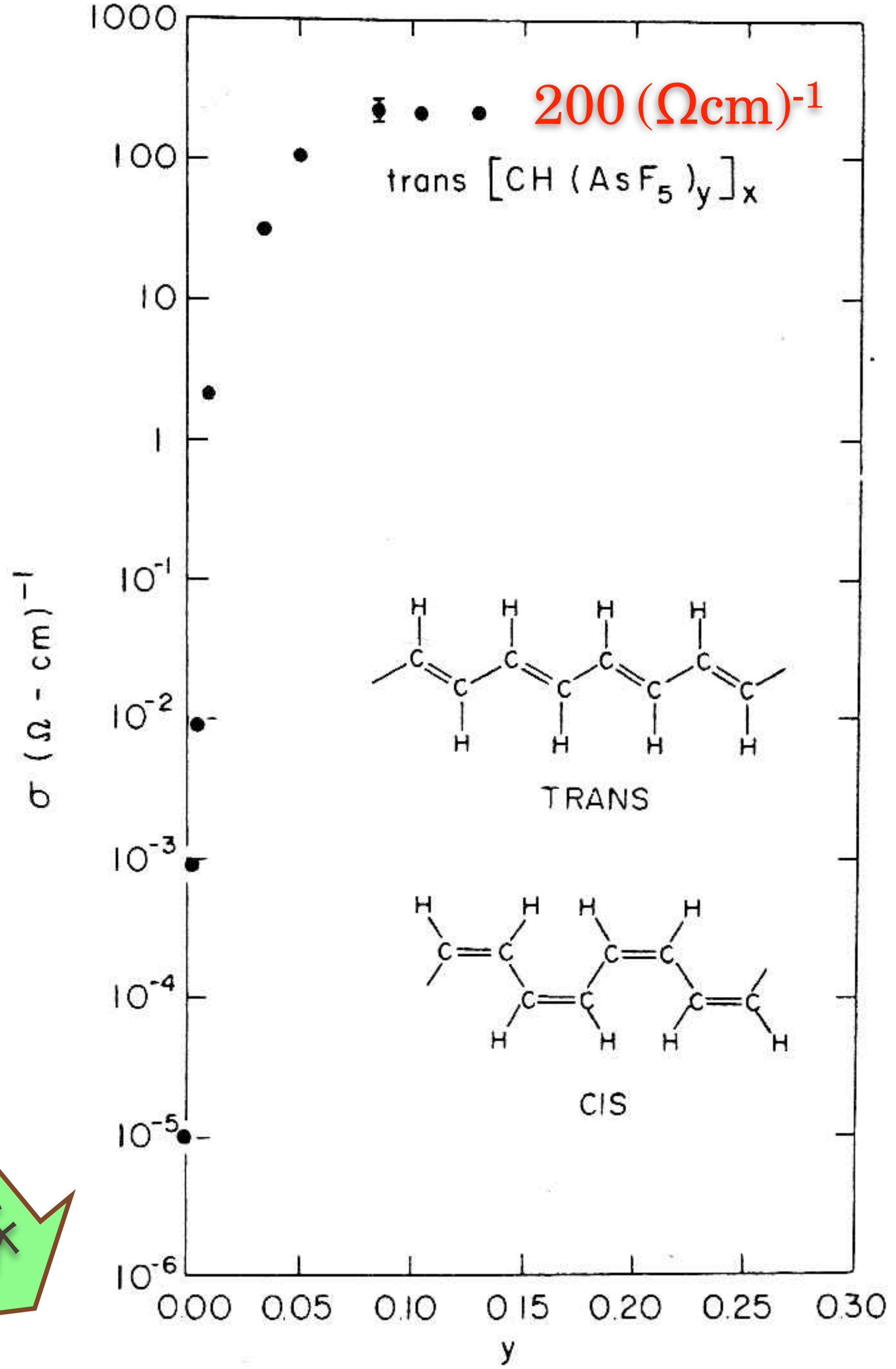
Electrical Conductivity in Doped Polyacetylene

C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
and
H. Shirakawa,(a) E. J. Louis, S. C. Gau, and Alan G. MacDiarmid
Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 23 June 1977)

Doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of eleven orders of magnitude. Transport studies and far-infrared transmission measurements imply a metal-to-insulator transition at dopant concentrations near 1%.

有機物質



$200\ (\Omega\mathrm{cm})^{-1}$

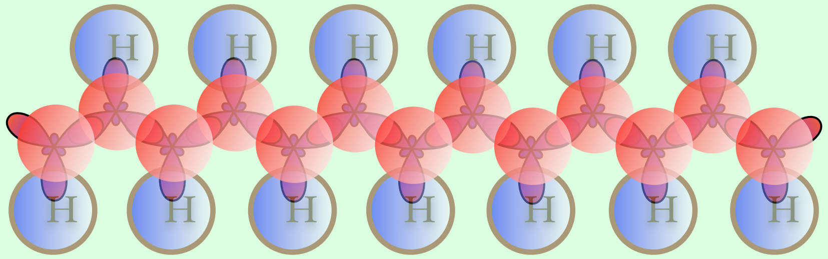
金属ではない!?

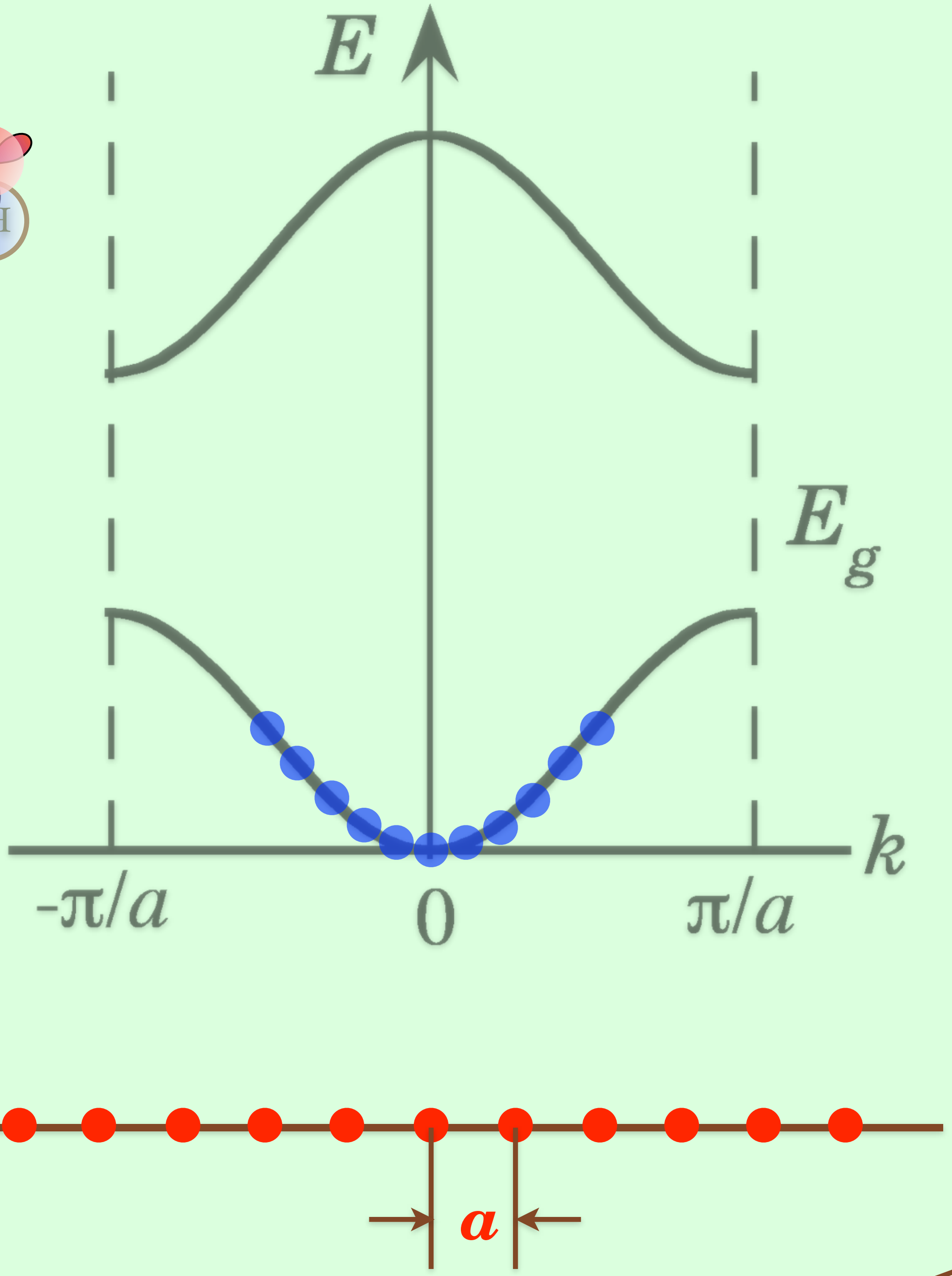
$10^{-9}\ (\Omega\mathrm{cm})^{-1}$ 半導体

FIG. 1. Electrical conductivity of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

有機物質

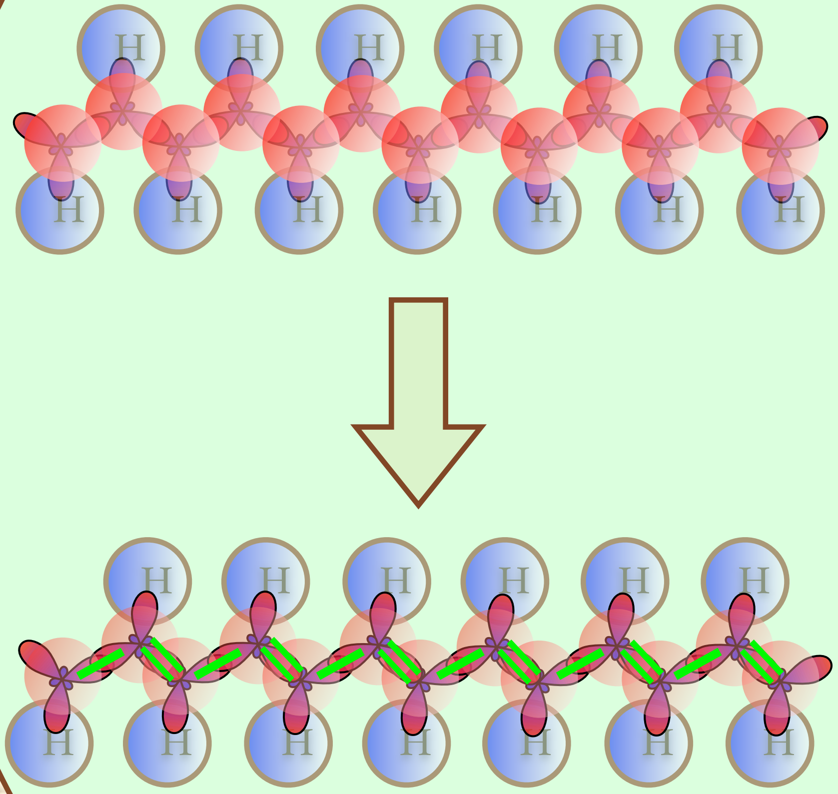
電荷密度波(CDW)
による半導体化現象

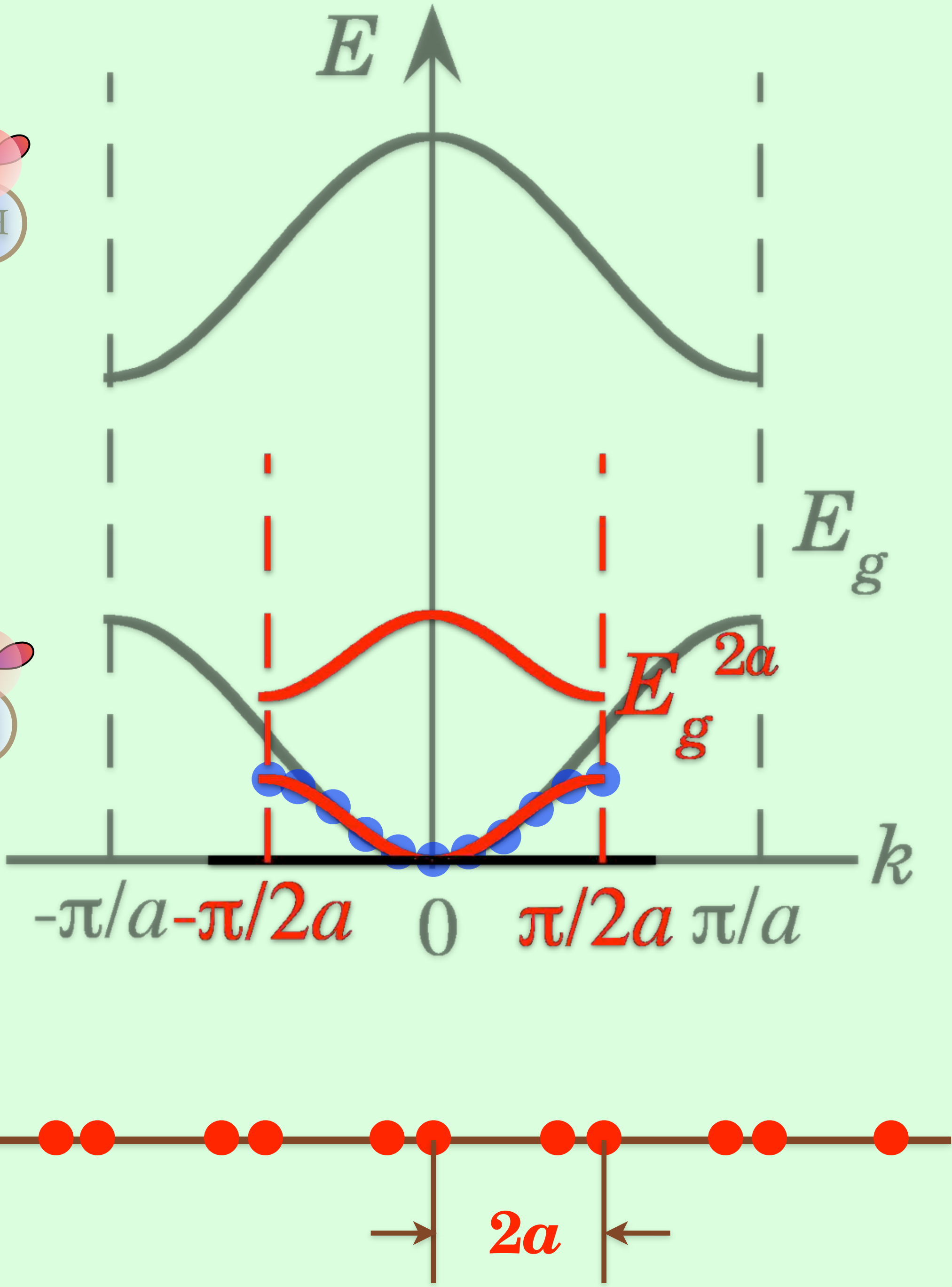




有機物質

電荷密度波(CDW)
による半導体化現象

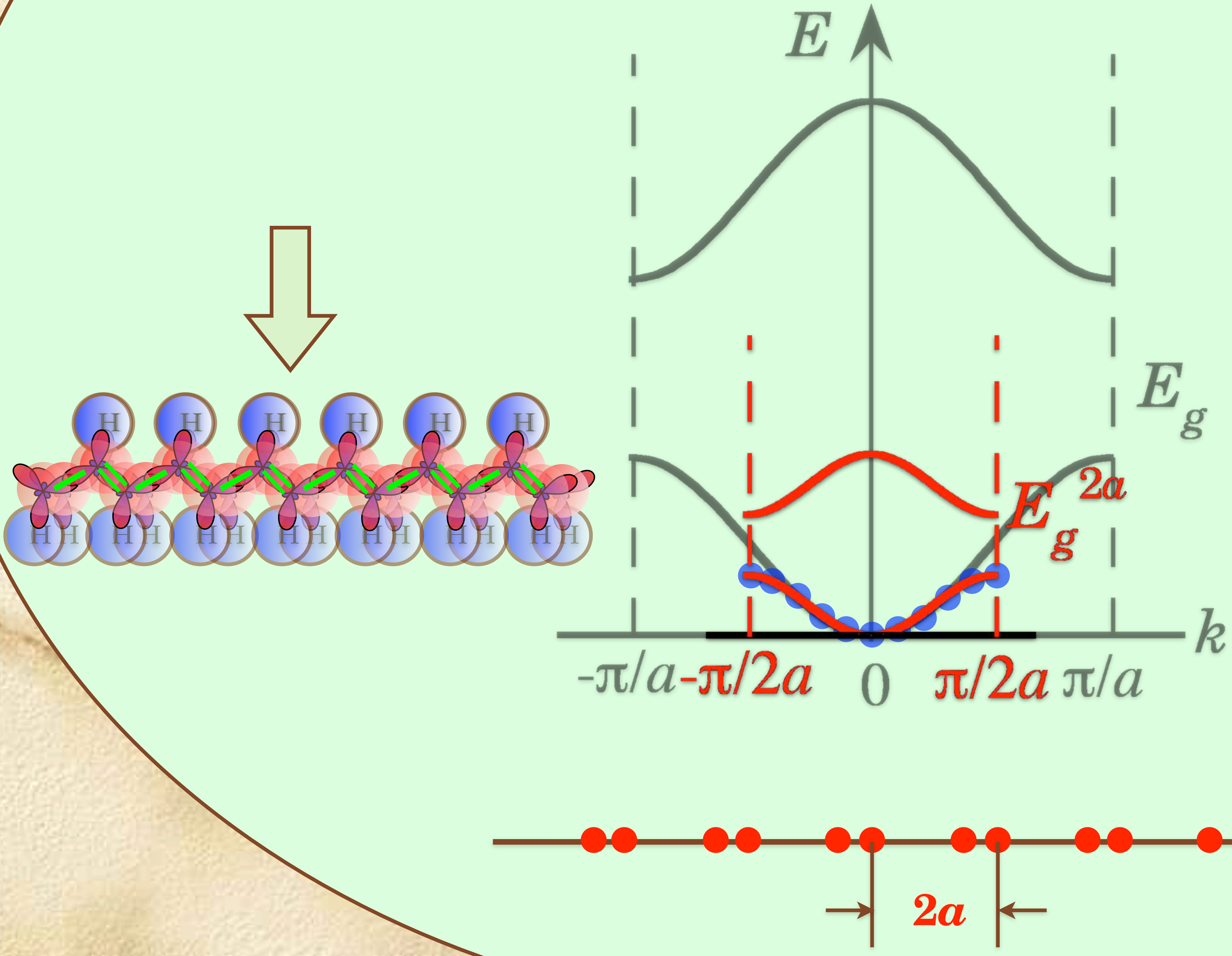




1次元電子系に
必ず起こる相転移
↓
Peierls transition
パイエルス転移

有機物質

電荷密度波(CDW)
による半導体化現象



1次元電子系に
必ず起こる相転移
↓
Peierls transition
パイエルス転移

有機物質

そこで、

半導体 => 導体

ドーピング

と

素励起

物理としての

面白さ

有機物質

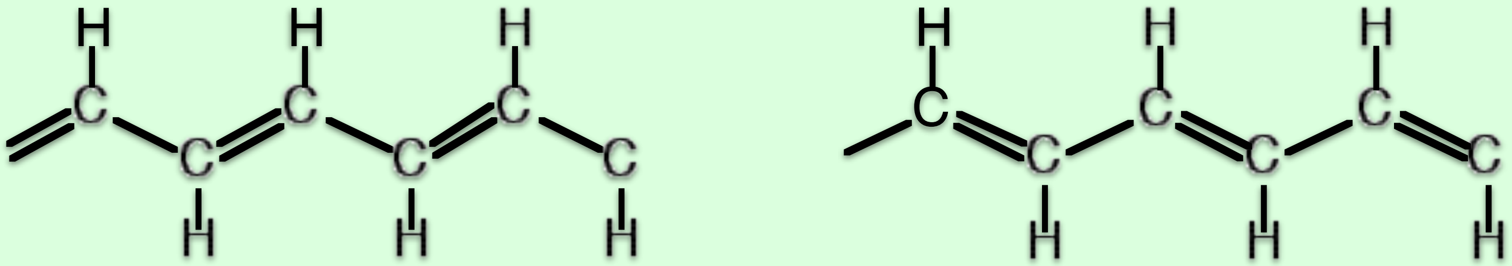
素励起

パイエルス転移: CDW状態

ソリトン・ポーラロン素励起

有機物質

エネルギーギャップ中の素励起



2つの構造のエネルギーが等しい

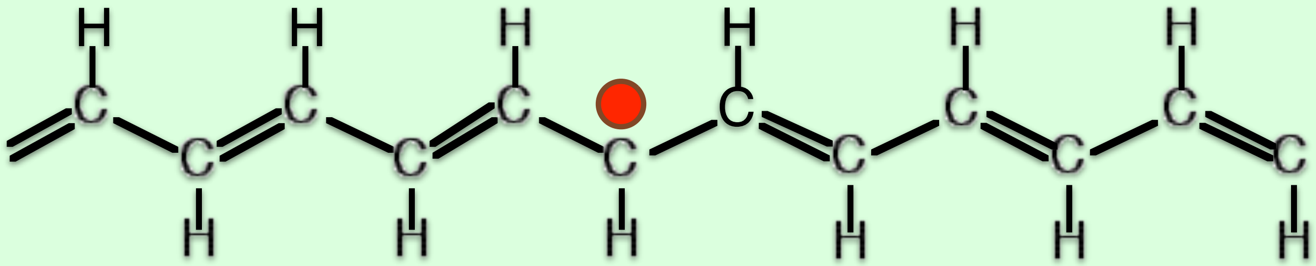
↓

縮退系

有機物質

エネルギーギャップ中の素励起

中性ソリトン



2つの構造のエネルギーが等しい

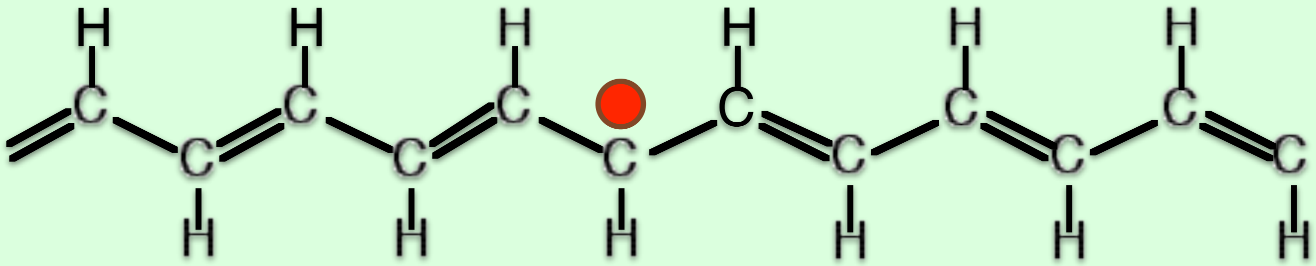
↓

縮退系

有機物質

エネルギーギャップ中の素励起

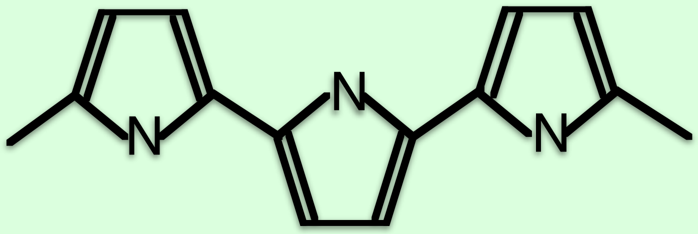
中性ソリトン



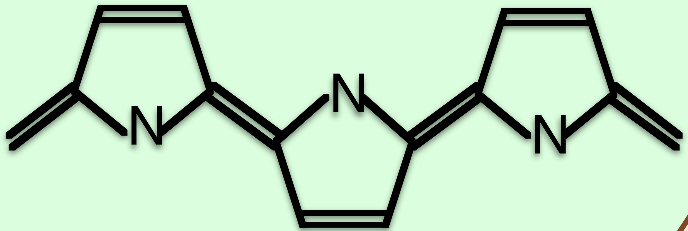
2つの構造のエネルギーが等しい

↓

縮退系



芳香族型



キノイド型

2つの構造のエネルギーが異なる

↓

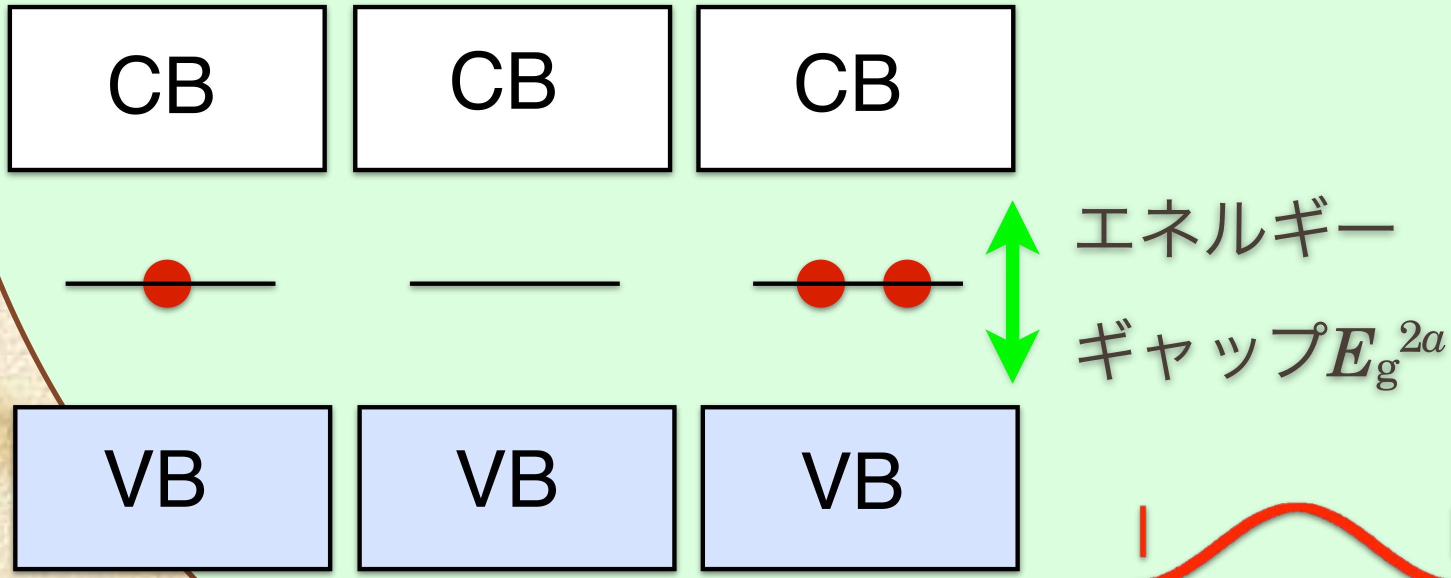
非縮退系

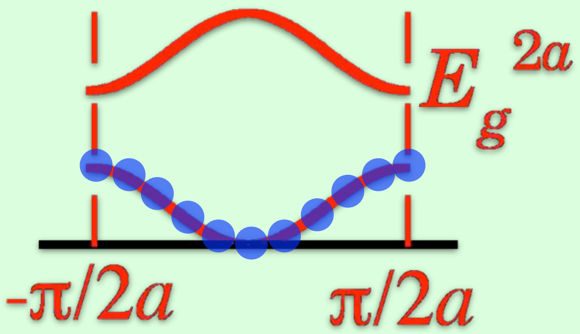
有機物質

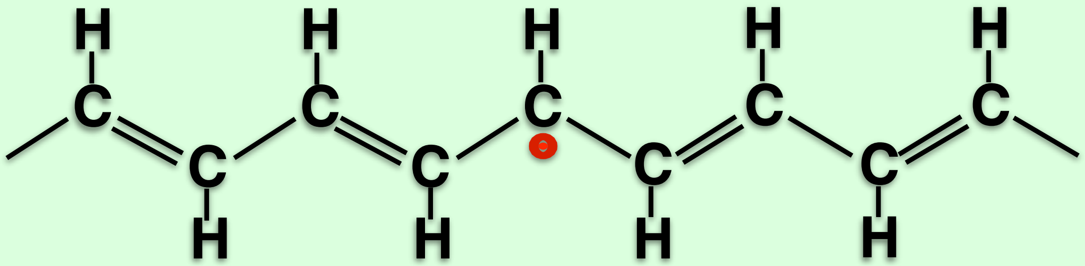
縮退系のソリトン

ソリトン

中性	正	負	
1/2	0	0	スピン
0	$+e$	$-e$	電荷







自由に動ける
結合交代の欠陥

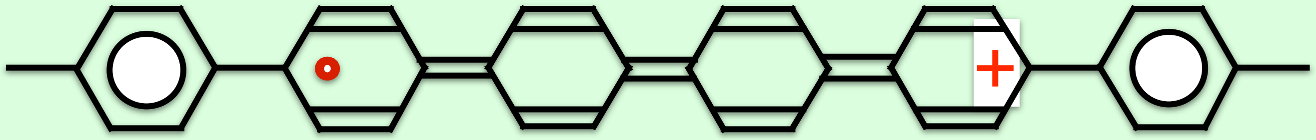
ソリトン

奇数個の炭素

有機物質

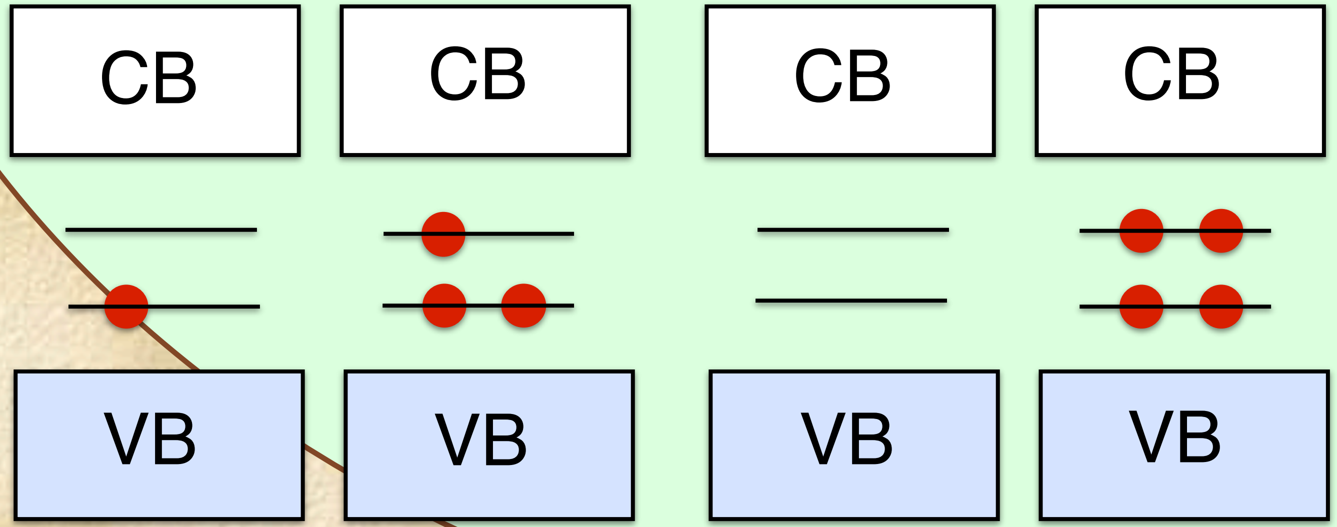
非縮退系のポーラロン

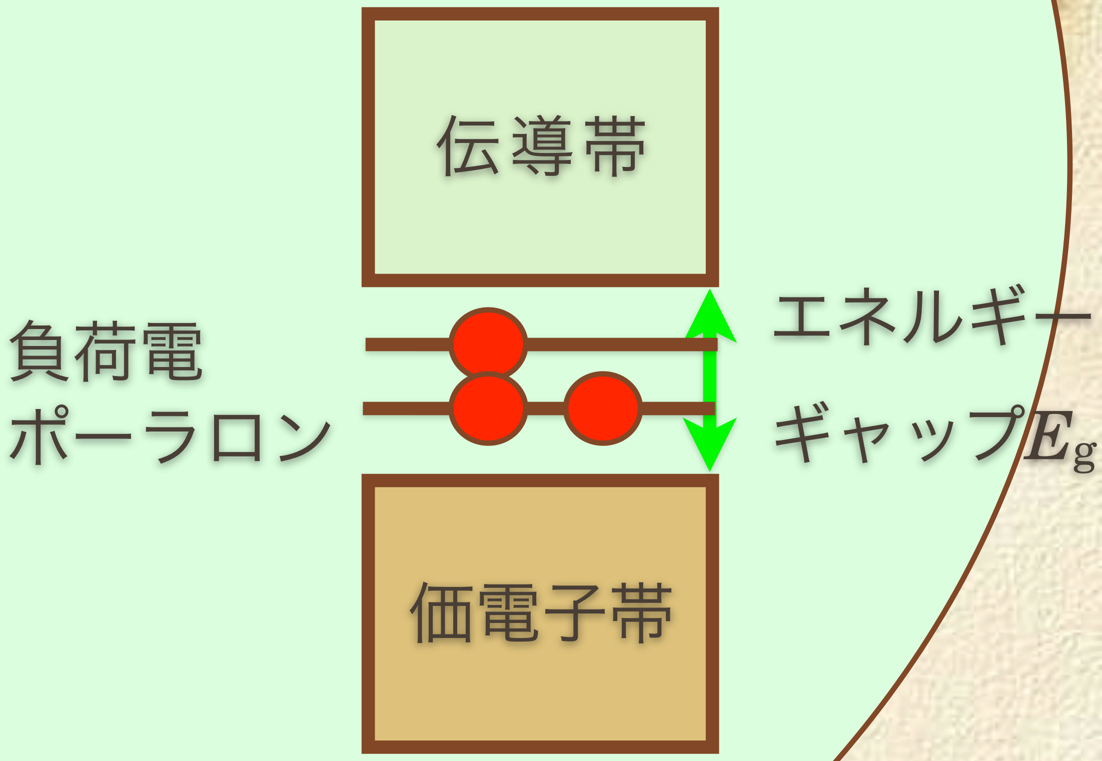
非縮退共役高分子の正ポーラロン



電子ドーピングによる
ポーラロン生成

	ポーラロン		バイポーラロン	
	正	負	正	負
スピン	1/2	1/2	0	0
電荷	$+e$	$-e$	$+2e$	$-2e$





ドーピングにより結合交代が
緩んで、ギャップが減少する

有機物質

半導体の応用素子の例

1. pn型接合ダイオード

2. 発光ダイオード

3. 太陽電池

応用としての

有用さ

有機物質

有機電界発光(EL)ディスプレー

明るい

きれい

軽い

安い（期待）

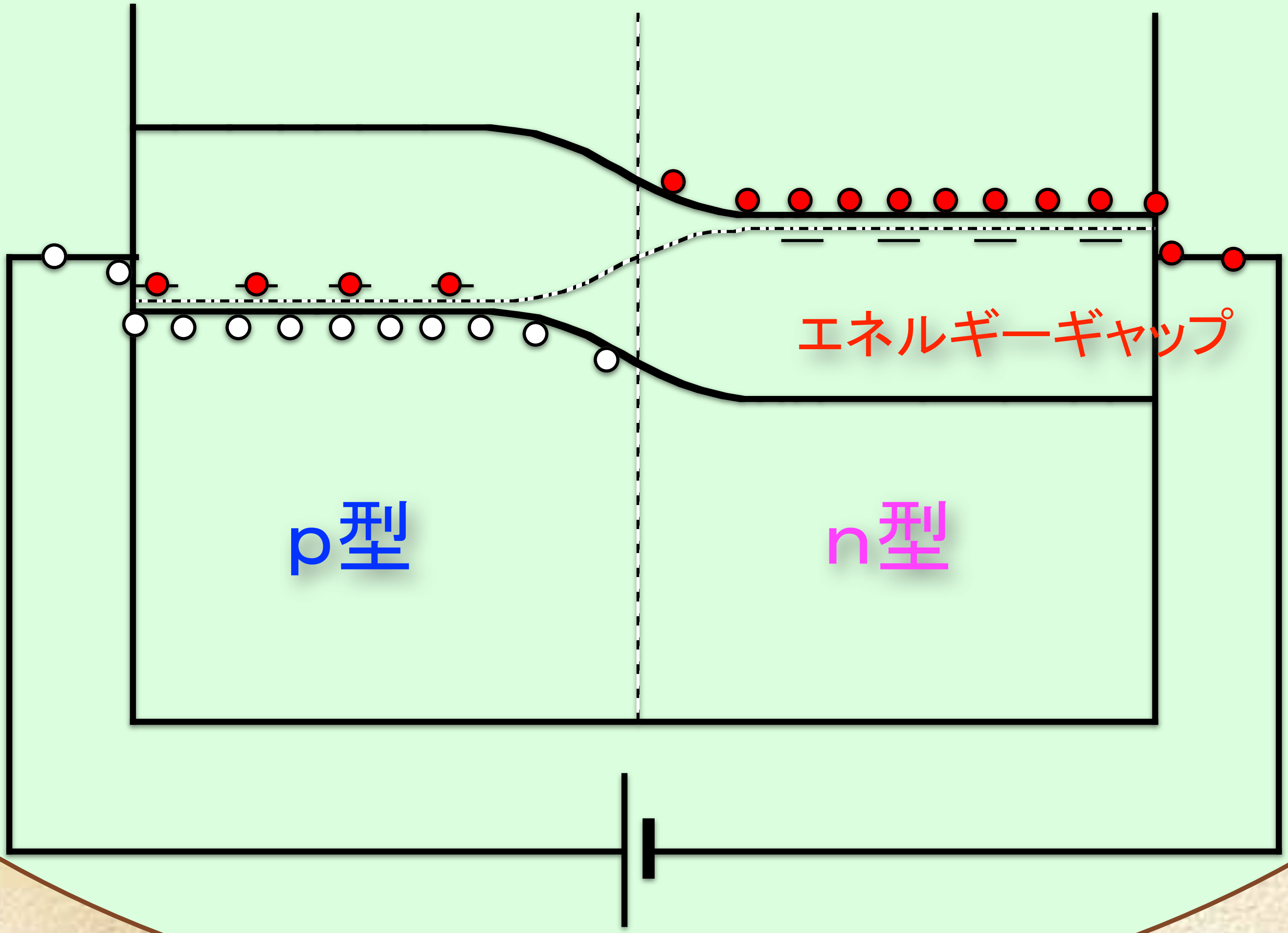
フレキシブル

薄型軽量、低消費電力、高コントラスト、広視野角、高速応答、高色再現が
可能な自発光タイプの表示素材

有機物質

電界発光の原理

電子ー正孔の対消滅が光に



有機物質

発光の色は？

エネルギーギャップ E_g

出てくる光の振動数: $\nu = E_\mathrm{g}/h$

エネルギーギャップの大きさ E_g

⇕

発光する色: 赤・青・緑

液晶ディスプレーとの比較

有機ELディスプレー	液晶ディスプレー
特徴	残された問題点
自発光	光源が必要
高輝度(600cd/m^2)	輝度（300cd/m^2）
視野角（360度も！）	視野角(170度)
早い応答性（μsec）	応答性（msec）
省エネ(<1/2)	電力
高いコントラスト（〜∞）	コントラスト（<5,000）
薄い（2-4mm）	厚い（15-20mm）

エプソン、40型有機ELディスプレイを開発 〜インクジェット技術を応用

2004年5月

http://pc.watch.impress.co.jp/docs/2004/0518/epson.htm

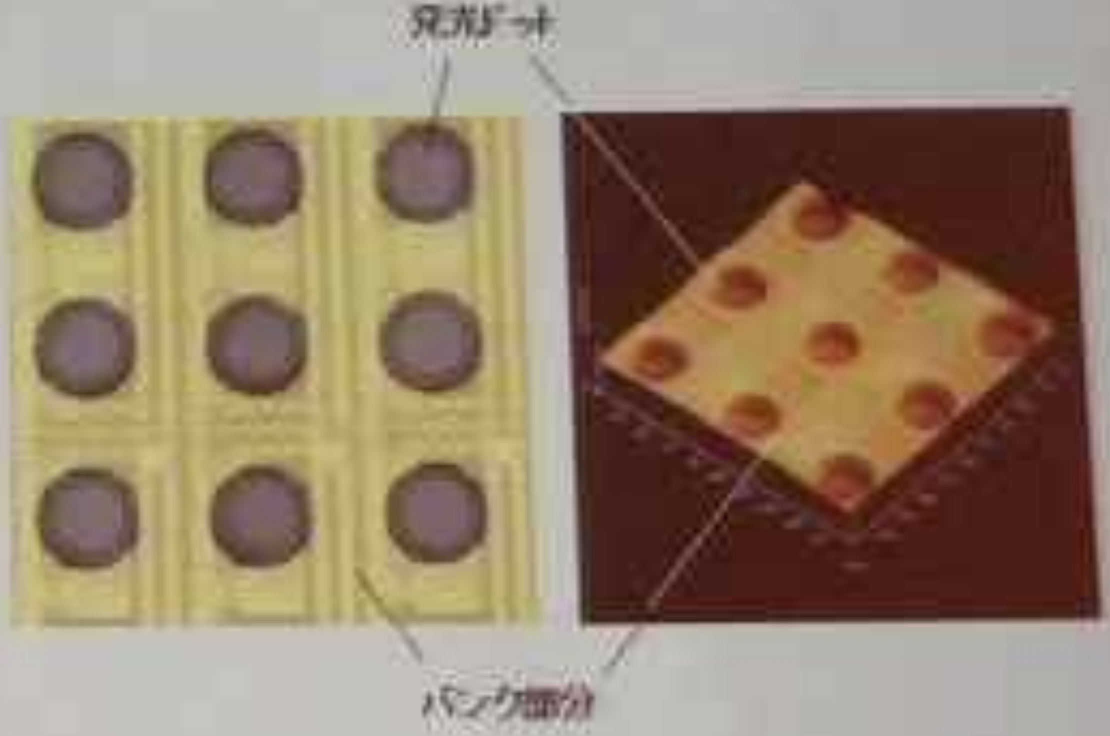
エプソンのOLED生産技術の特長（1）

EPSON

エプソン独自のインクジェット技術（マイクロピエゾヘッド技術）の活用

非加熱方式の技術のためインクジェットプリンタヘッドの工業応用が容易

- **大面積パターニングが可能**
  - 1200 mm x 820 mm
- **高精細パターニングが可能**
  - 2,880 dpi
- **発光材料の有効利用**
  - 必要な画素にだけ吐出
  （オンデマンドプリンティング）



公開された40型有機ELディスプレイ試作機。パネル上に十字の継ぎ目が見えるが、これは小型の基板を貼り合わせているため。成膜自体は40型での一括形成が可能

横から見たところ。薄型で、広視野角なのが確認できる


ed
CD
wise
view™
SAMSUNG

世界初の
有機ELテレビ

２００７年１０月

高い輝度：600 cd/m^2

高いコントラスト比：
>1,000,000

早い応答時間：
数μs

高い色再現性：NTSC 110 %

有機物質

半導体の応用素子の例

1. pn型接合ダイオード
2. 発光ダイオード
3. 太陽電池

有機物質

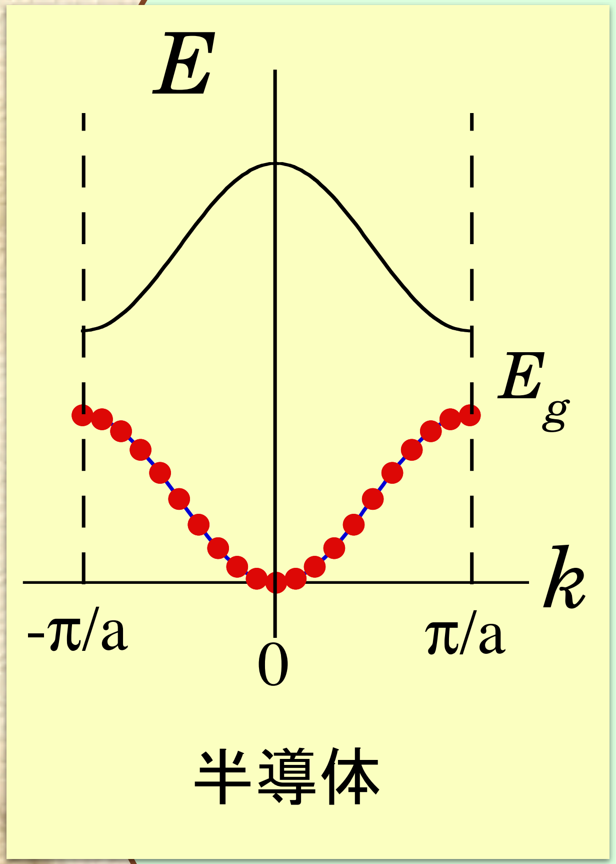
プラスチック太陽電池

軽い

安い

フレキシブル

太陽電池の原理



太陽光のエネルギー $h\nu$

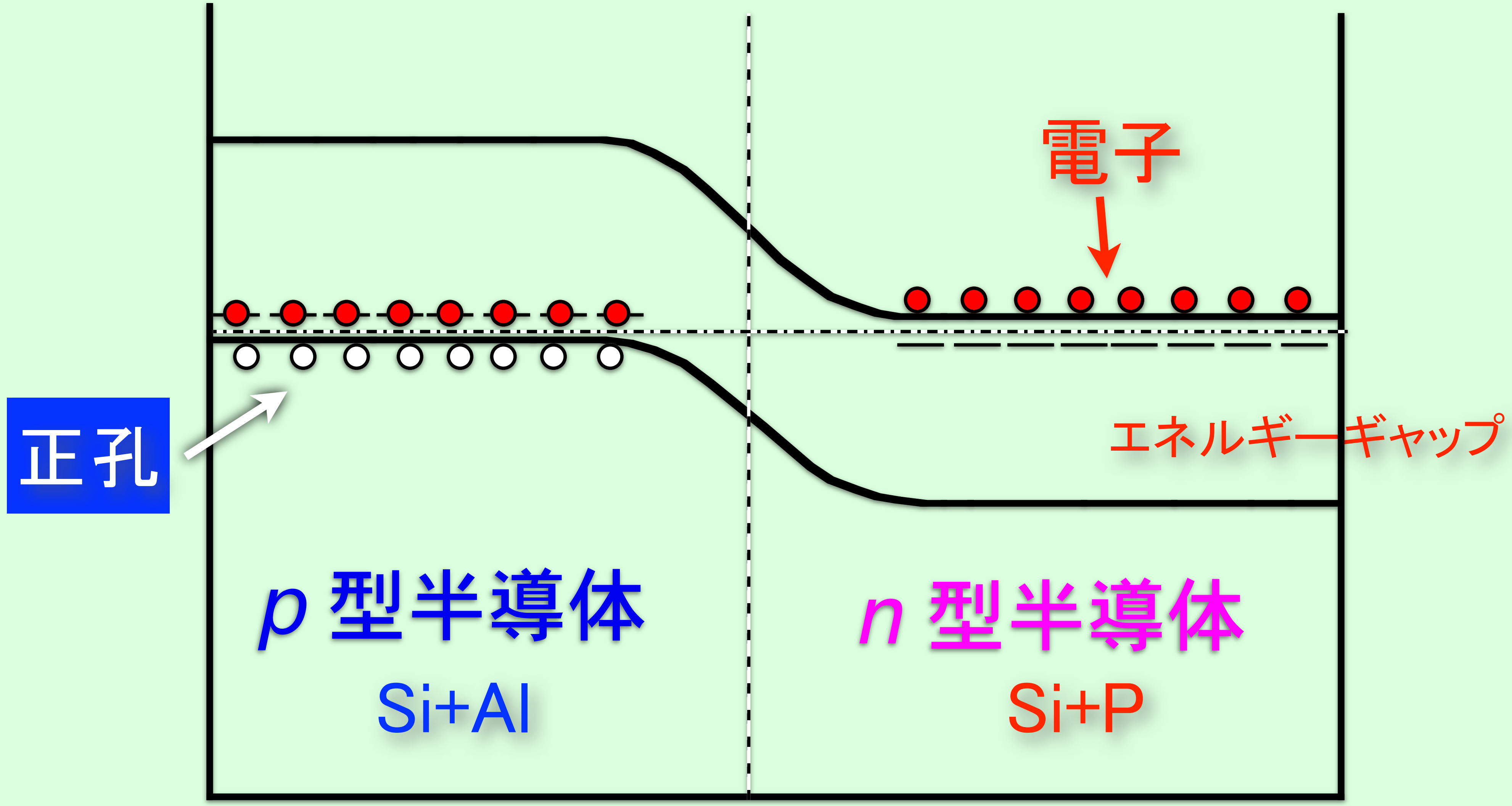
$h\nu =$ エネルギーギャップ E_g

電子ー正孔対の生成

電荷（電子、正孔）の分離

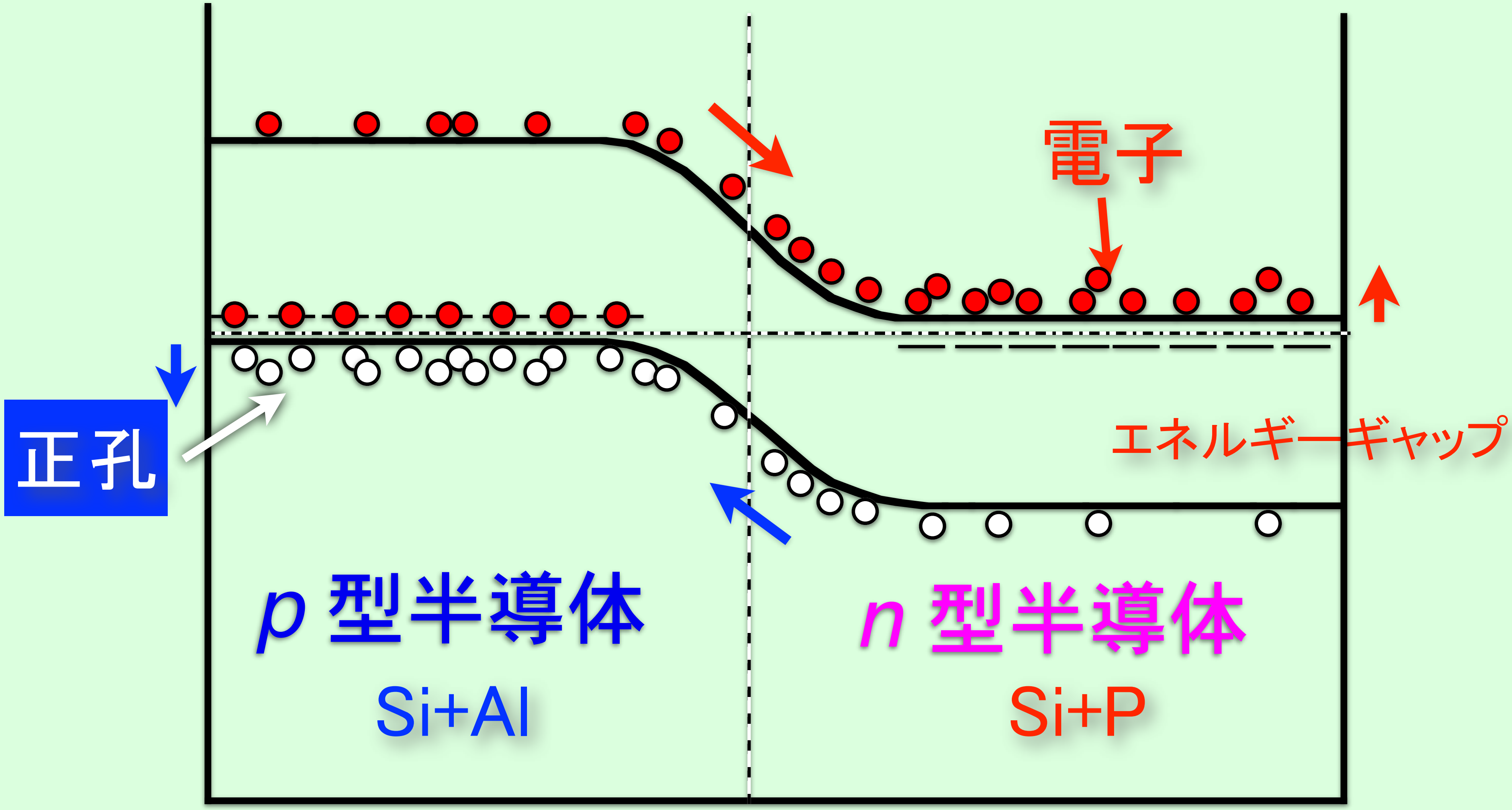
起電力の発生

太陽電池の原理



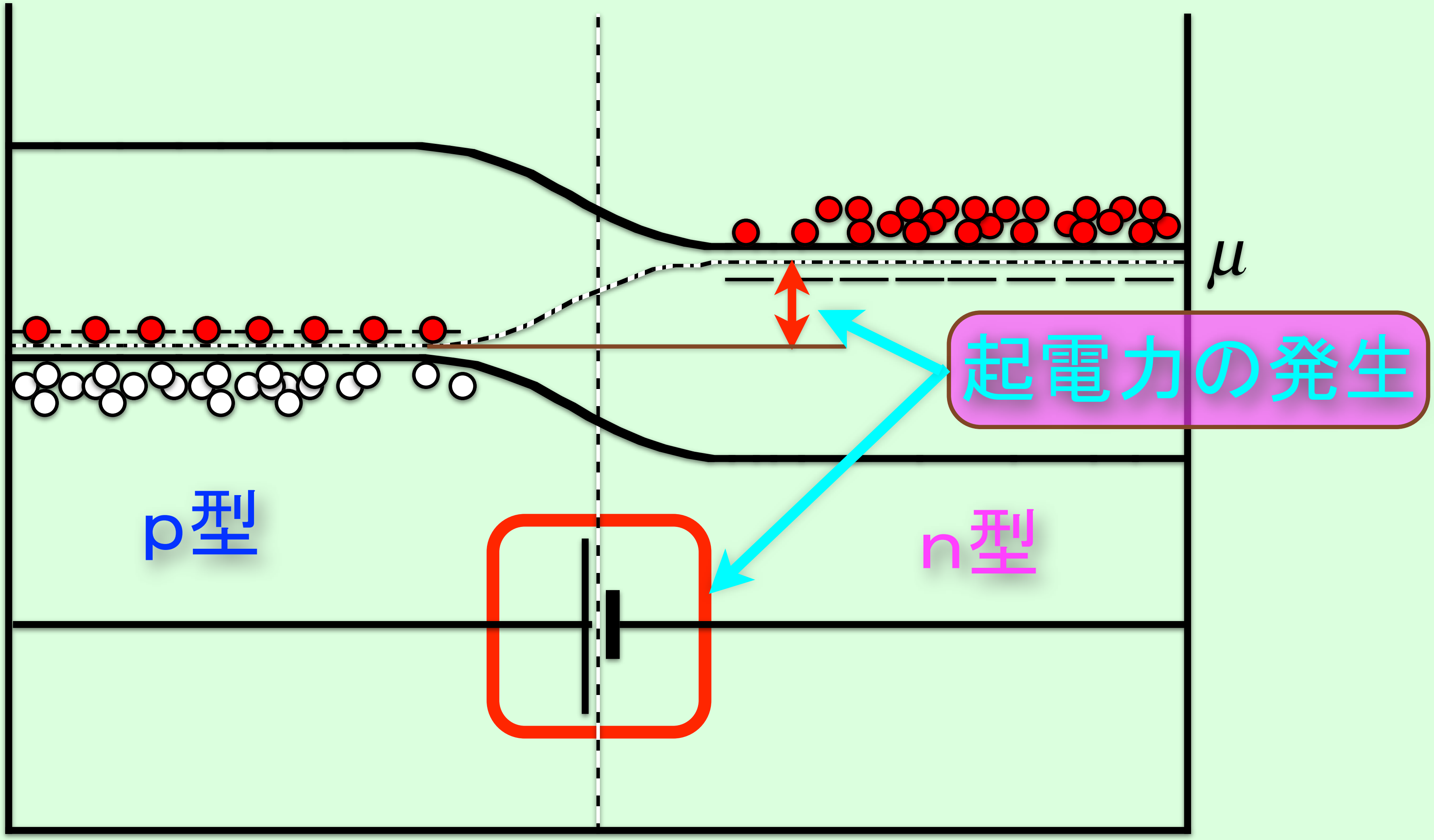
光のエネルギーを受け、電子がエネルギーギャップを上がる

太陽電池の原理

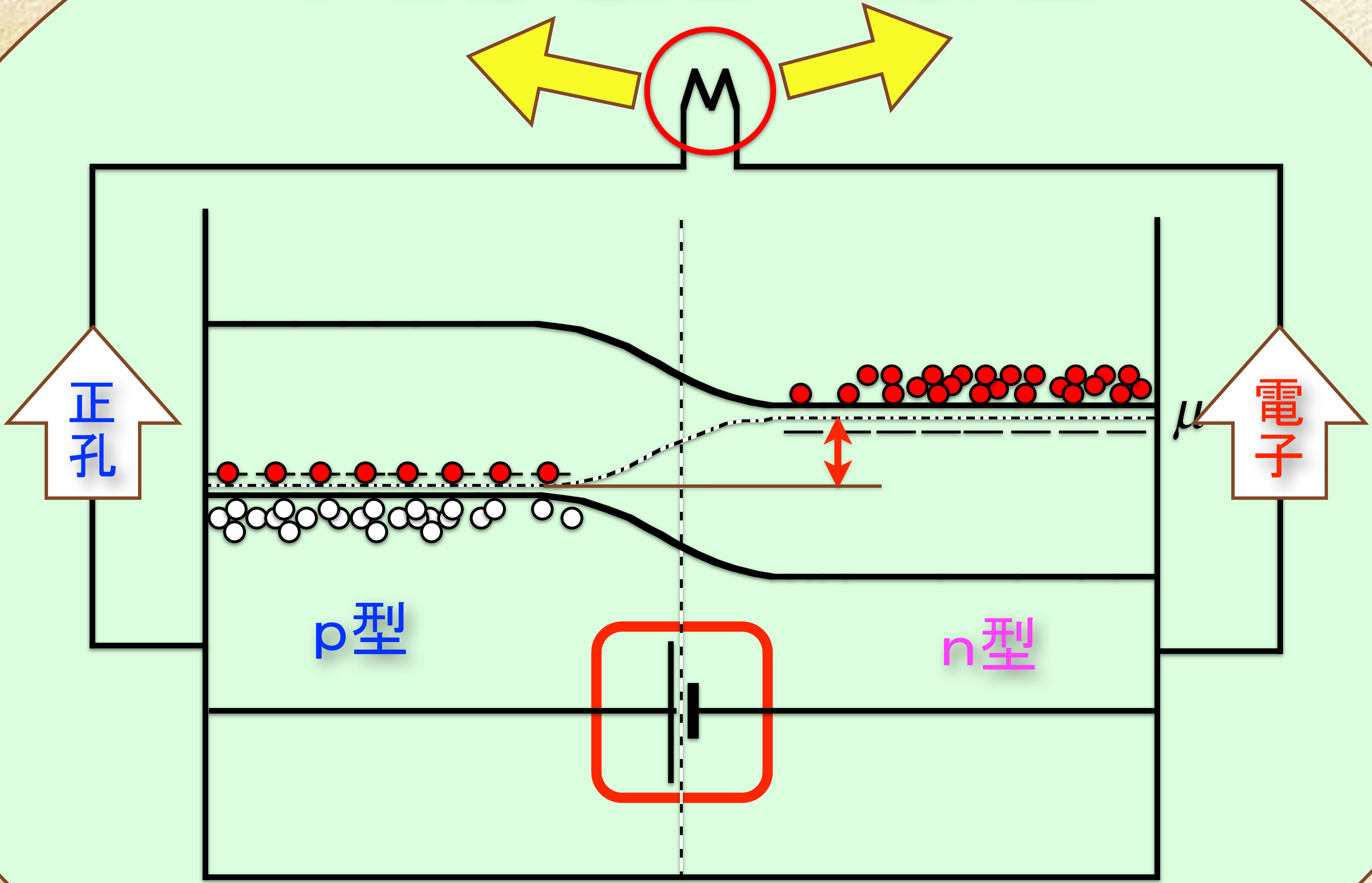


光のエネルギーを受け、電子がエネルギーギャップを上がる

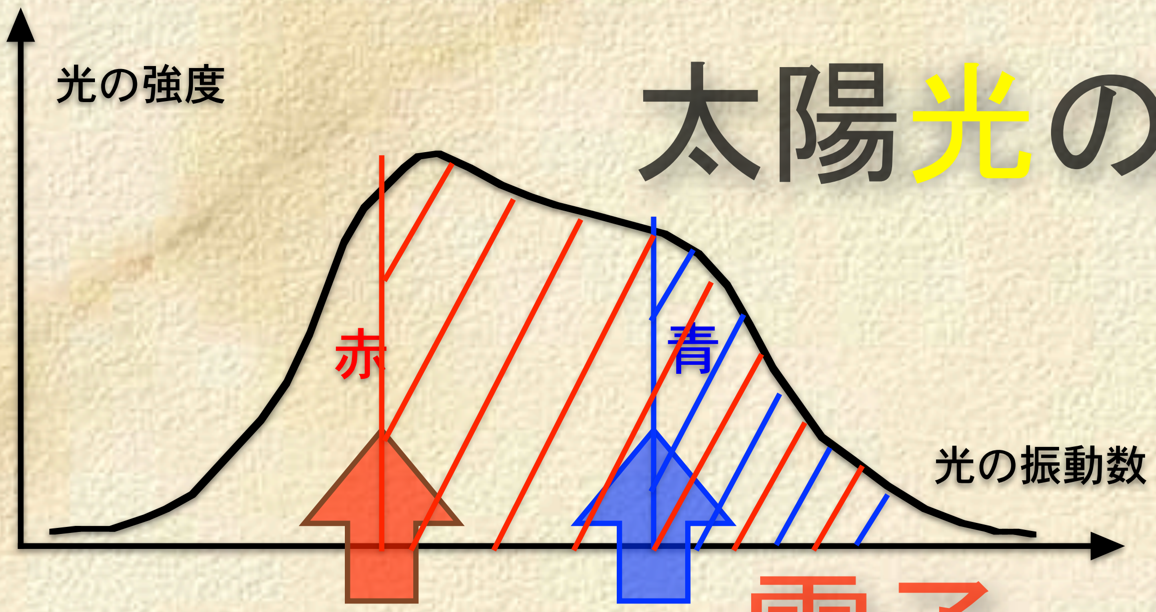
太陽電池の原理



太陽電池の原理



太陽電池の変換効率

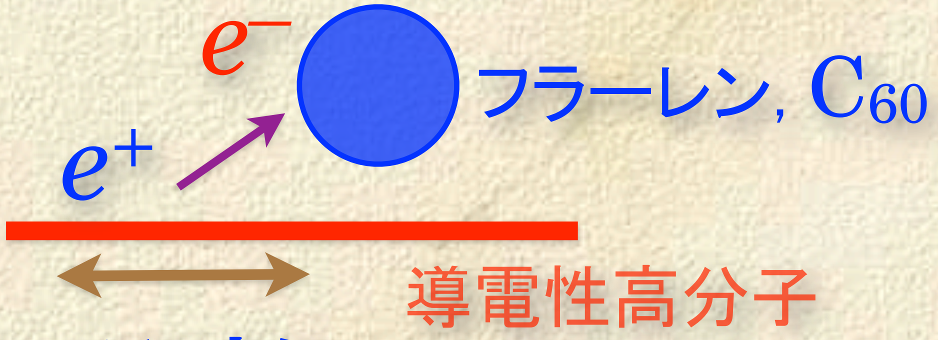


太陽光のエネルギー $h\nu$

太陽光のスペクトルにマッチしたエネルギーギャップの分布

電子ー正孔対の生成

効率的な電荷の分離



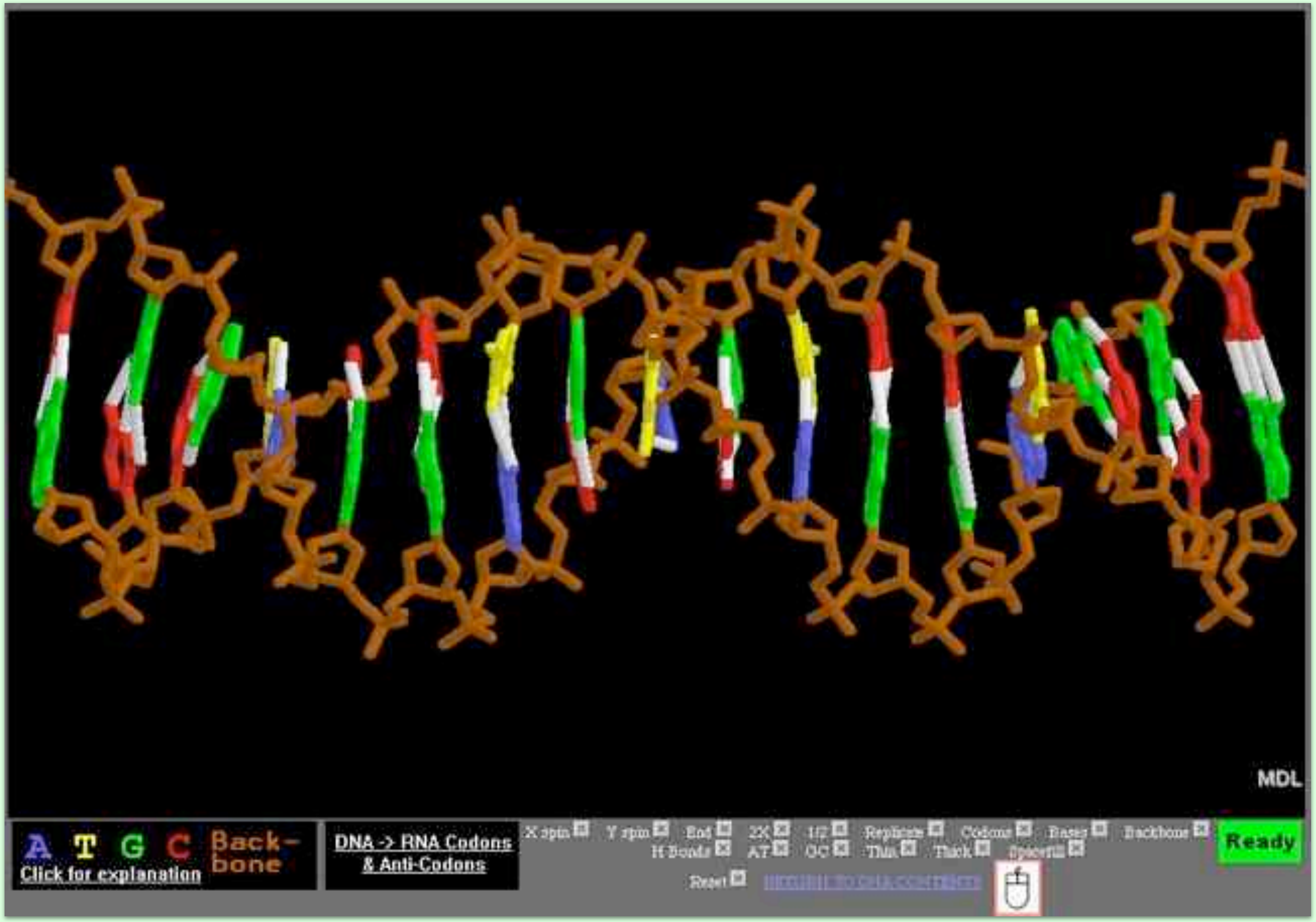
電荷（電子、正孔）の分離

起電力の発生

有機物質

DNAの物性：構造

DeoxyriboNucleic Acid



http://www.umass.edu/microbio/chime/dna/index1.htm
http://molvis.sdsc.edu/dna/index.htm (*mirror* site)

構造

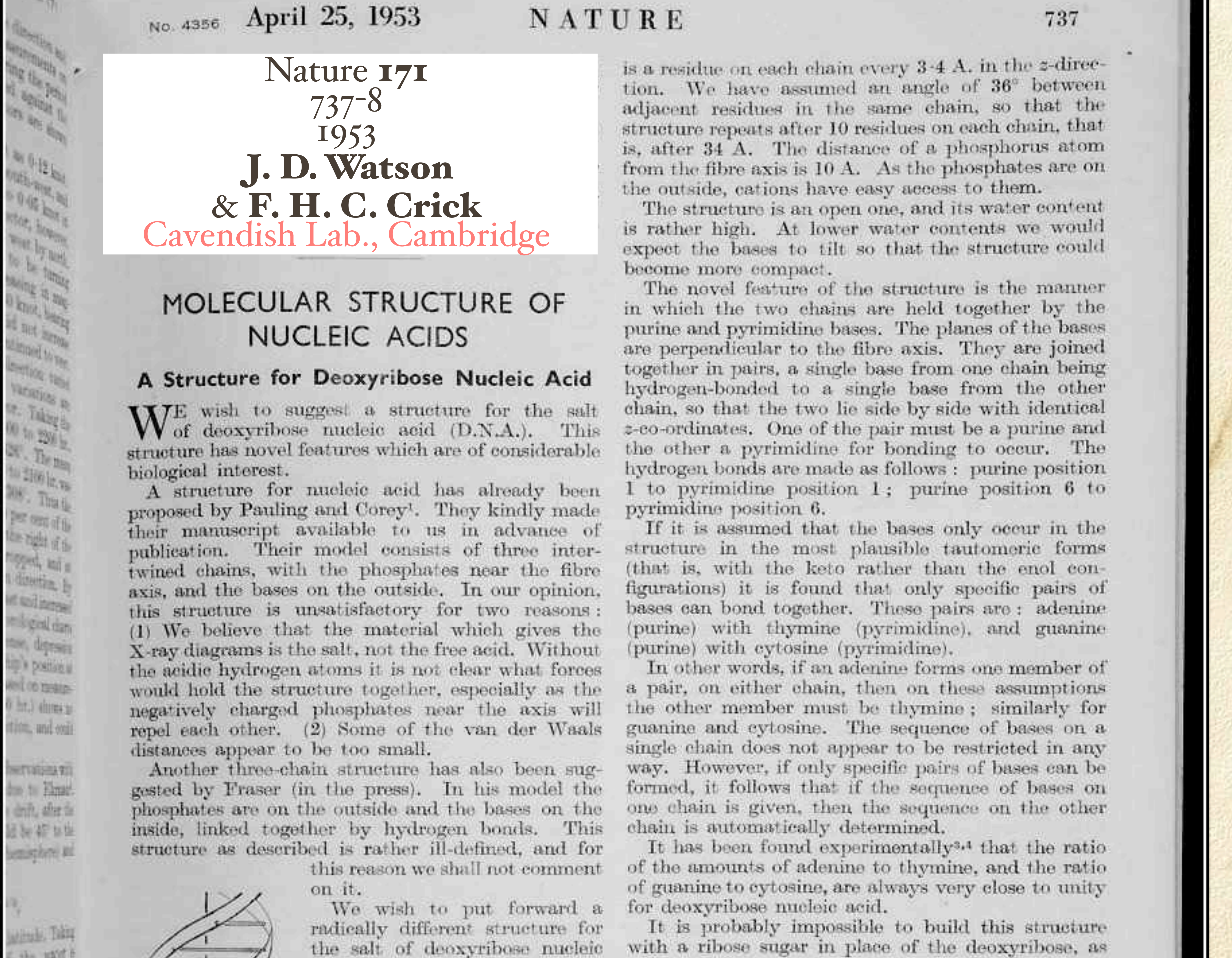
James Watson and Francis Crick, crackers of the DNA code, in 1953

James Watson & Francis Crick

It took an ex-physicist and a former ornithology student – along with some unwitting help from a competitor – to crack the secret of life By ROBERT WRIGHT

http://www.time.com/time/time100/scientist/profile/watsoncrick.html

Nature **171**
737-8
1953
J. D. Watson
& **F. H. C. Crick**
Cavendish Lab., Cambridge



MOLECULAR STRUCTURE OF NUCLEIC ACIDS

A Structure for Deoxyribose Nucleic Acid

WE wish to suggest a structure for the salt of deoxyribose nucleic acid (D.N.A.). This structure has novel features which are of considerable biological interest.

A structure for nucleic acid has already been proposed by Pauling and Corey[1]. They kindly made their manuscript available to us in advance of publication. Their model consists of three intertwined chains, with the phosphates near the fibre axis, and the bases on the outside. In our opinion, this structure is unsatisfactory for two reasons: (1) We believe that the material which gives the X-ray diagrams is the salt, not the free acid. Without the acidic hydrogen atoms it is not clear what forces would hold the structure together, especially as the negatively charged phosphates near the axis will repel each other. (2) Some of the van der Waals distances appear to be too small.

Another three-chain structure has also been suggested by Fraser (in the press). In his model the phosphates are on the outside and the bases on the inside, linked together by hydrogen bonds. This structure as described is rather ill-defined, and for this reason we shall not comment on it.

We wish to put forward a radically different structure for the salt of deoxyribose nucleic

is a residue on each chain every 3·4 A. in the z-direction. We have assumed an angle of 36° between adjacent residues in the same chain, so that the structure repeats after 10 residues on each chain, that is, after 34 A. The distance of a phosphorus atom from the fibre axis is 10 A. As the phosphates are on the outside, cations have easy access to them.

The structure is an open one, and its water content is rather high. At lower water contents we would expect the bases to tilt so that the structure could become more compact.

The novel feature of the structure is the manner in which the two chains are held together by the purine and pyrimidine bases. The planes of the bases are perpendicular to the fibre axis. They are joined together in pairs, a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical z-co-ordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur. The hydrogen bonds are made as follows: purine position 1 to pyrimidine position 1; purine position 6 to pyrimidine position 6.

If it is assumed that the bases only occur in the structure in the most plausible tautomeric forms (that is, with the keto rather than the enol configurations) it is found that only specific pairs of bases can bond together. These pairs are: adenine (purine) with thymine (pyrimidine), and guanine (purine) with cytosine (pyrimidine).

In other words, if an adenine forms one member of a pair, on either chain, then on these assumptions the other member must be thymine; similarly for guanine and cytosine. The sequence of bases on a single chain does not appear to be restricted in any way. However, if only specific pairs of bases can be formed, it follows that if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined.

It has been found experimentally[3,4] that the ratio of the amounts of adenine to thymine, and the ratio of guanine to cytosine, are always very close to unity for deoxyribose nucleic acid.

It is probably impossible to build this structure with a ribose sugar in place of the deoxyribose, as

Nature **171**
738-40
1953
M. H. F. Wilkins,
A. R. Stokes,
& H. R. Wilson
King's College, London

10, 192 (1953).

Molecular Structure of Deoxypentose Nucleic Acids

WHILE the biological properties of deoxypentose nucleic acid suggest a molecular structure containing great complexity, X-ray diffraction studies described here (cf. Astbury[1]) show the basic molecular configuration has great simplicity. The purpose of this communication is to describe, in a preliminary way, some of the experimental evidence for the polynucleotide chain configuration being helical, and existing in this form when in the natural state. A fuller account of the work will be published shortly.

The structure of deoxypentose nucleic acid is the same in all species (although the nitrogen base ratios alter considerably) in nucleoprotein, extracted or in cells, and in purified nucleate. The same linear group of polynucleotide chains may pack together parallel in different ways to give crystalline[1-3], semi-crystalline or paracrystalline material. In all cases the X-ray

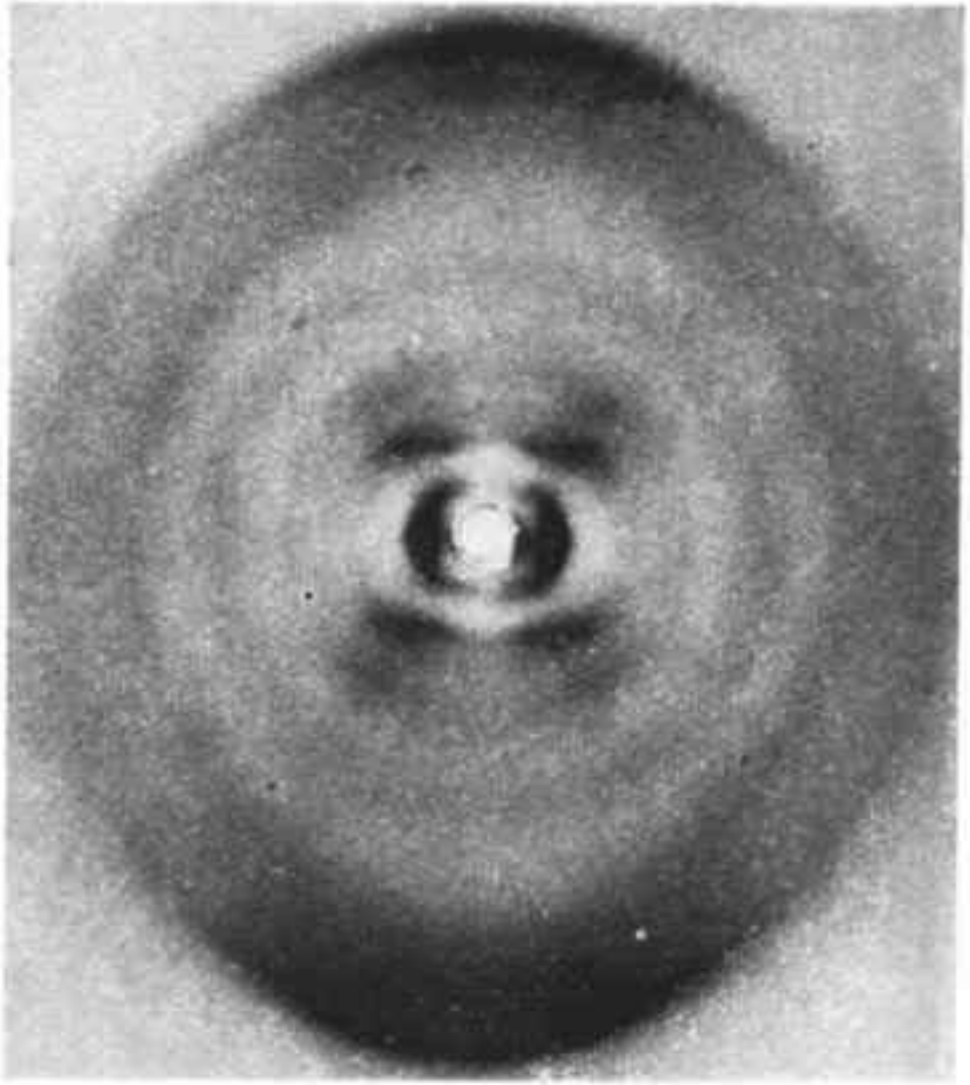


Fig. 1. Fibre diagram of deoxypentose nucleic acid from *B. coli*. Fibre axis vertical

the innermost maxima of each Bessel function and the origin. The angle this line makes with the equator is roughly equal to the angle between an element of the helix and the helix axis. If a unit repeats n times along the helix there will be a meridional reflexion (J_0^2) on the nth layer line. The helical configuration produces side-bands on this fundamental frequency, the effect[5] being to reproduce the intensity distribution about the origin around the new origin, on the nth layer line, corresponding to C in Fig. 2.

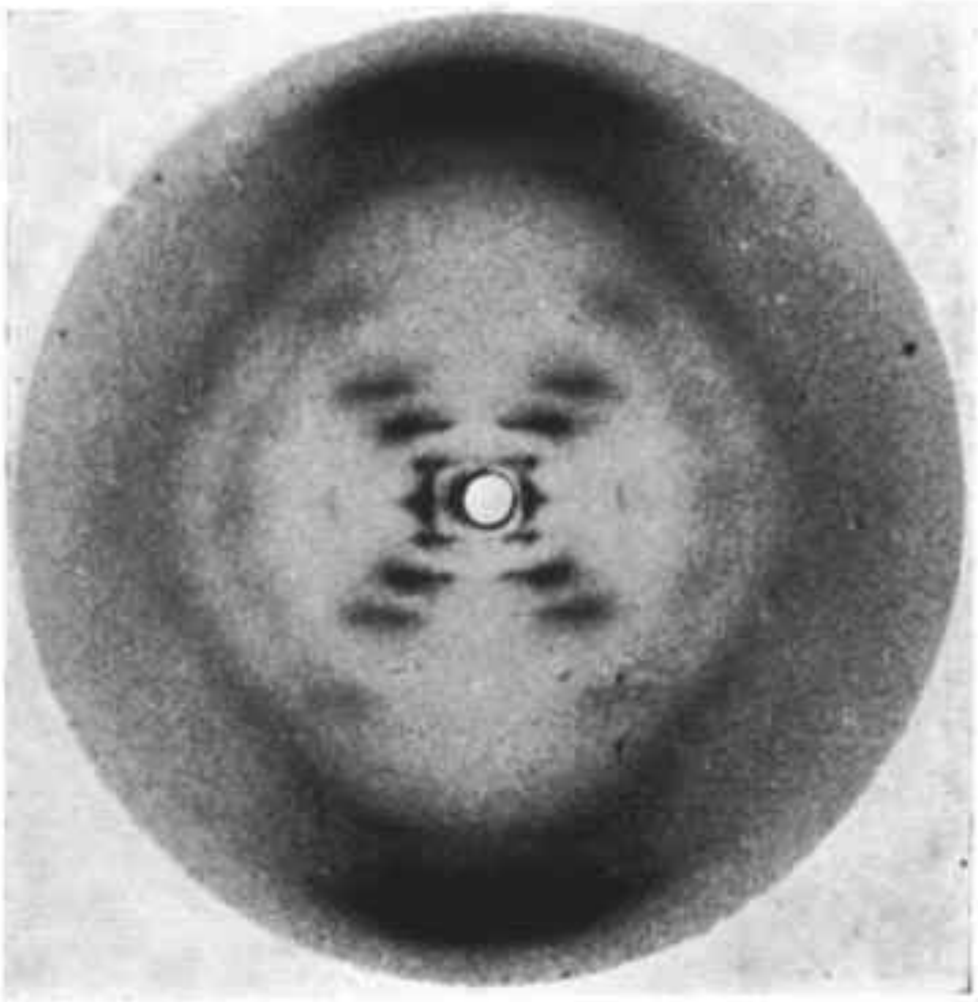
We will now briefly analyse in physical terms some of the effects of the shape and size of the repeat unit or nucleotide on the diffraction pattern. First, if the nucleotide consists of a unit having circular symmetry

Nature **171**
740–41
1953

Rosalind E. Franklin,
& R. G. Gosling
King's College, London

Molecular Configuration in Sodium Thymonucleate

SODIUM thymonucleate fibres give two distinct types of X-ray diagram. The first corresponds to a crystalline form, structure *A*, obtained at about 75 per cent relative humidity; a study of this is described in detail elsewhere[1]. At higher humidities a different structure, structure *B*, showing a lower degree of order, appears and persists over a wide



Sodium deoxyribose nucleate from calf thymus. Structure *B*

molecules, each unit being shielded by a sheath of water. Each unit is then free to take up its least-energy configuration independently of its neighbours and, in view of the nature of the long-chain molecules involved, it is highly likely that the general form will be helical[3]. If we adopt the hypothesis of a helical structure, it is immediately possible, from the X-ray diagram of structure *B*, to make certain deductions as to the nature and dimensions of the helix.

The innermost maxima on the first, second, third and fifth layer lines lie approximately on straight lines radiating from the origin. For a smooth single-strand helix the structure factor on the *n*th layer line is given by :

$$F_n = J_n(2\pi rR) \exp i\, n(\psi + \tfrac{1}{2}\pi),$$

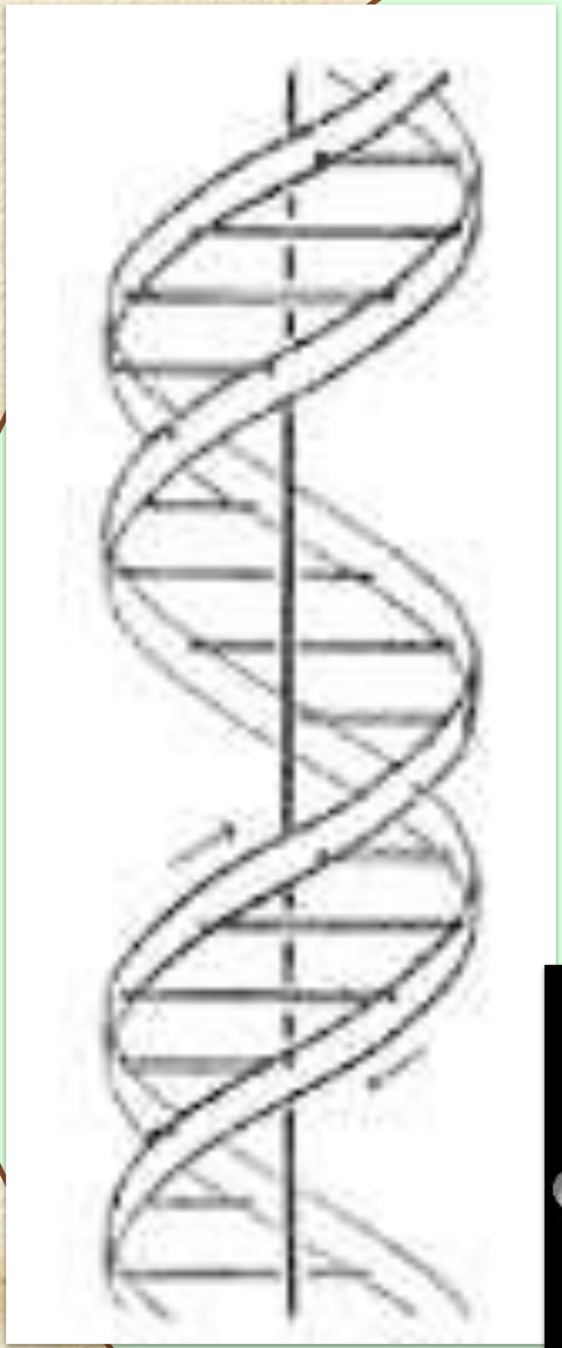
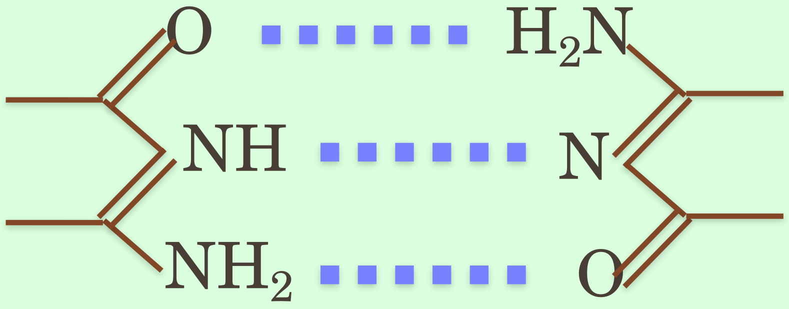
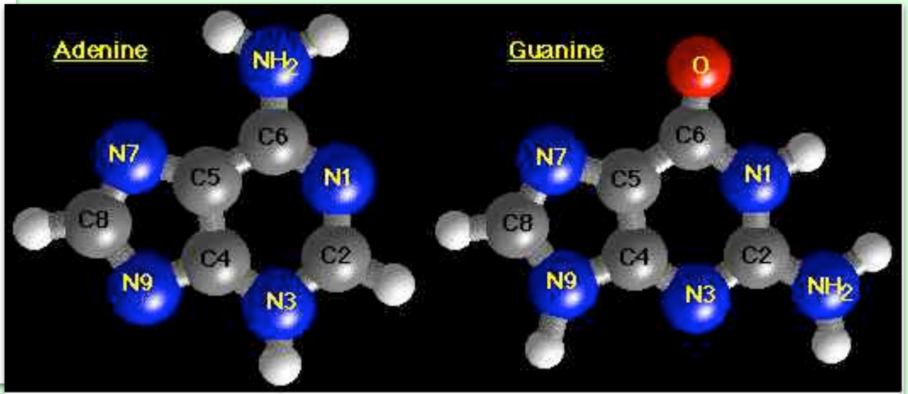


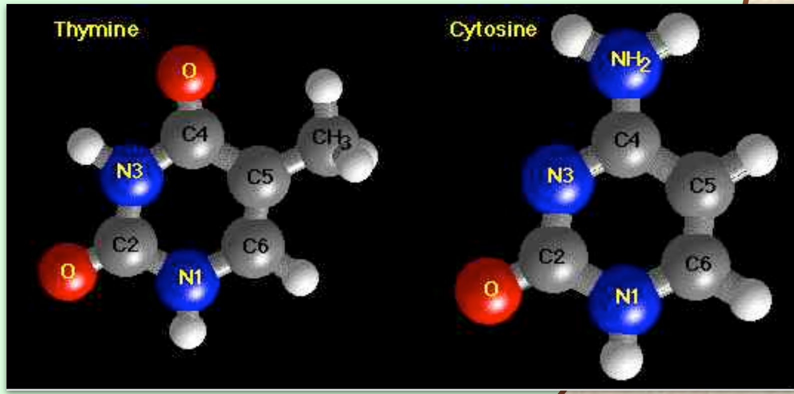
Figure 1

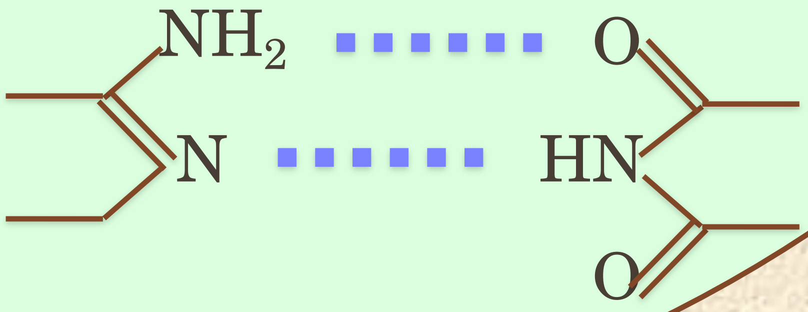
This figure is purely diagrammatic. The two ribbons symbolize the two phosphate-sugar chains, and the horizonal rods the pairs of bases holding the chains together. The vertical line marks the fibre axis.



Guanine **Cytosine**







Adenine **Thymine**

Chargaff's rules

有機物質

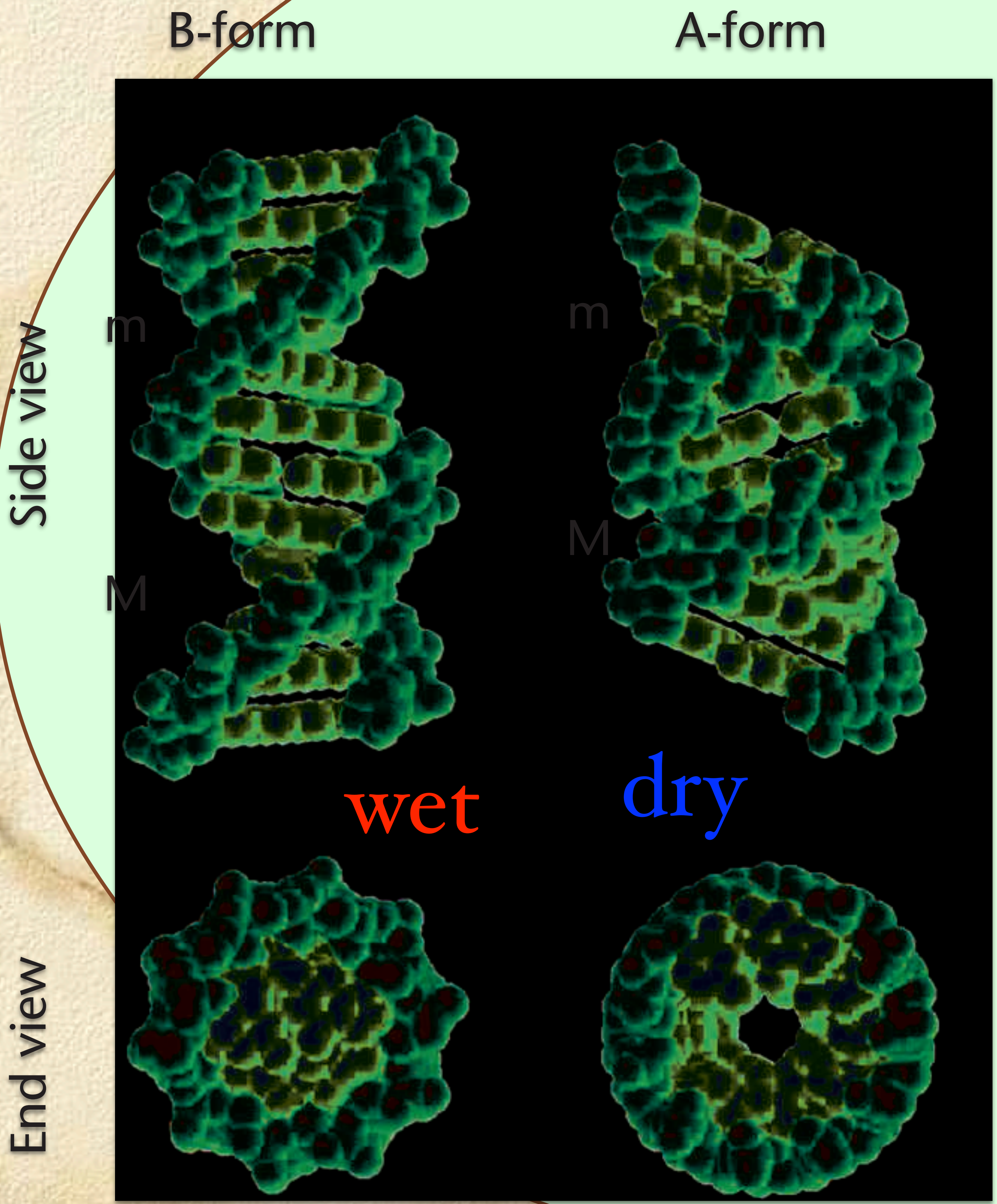


Table 1 Average structural parameters for various helical f

Parameter	B-form	A-form
Helix handedness	Right	Right
Base pairs per turn (helical repeat)	10.5	11
Base pairs per repeating unit	1	1
Rise per base pair (Å)[a]	3.4	2.6
Major groove width (Å)	11.7	2.7
Major groove depth (Å)	8.8	13.5
Minor groove width (Å)	5.7	11.0
Minor groove depth (Å)	7.5	2.8

[a] One angstrom (Å) is equal to 10^{-10} m.

From Encyclopedia of the Human Genome
Richard P. Bowater, 2003, Nature Pub.
www.ehgonline.net

有機物質

走査トンネル顕微鏡
Scanning Tunnel Microscope

ノーベル賞受賞(1986): Binnig and Rohrer

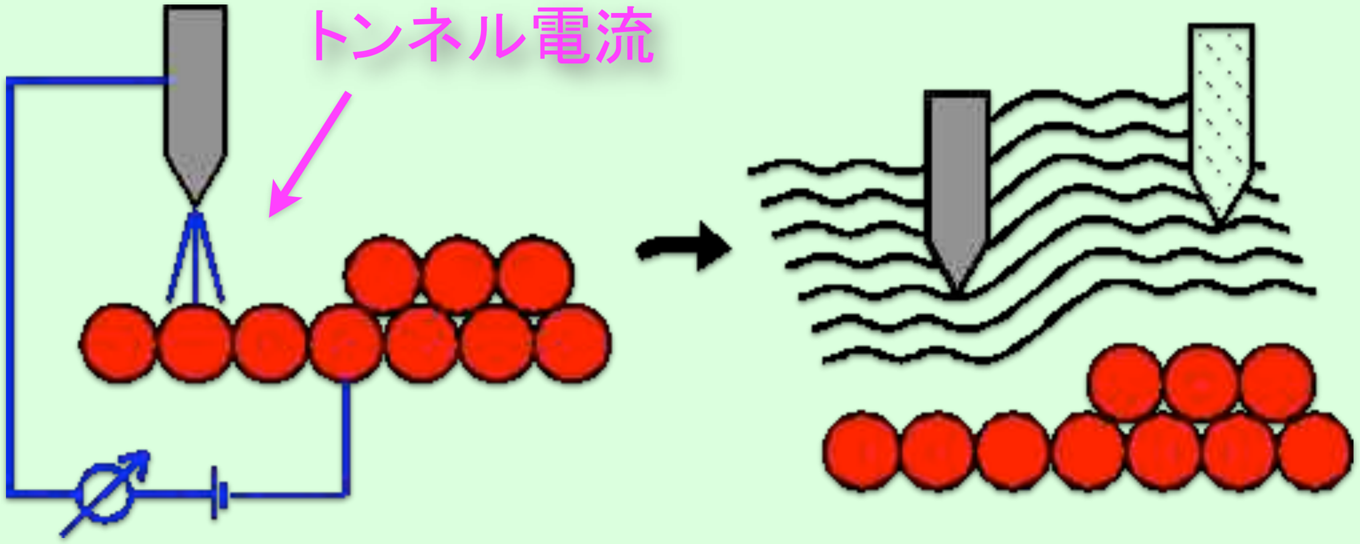
IBM ギャラリー

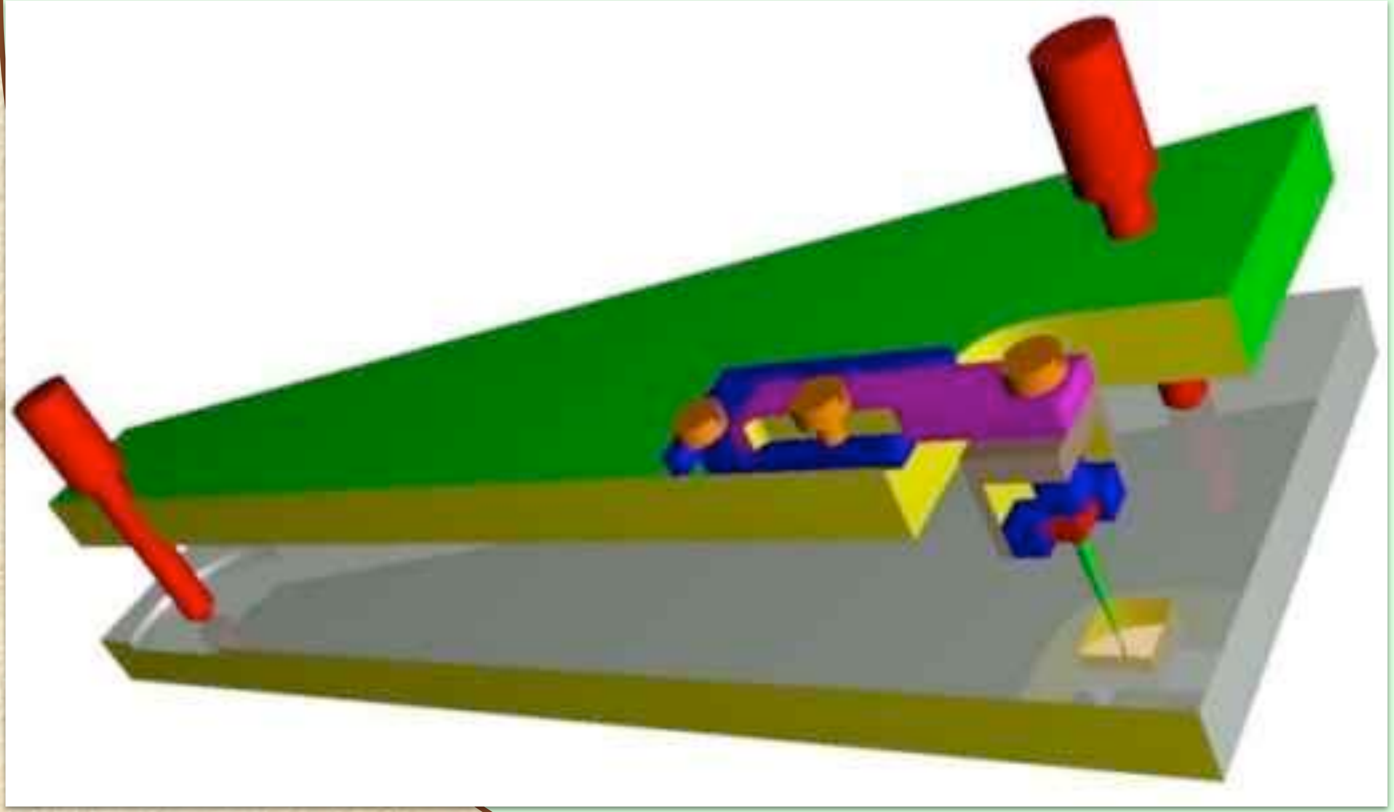
電子の波を見る

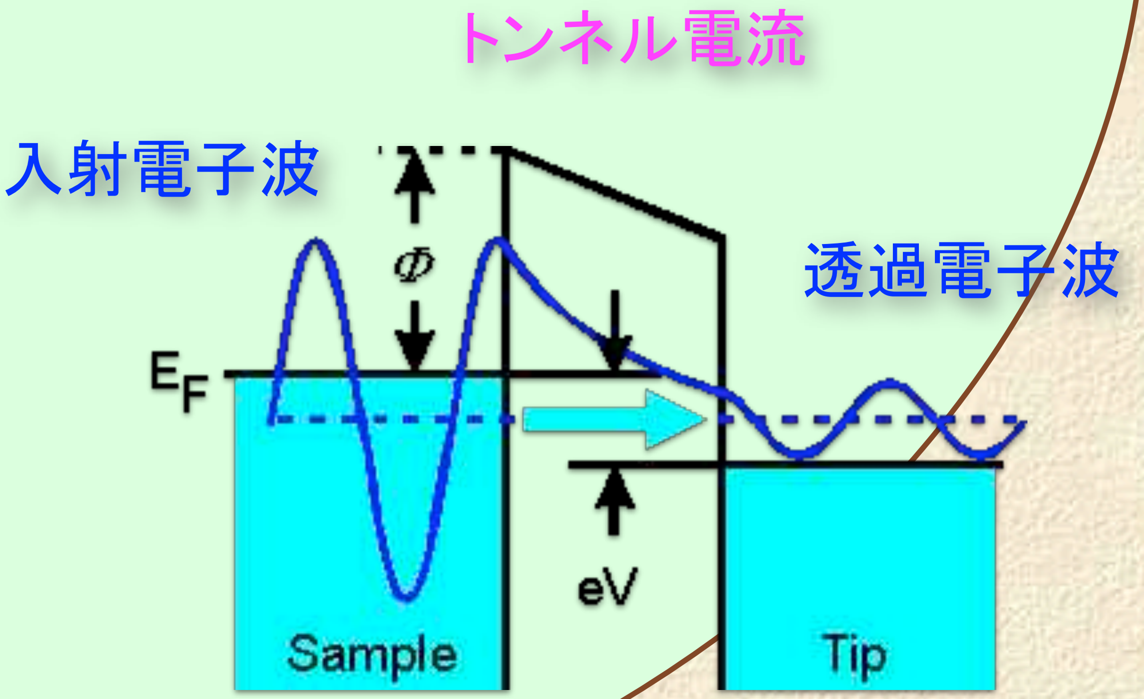
構造を見る

http://www.almaden.ibm.com/vis/stm/gallery.html

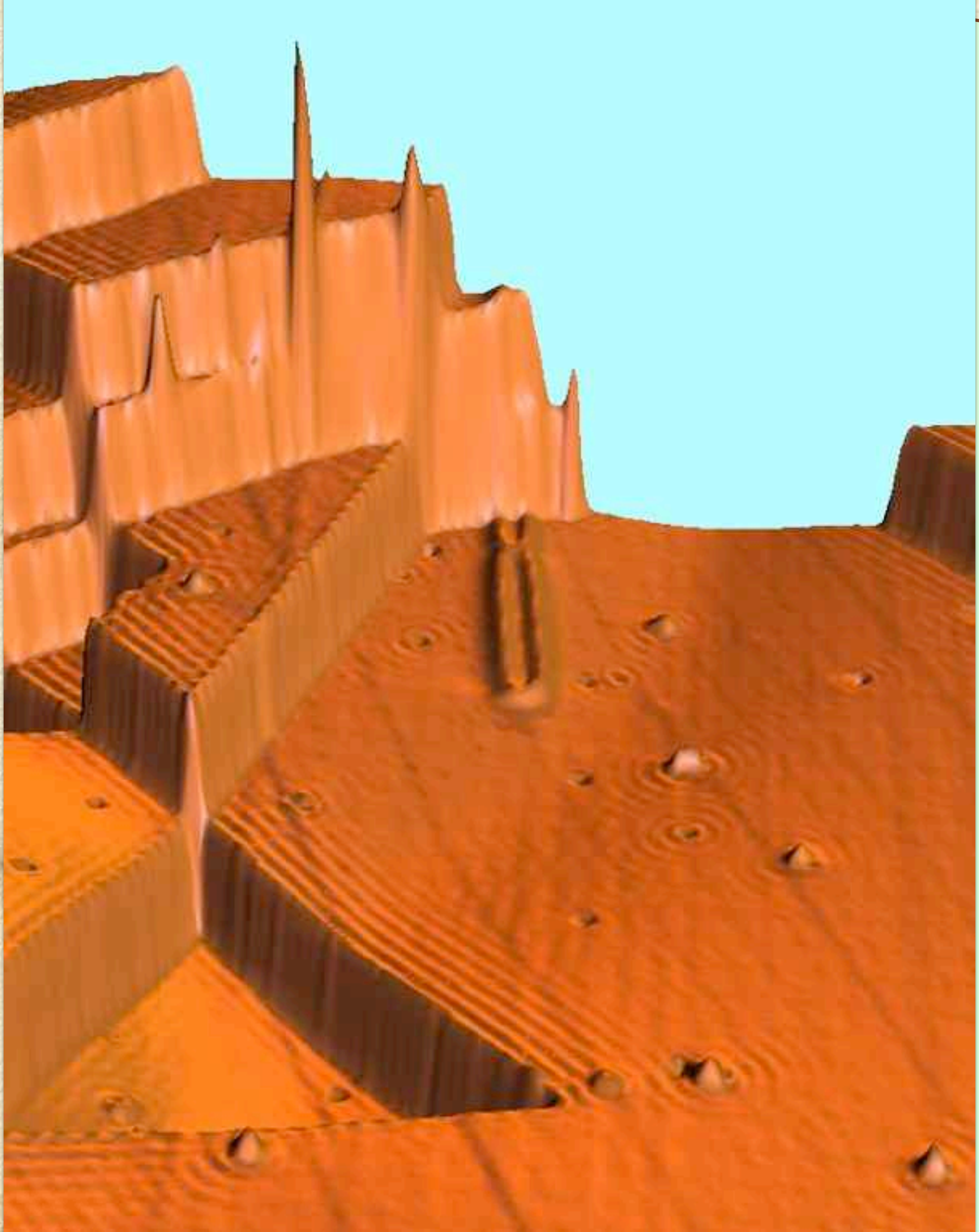
走査トンネル顕微鏡の原理





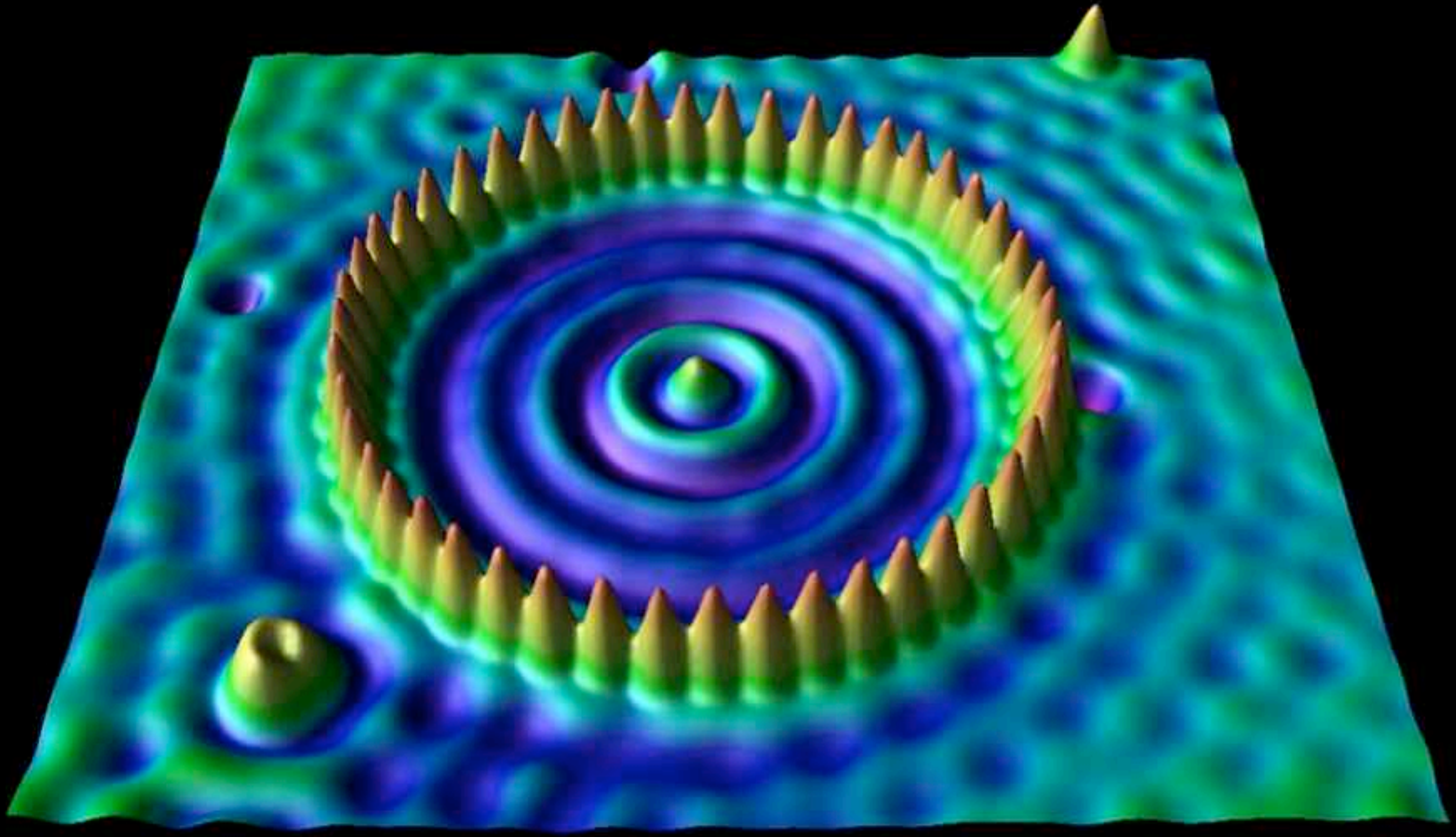


http://sxm4.uni-muenster.de/stm-en/



Reminiscent of formal Japanese rock gardens, here we see ripples surrounding features on the copper (111) surface. The artists' fortunes took a major turn upward when they determined that the ripples were due to "surface state electrons." These electrons are free to roam about the surface but not to penetrate into the solid. When one of these electrons encounters an obstacle like a step edge, it is partially reflected. The ripples extending away from the step edges and the various defects in the crystal surface are just the standing waves that are created whenever a wave scatters off of something. The standing waves are about 15 Angstroms (roughly 10 atomic diameters) from crest to crest. The amplitude is largest adjacent to the step edge where it is about 0.04 Angstroms from crest to trough.

Scientists discovered a new method for confining electrons to artificial structures at the nanometer lengthscale. Surface state electrons on Cu(111) were confined to closed structures (corrals) defined by barriers built from Fe adatoms. The barriers were assembled by individually positioning Fe adatoms using the tip of a low temperature scanning tunneling microscope (STM). A circular corral of radius 71.3 Angstrom was constructed in this way out of 48 Fe adatoms.



This STM image shows the direct observation of standing-wave patterns in the local density of states of the Cu (111) surface. These spatial oscillations are quantum-mechanical interference patterns caused by scattering of the two-dimensional electron gas off the Fe adatoms and point defects.

有機物質

DNAの構造はSTMで見えるか?

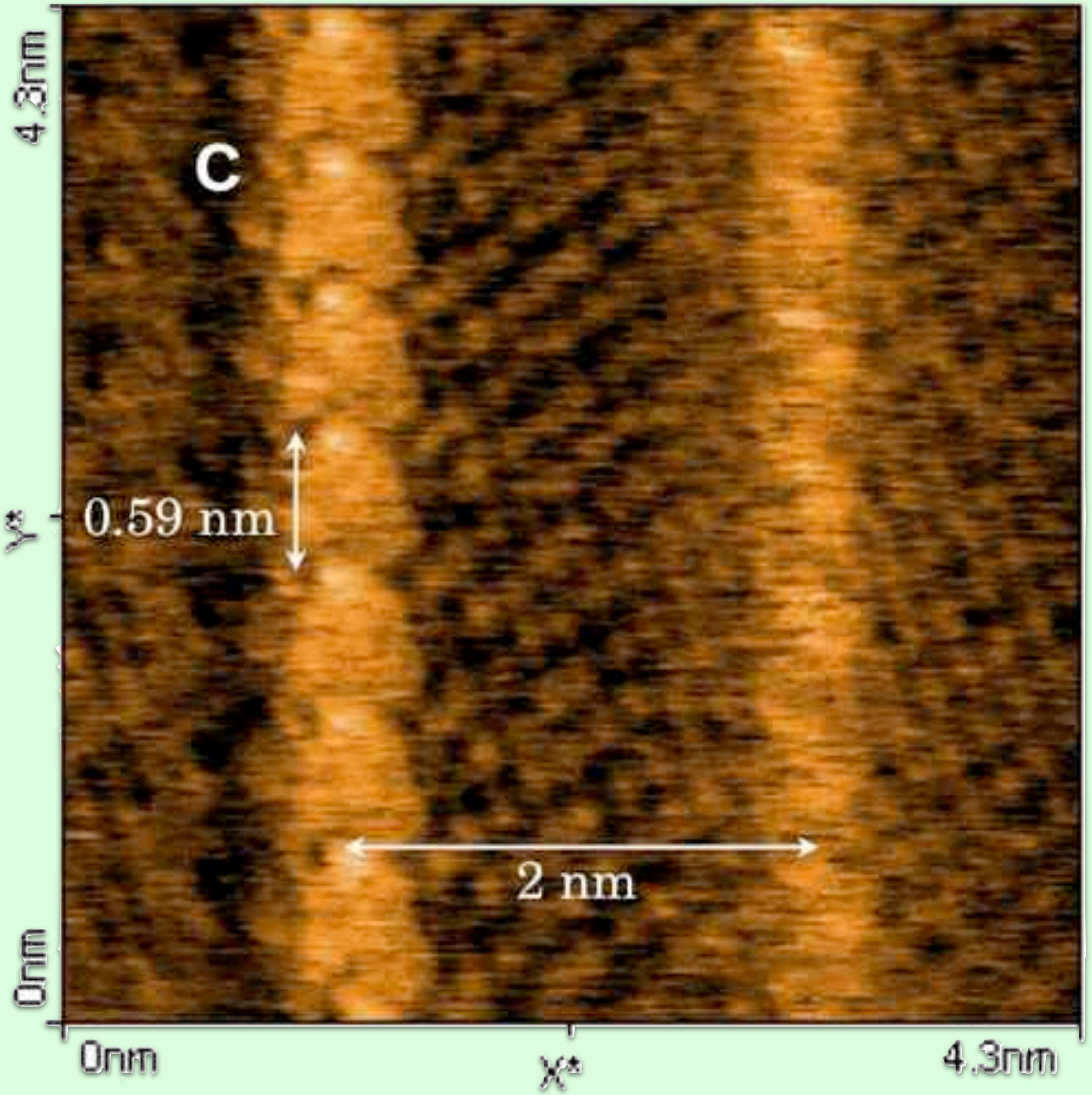
STMは、チップ電位における
電子状態密度の等高線を見る

DNAは半導体!

エネルギーギャップ内には状態密度無し!!

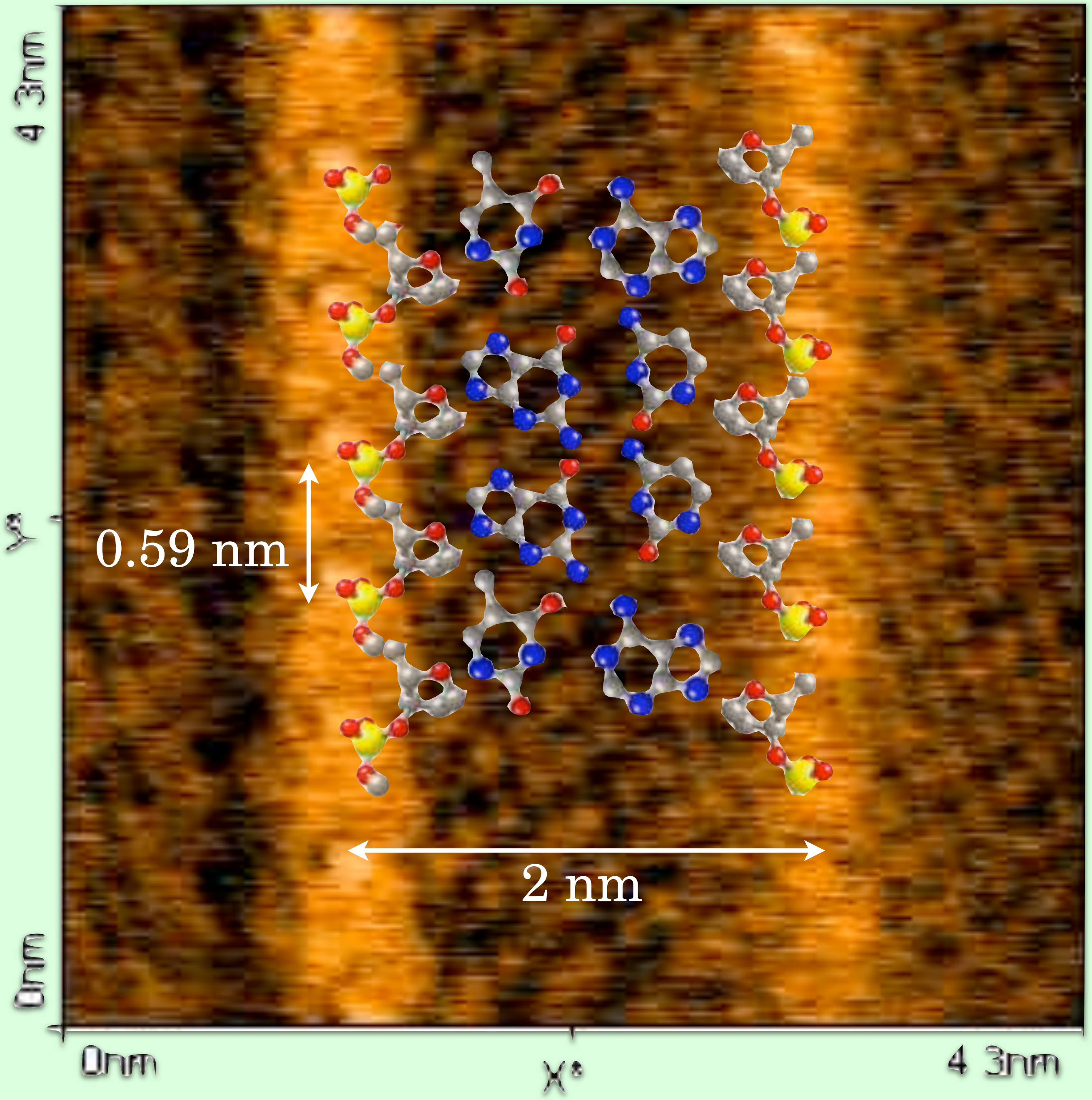
有機物質

DNAのSTMによる可視化（M1:臼井くん）



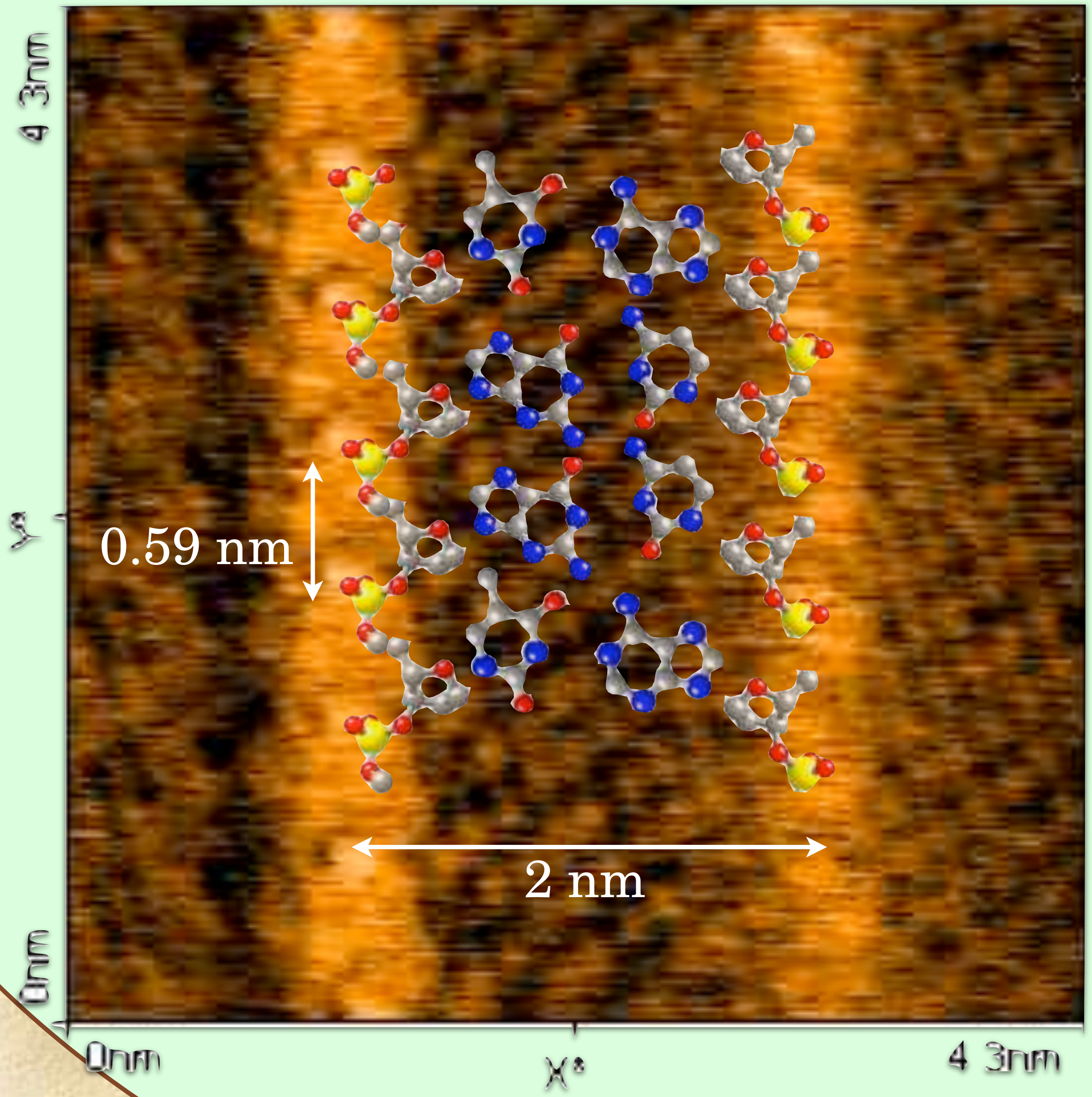
有機物質

DNAのSTMによる可視化（M1:臼井くん）



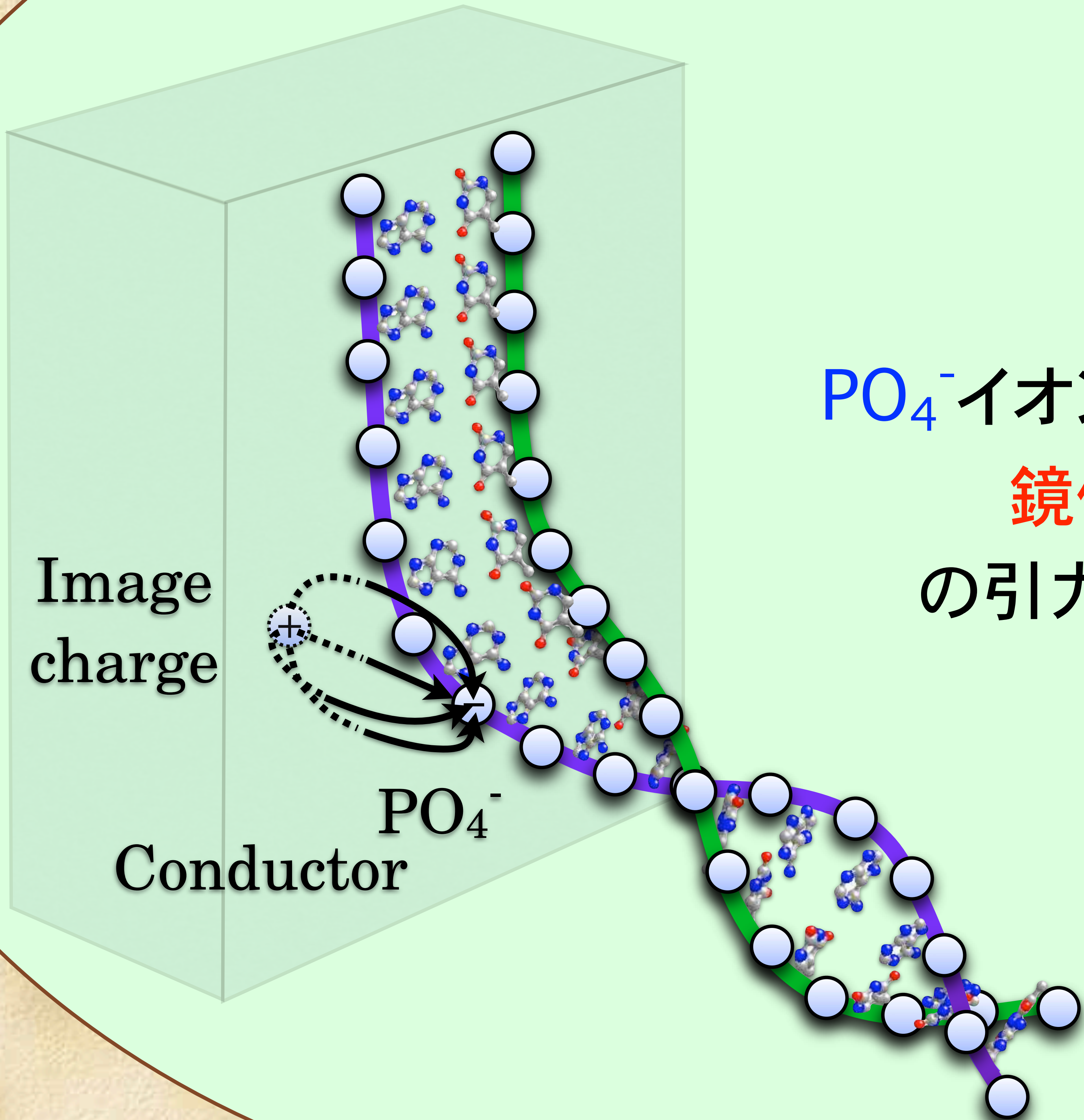
有機物質

DNAのSTMによる可視化（M1:臼井くん）



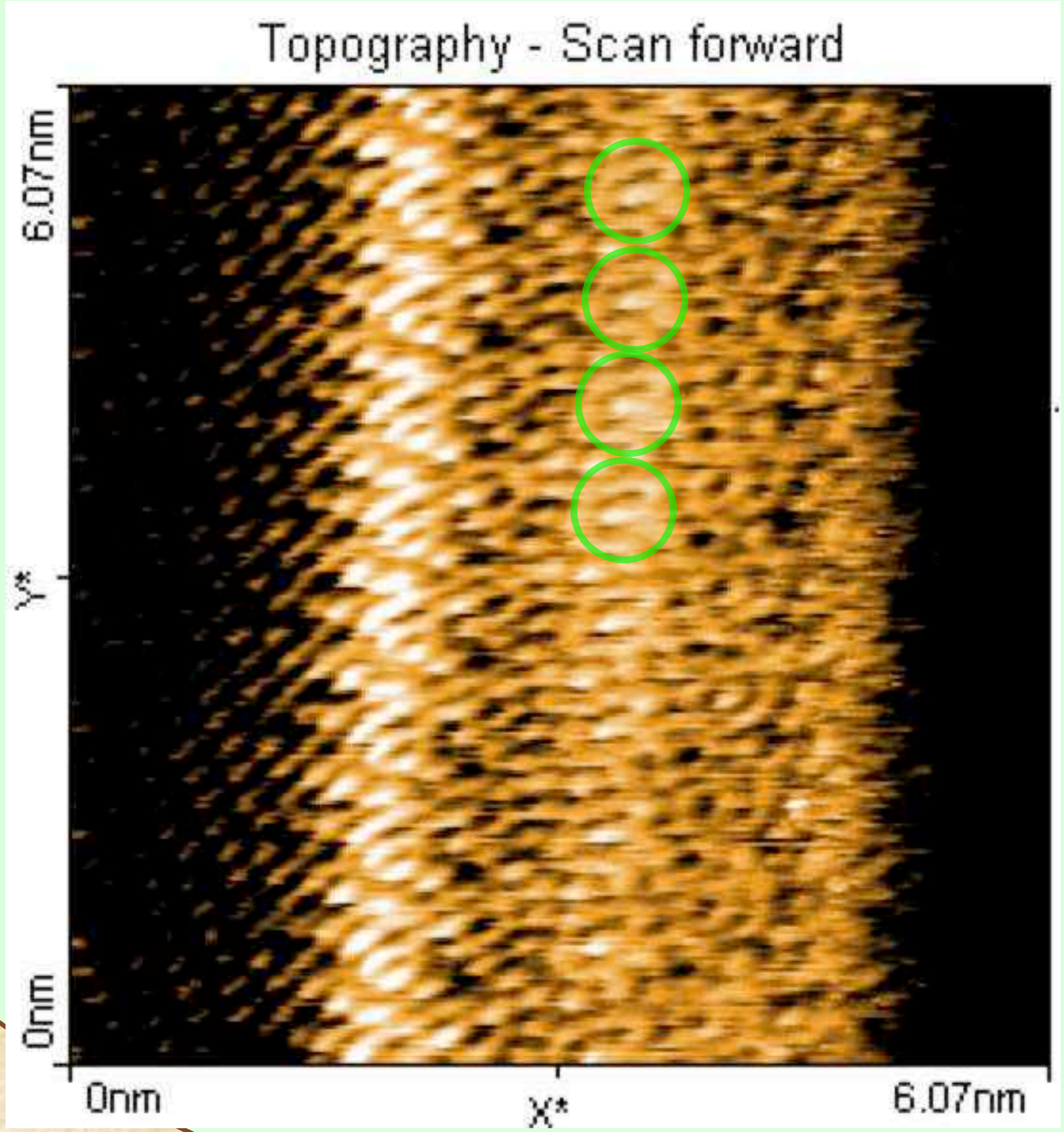
世界で初めて見えた
新種の構造を持つ
DNA！

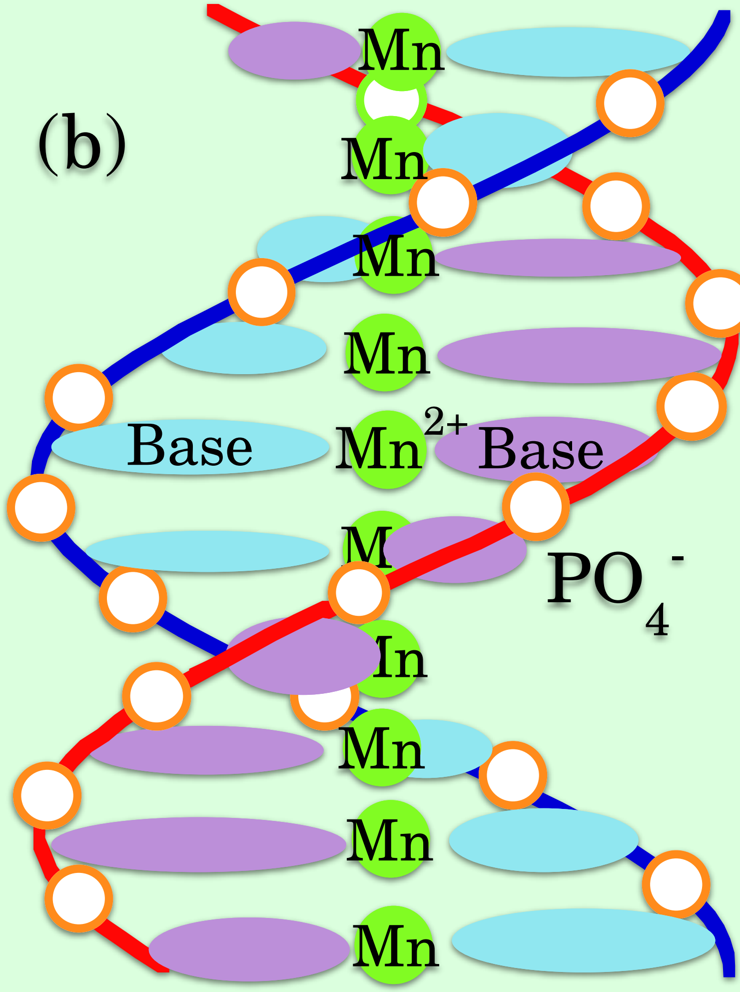
有 機 物 質



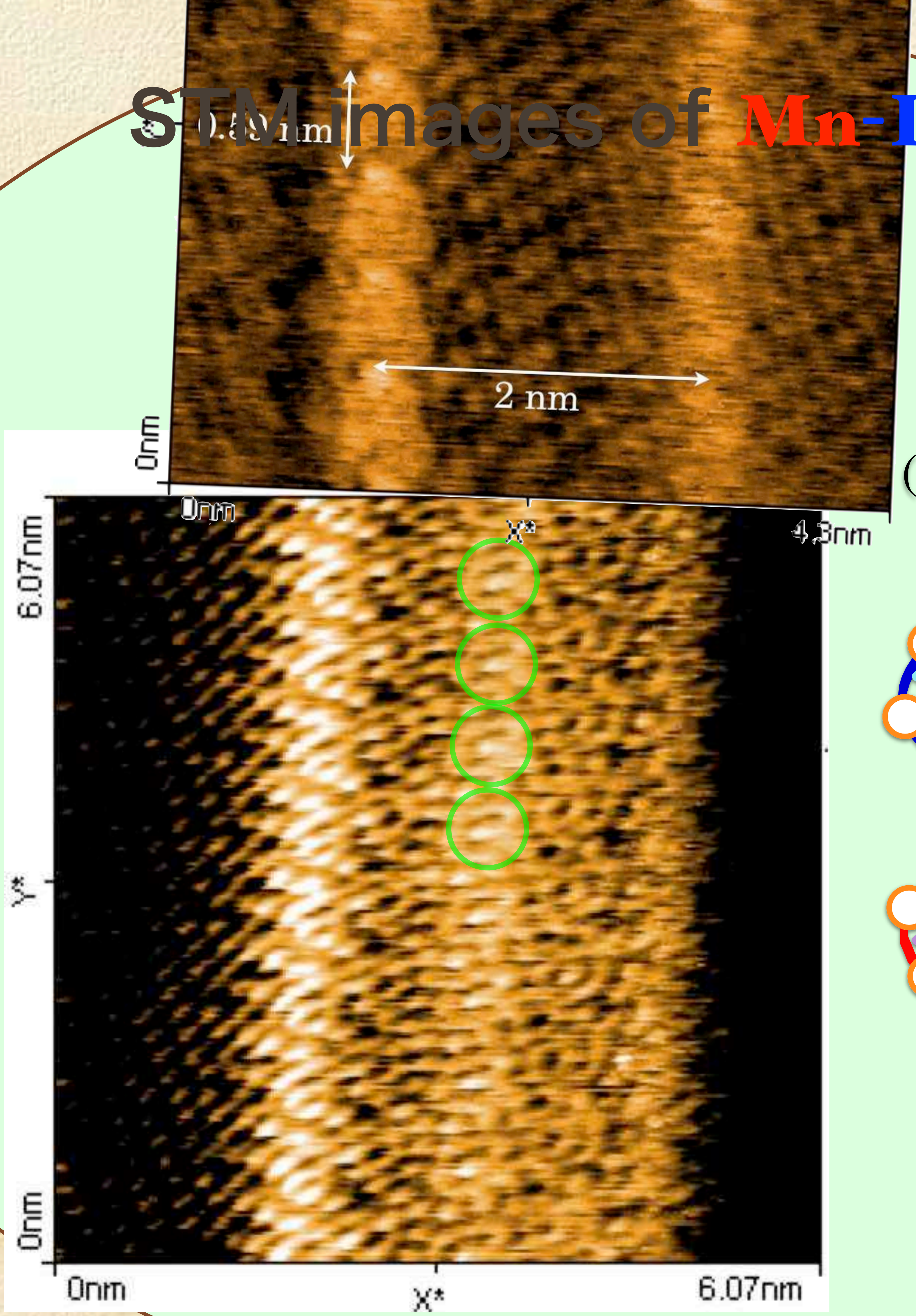
PO_4^-イオンと導体表面の
鏡像電荷と
の引力が原因か?

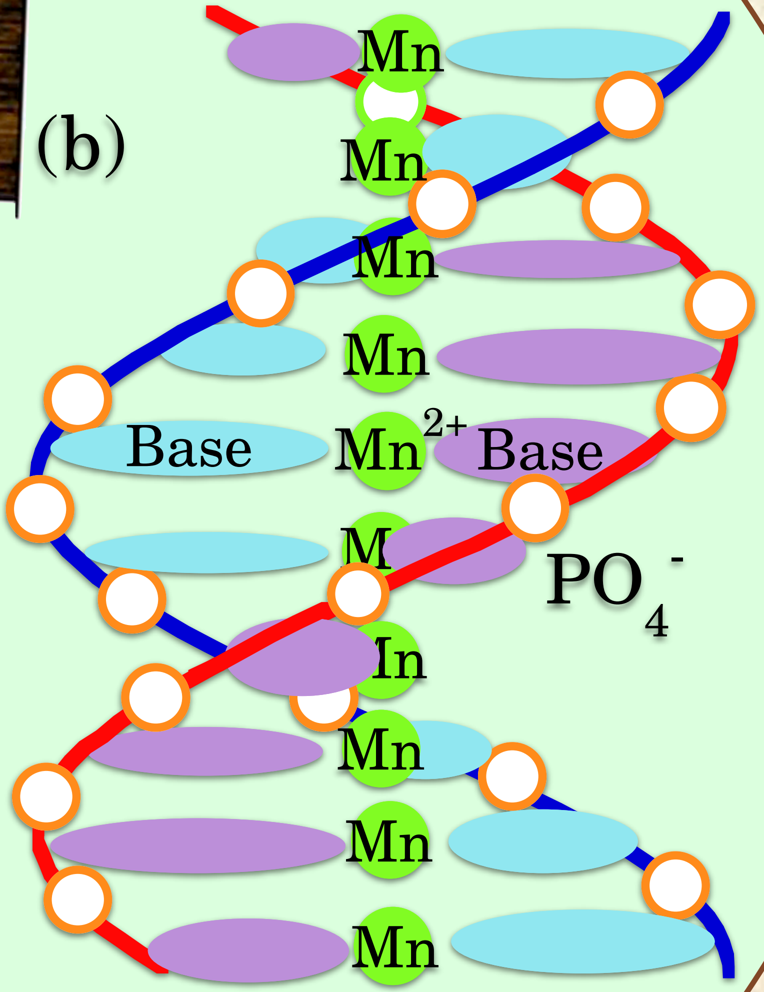
STM images of Mn-DNA



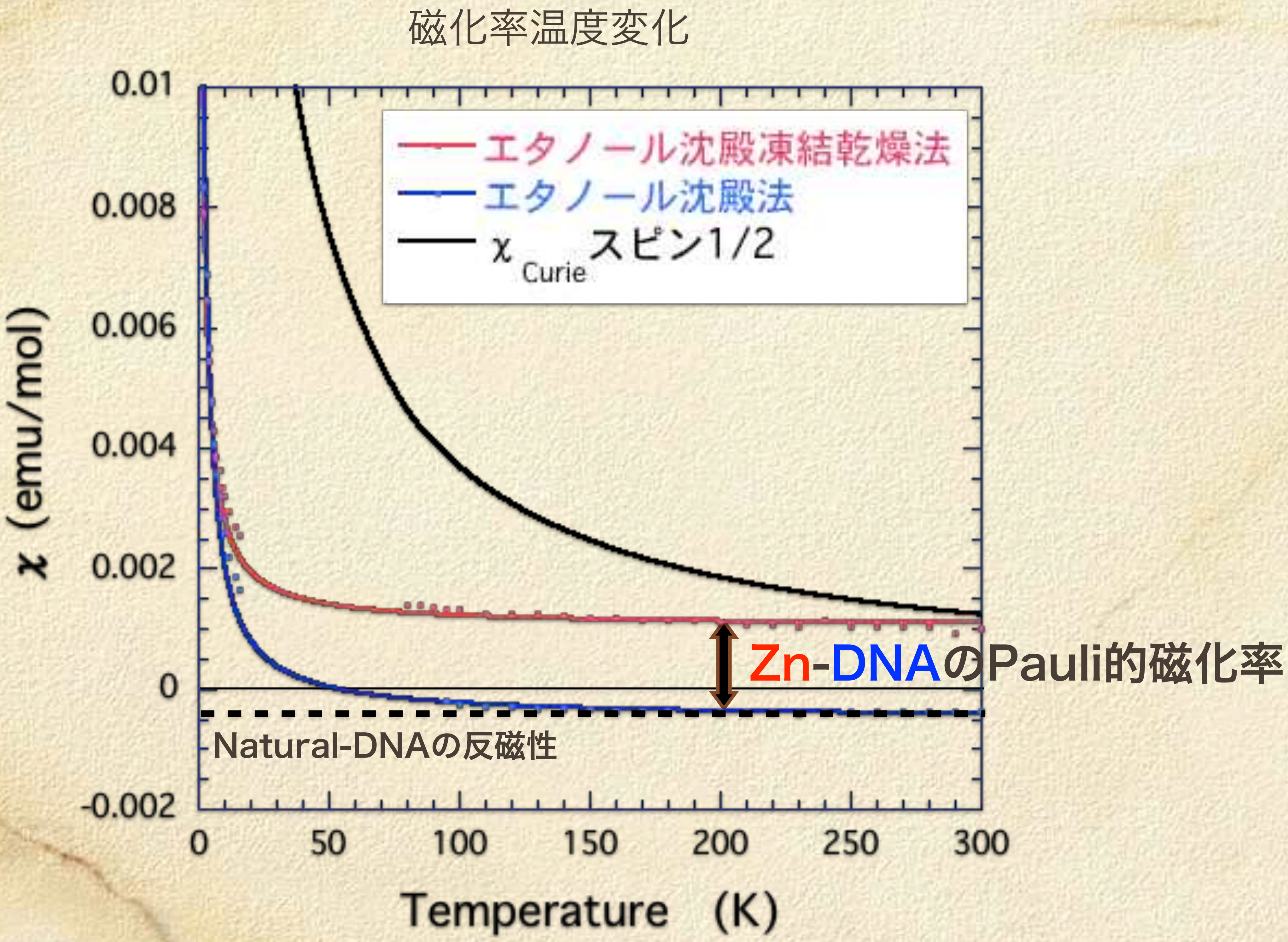


STM images of Mn-DNA





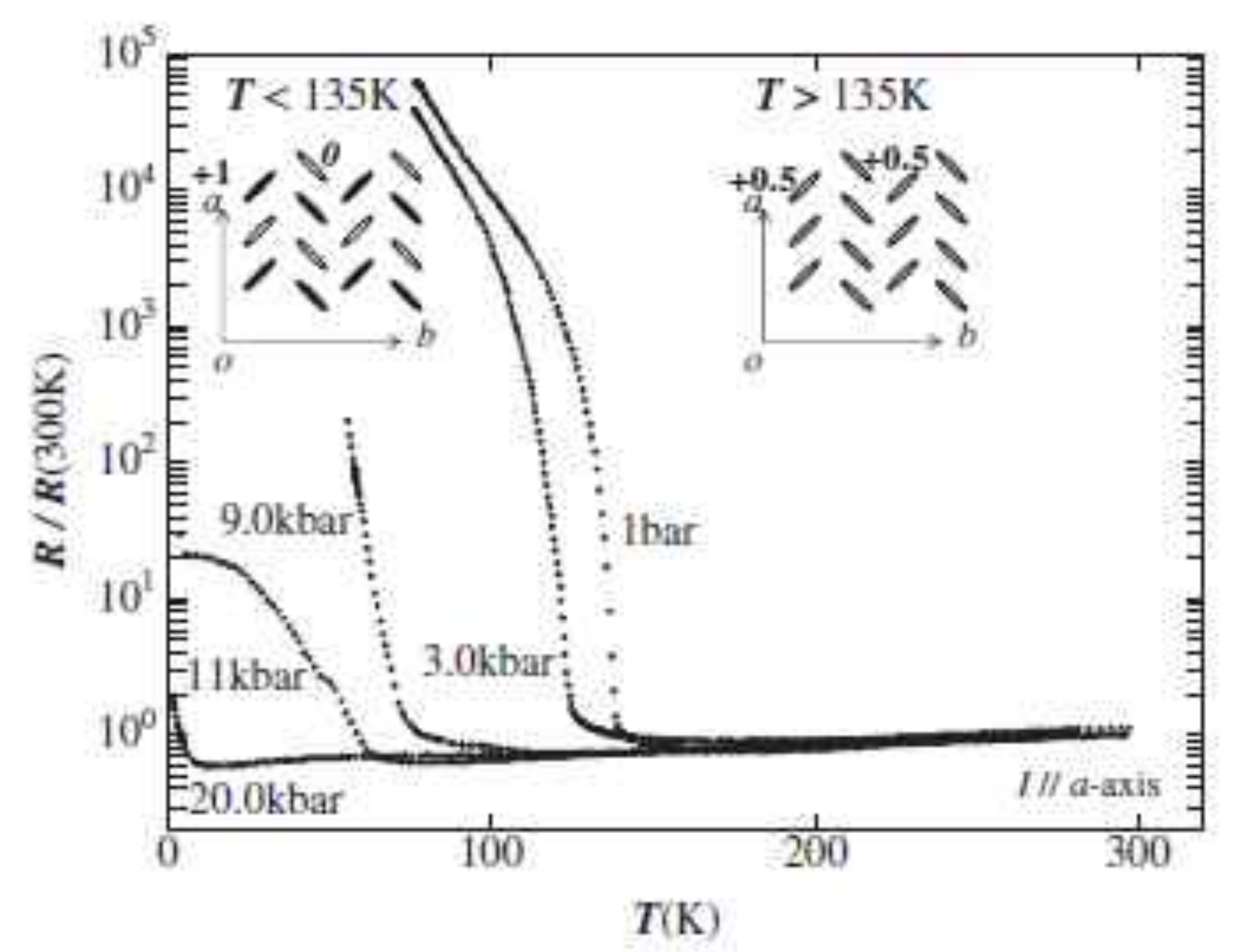
Zn-DNAの磁化率

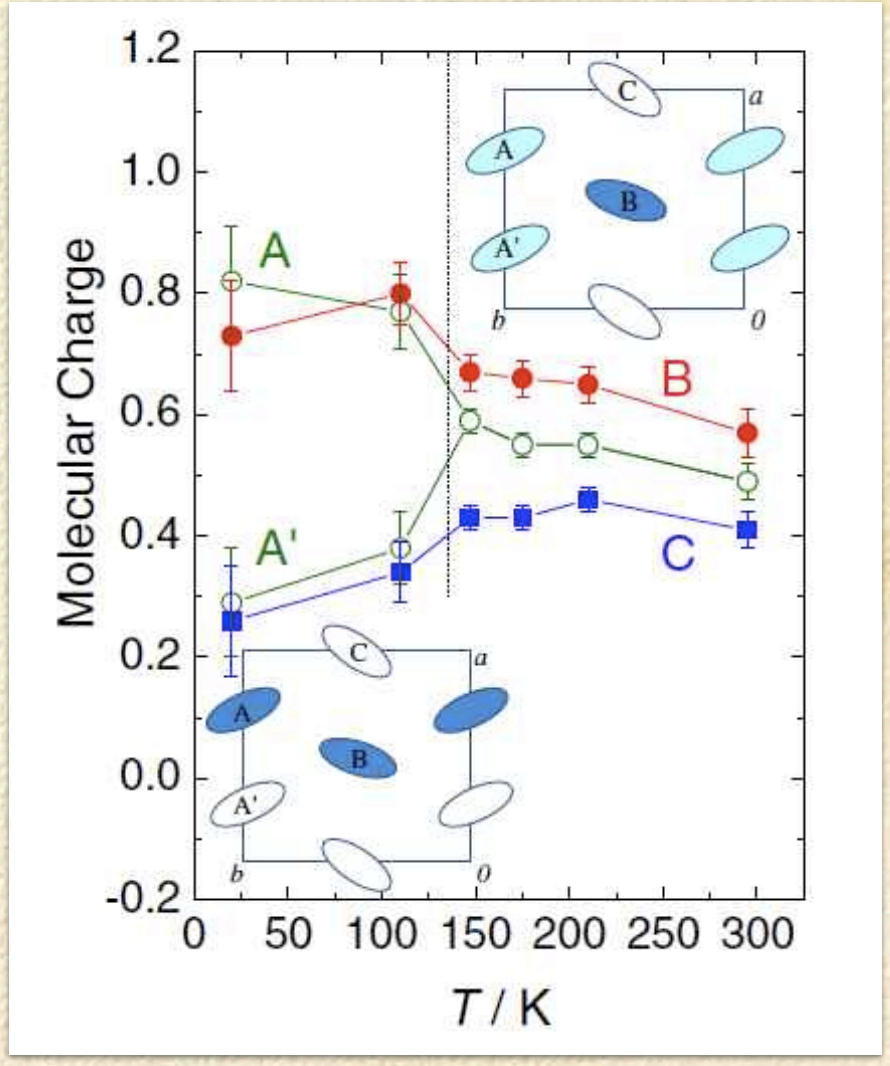

磁化率温度変化
エタノール沈殿凍結乾燥法
エタノール沈殿法
χ Curie スピン1/2
χ (emu/mol)
0.01
0.008
0.006
0.004
0.002
0
-0.002
0
50
100
150
200
250
300
Temperature (K)
Zn-DNAのPauli的磁化率
Natural-DNAの反磁性

有機物質

α-$(ET)_2I_3$ の表面電子状態

α-$(ET)_2I_3$ の物性

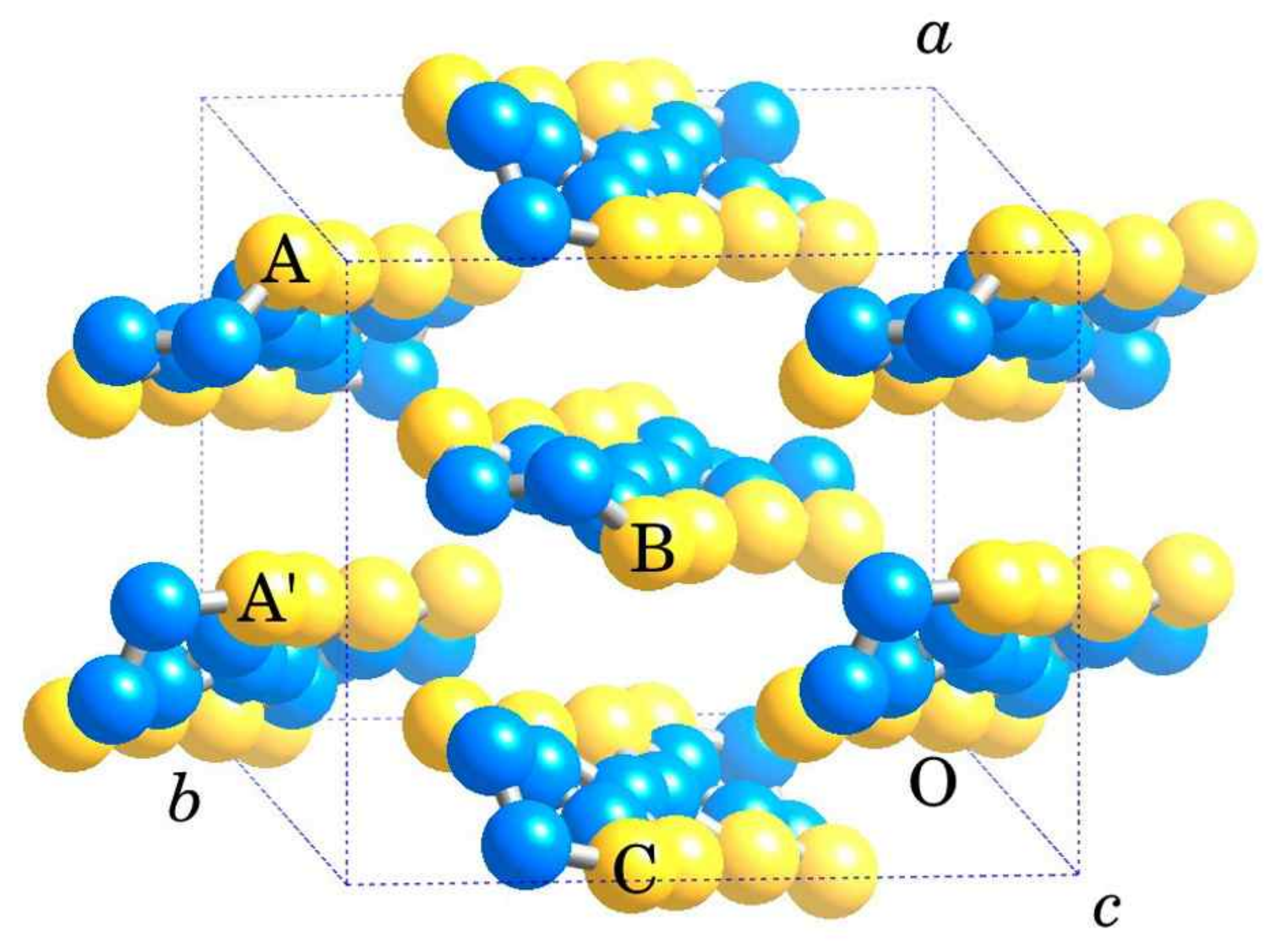




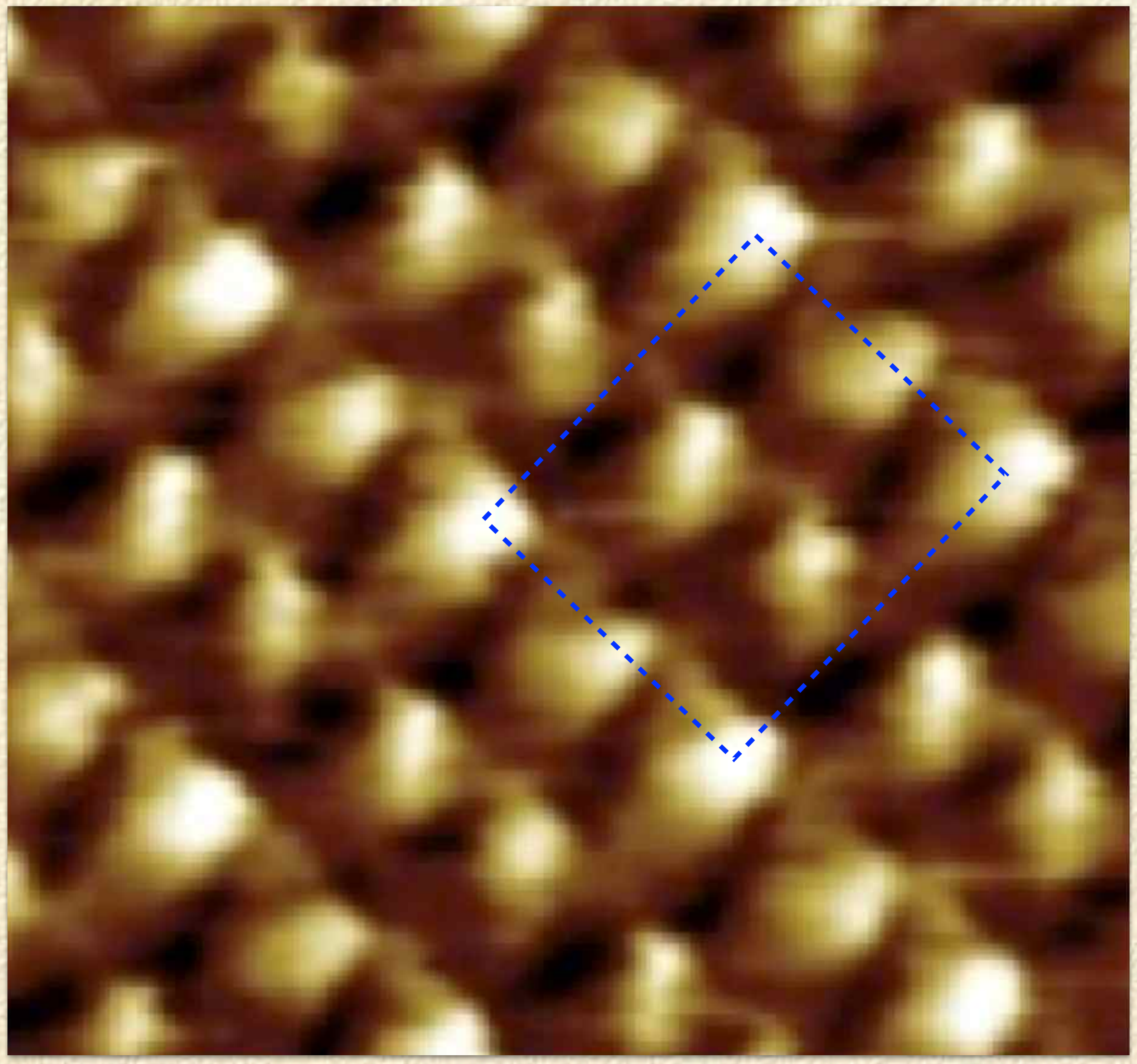
N. Tajima et al., JPSJ 69, (2000) 543
T. Kakiuchi, et al., JPSJ 76 (2007) 113702

室温：電荷不均化 金属相

135K以下：電荷秩序相


a
A
B
A'
O
b
C
c

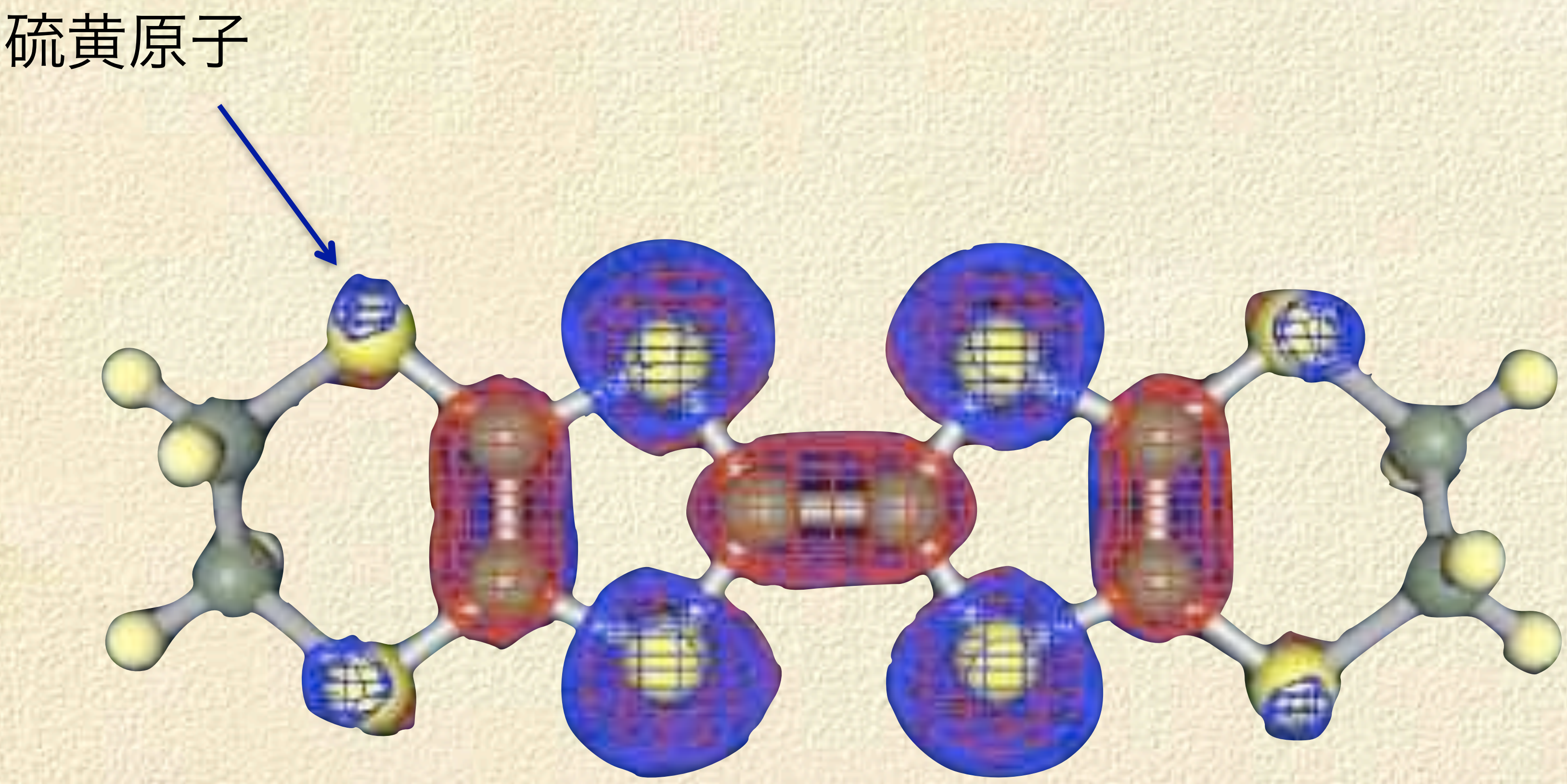
$\approx 2.8 \times 2.6 \text{ nm}^2$



$I = 1$ nA、$V = 10$ mV、*a*-*b* plane

観測している波動関数

MOPACを用いて計算したET分子のHOMO軌道



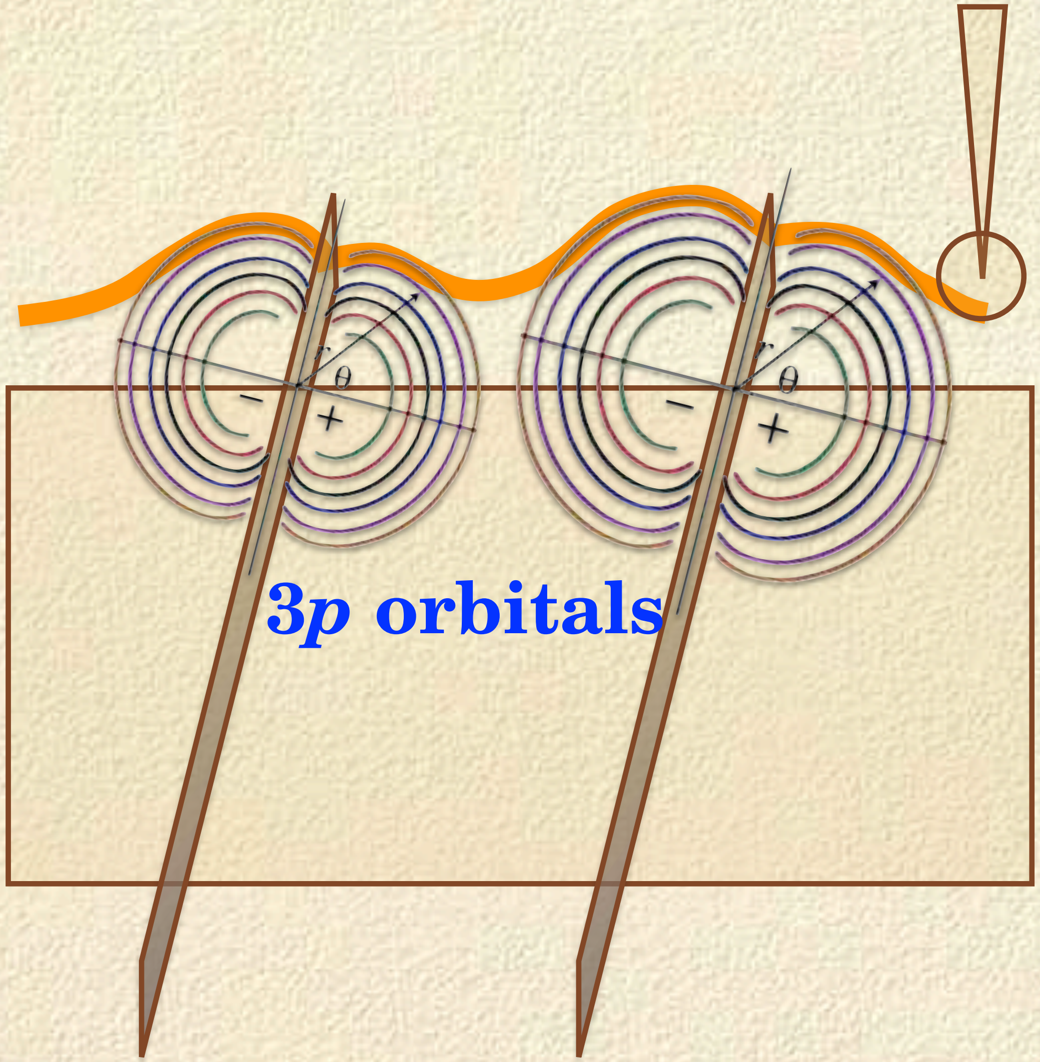
a-*b*面

STMでは端の硫黄3*p*軌道

弱い分子間相互作用

＝＞　**水素の波動関数**

Schematic image of topography

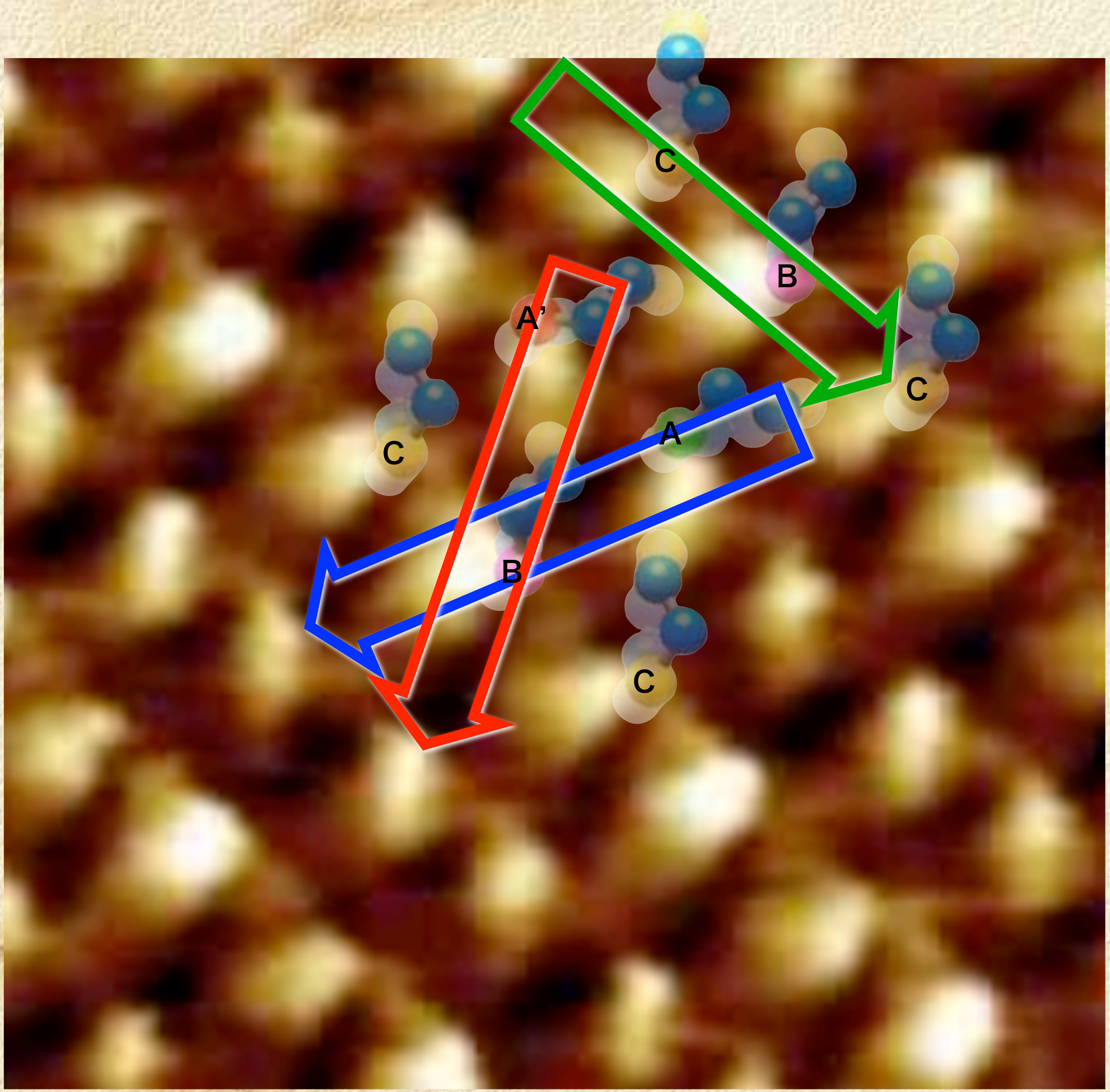


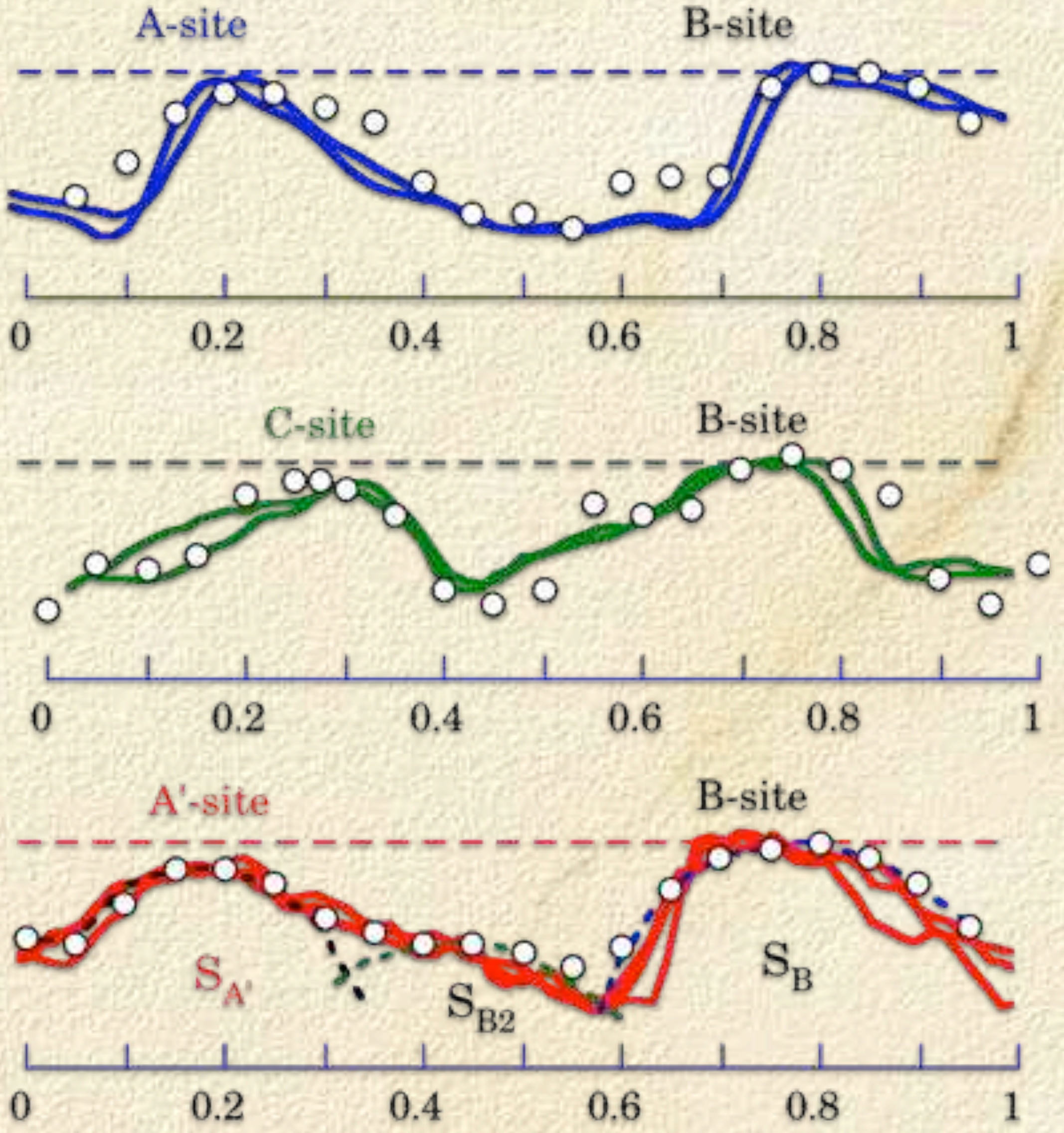
3*p* orbitals

molecular planes

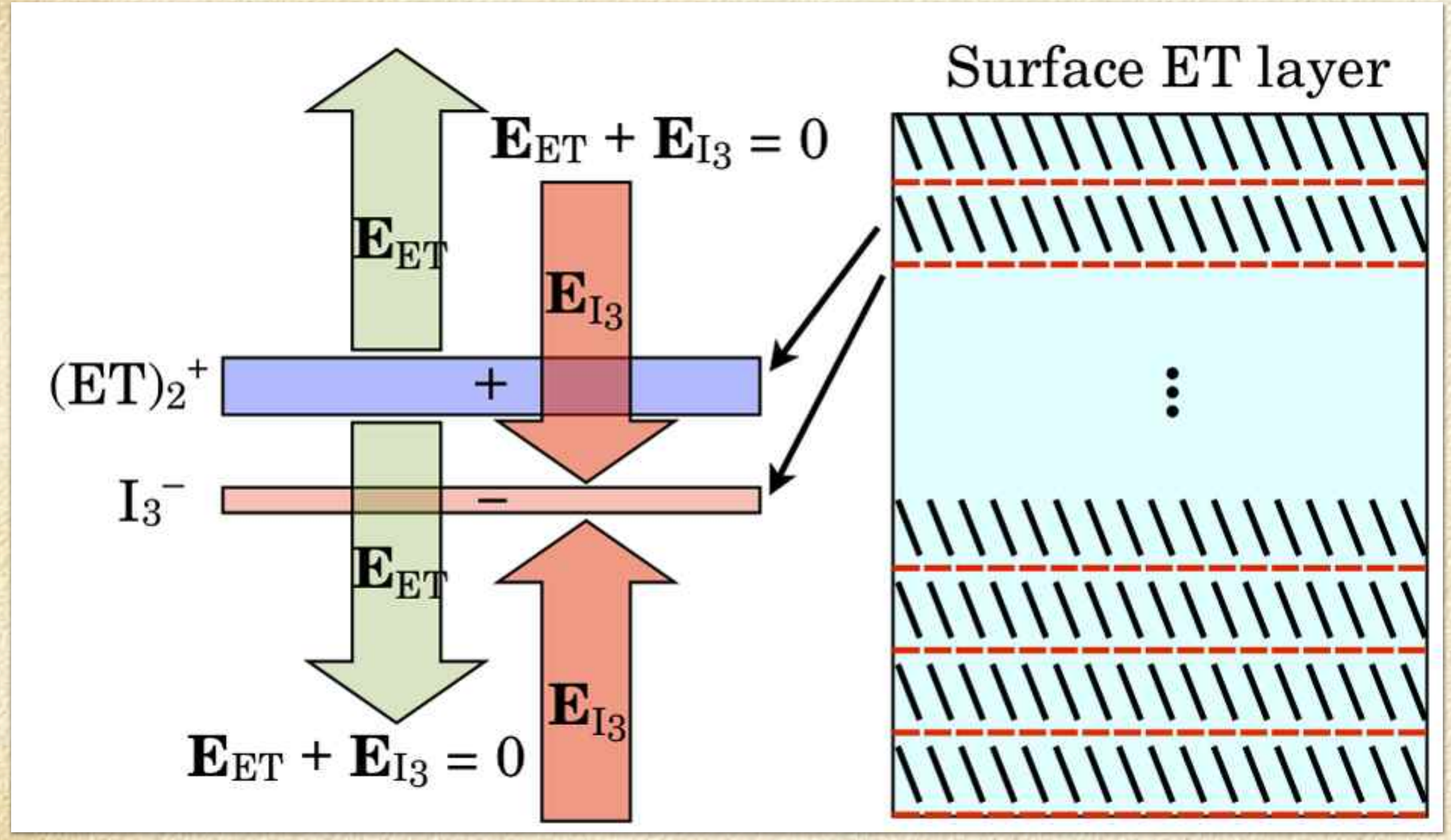
α-ET$_2$I$_3$: STM image in the *a*-*b* plane

Site assignment

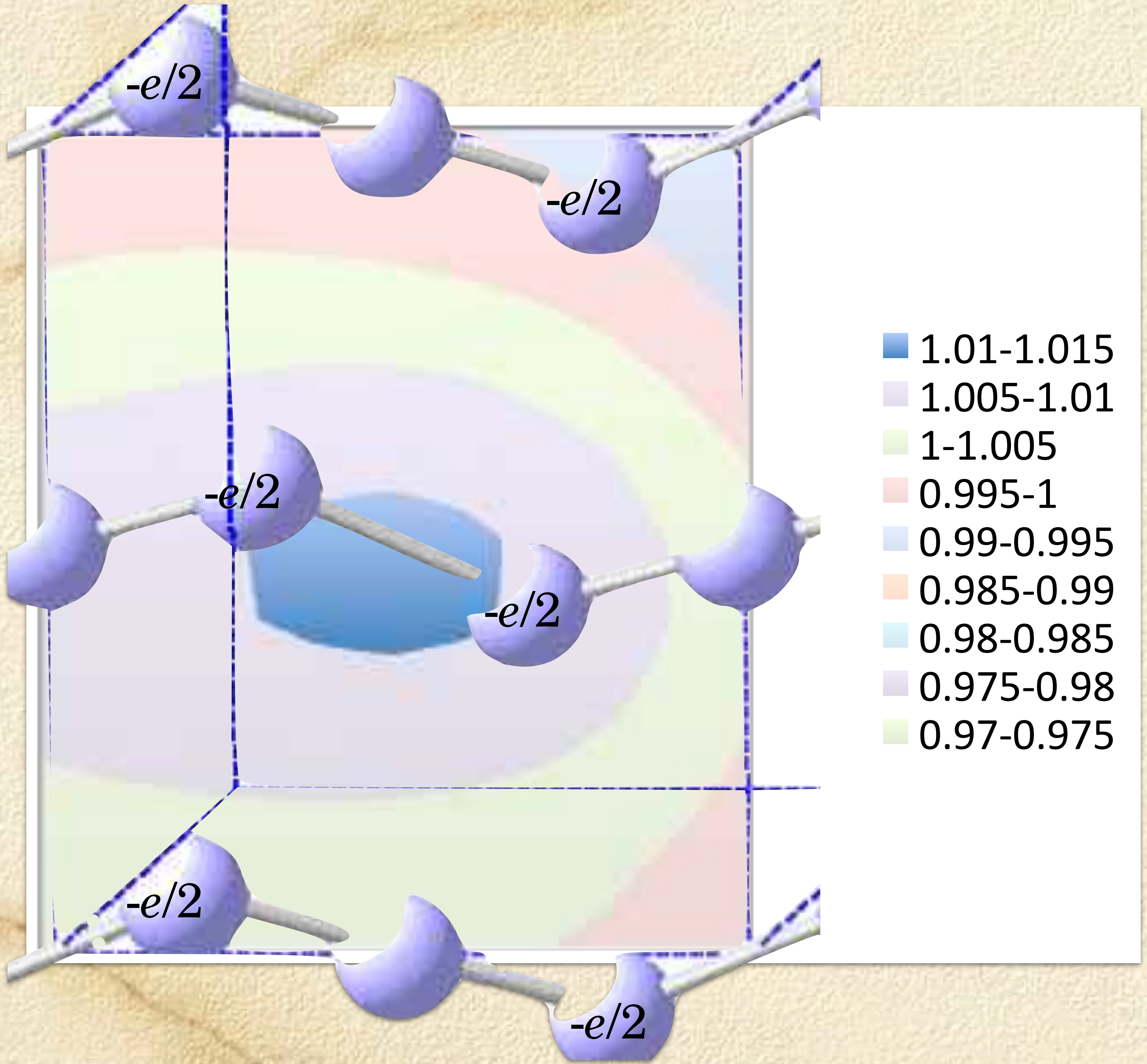




B) I_3 層と ET_2 層間のクーロン引力



I_3 層の作る電場



c^* ~~軸方向の表面再構成~~ ？

B サイト

分子電荷最大 => I_3 層への引力最大

STM チップ高さ最小？

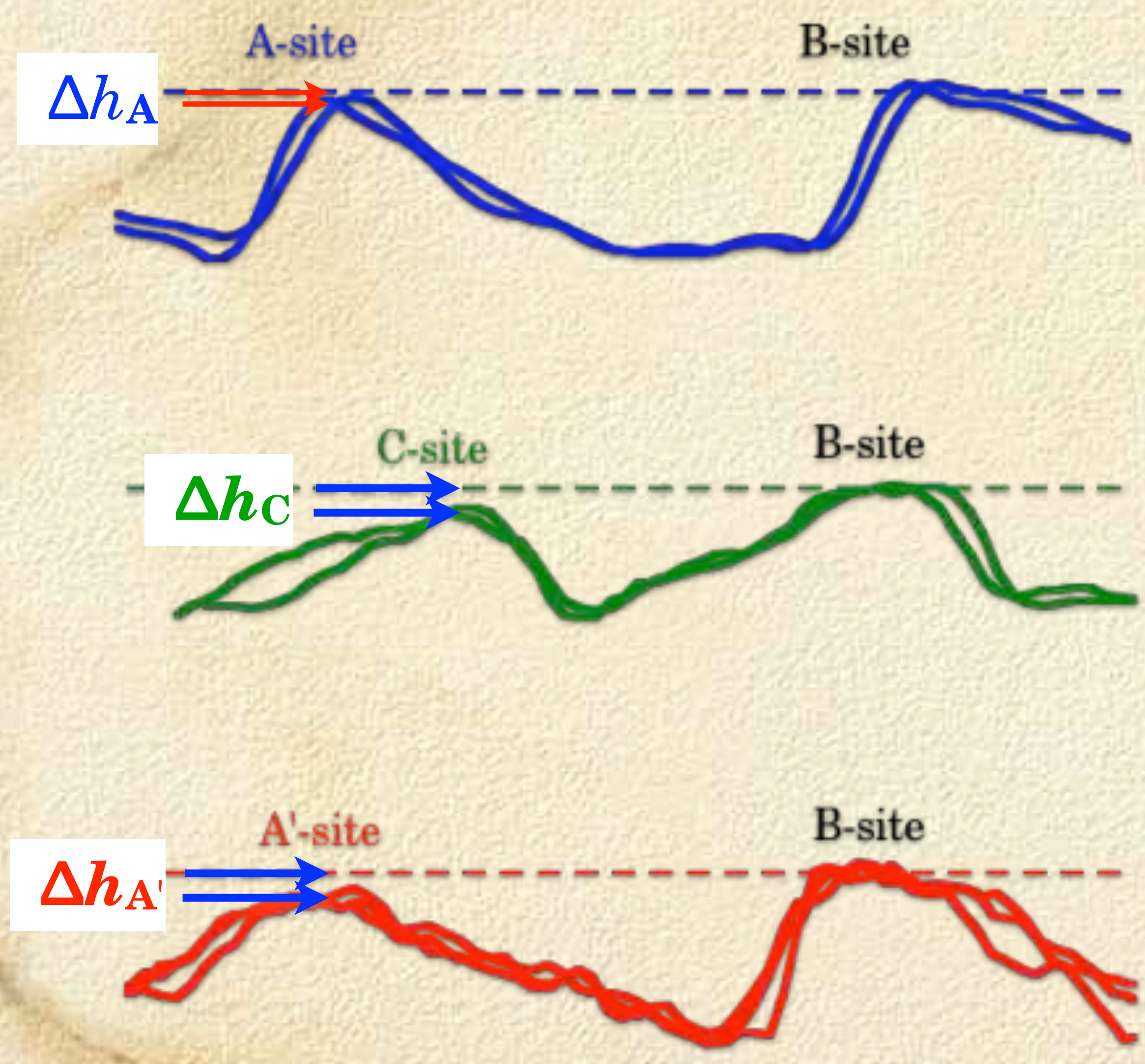
No！（最大）

⬇

ET$_2$ 層内の２次元電子状態

による分子電荷の表面再構成

Relative Molecular Charge $\rho_i / \Sigma\rho_i$

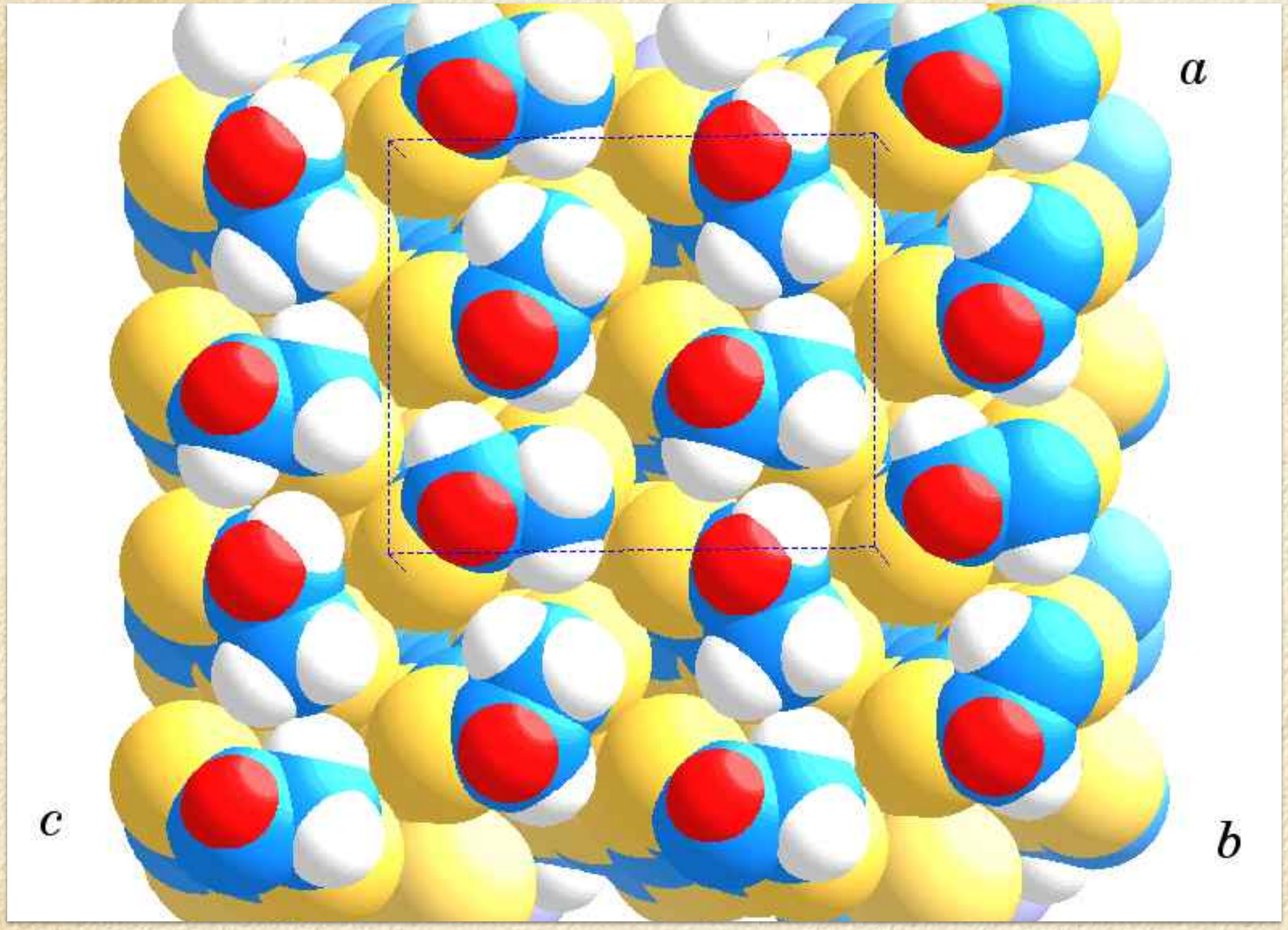


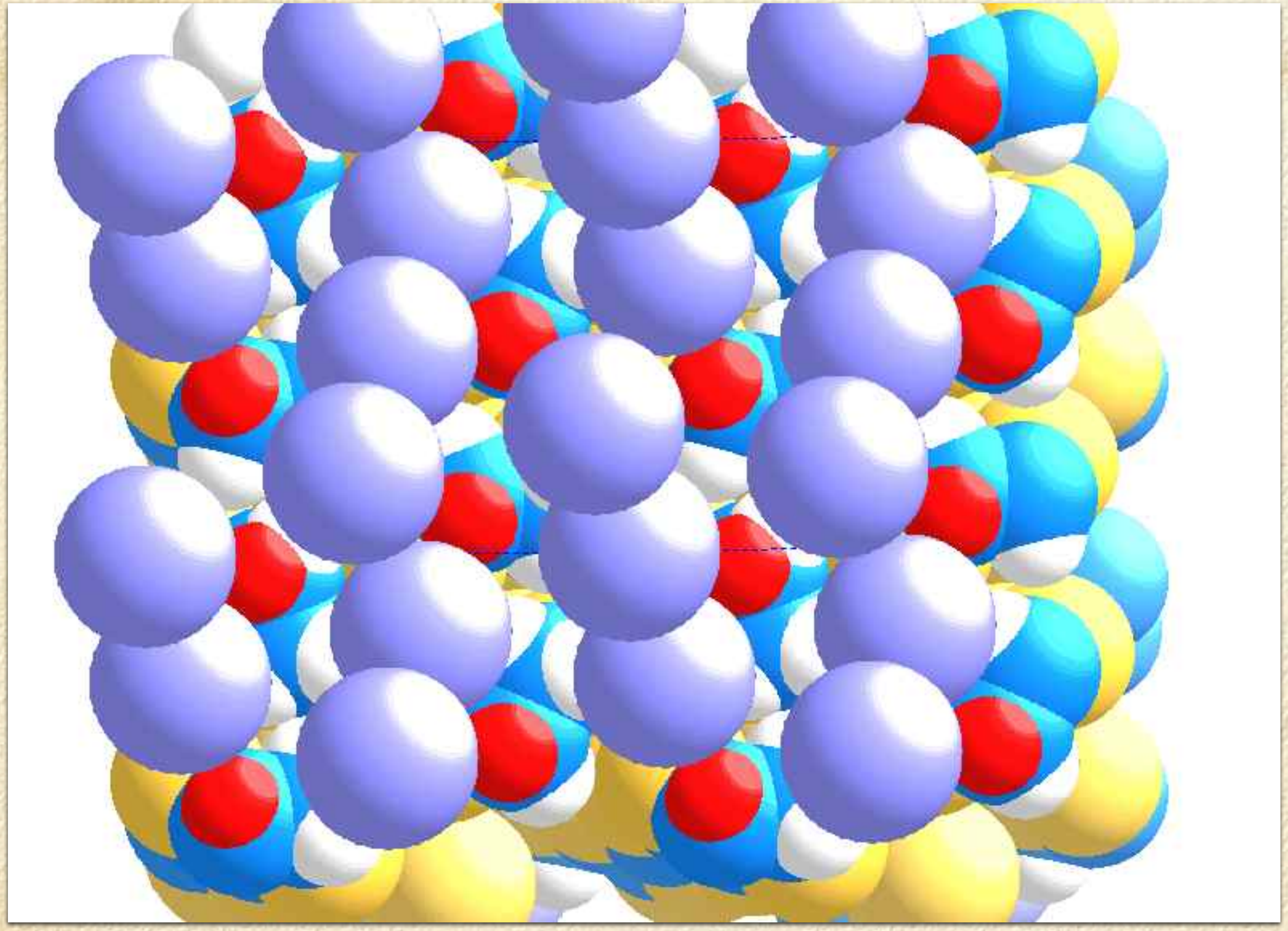
site	The present results	X-ray results	
	RT	RT	20 K
B	0.42(8)	0.29(2)	0.35(4)
C	0.16(2)	0.21(3)	0.12(5)
A	0.26(5)	0.25(2)	0.39(5)
A’	0.16(2)	0.25(2)	0.14(5)
	CO?	**CD**	**CO**

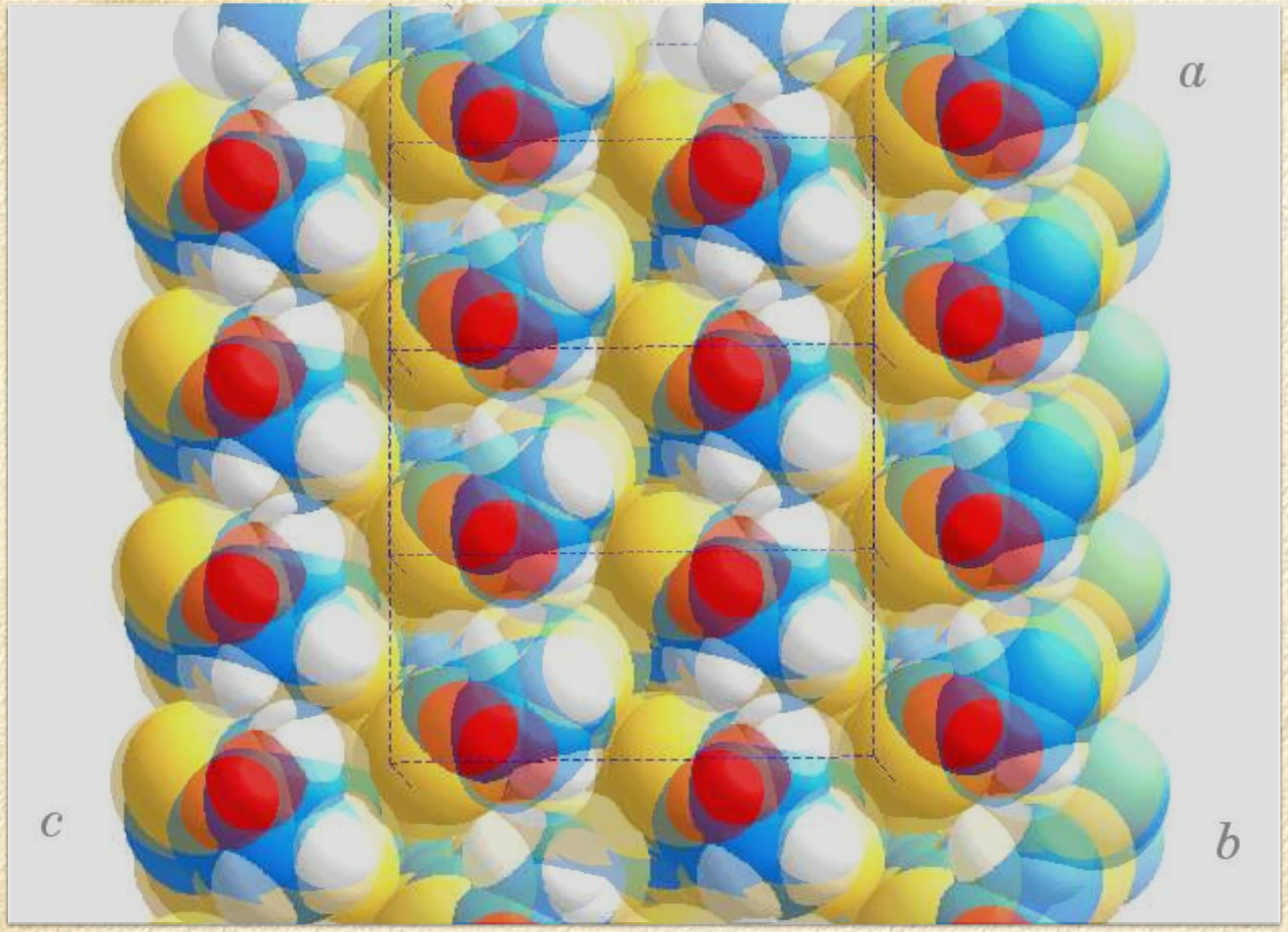
室温にて

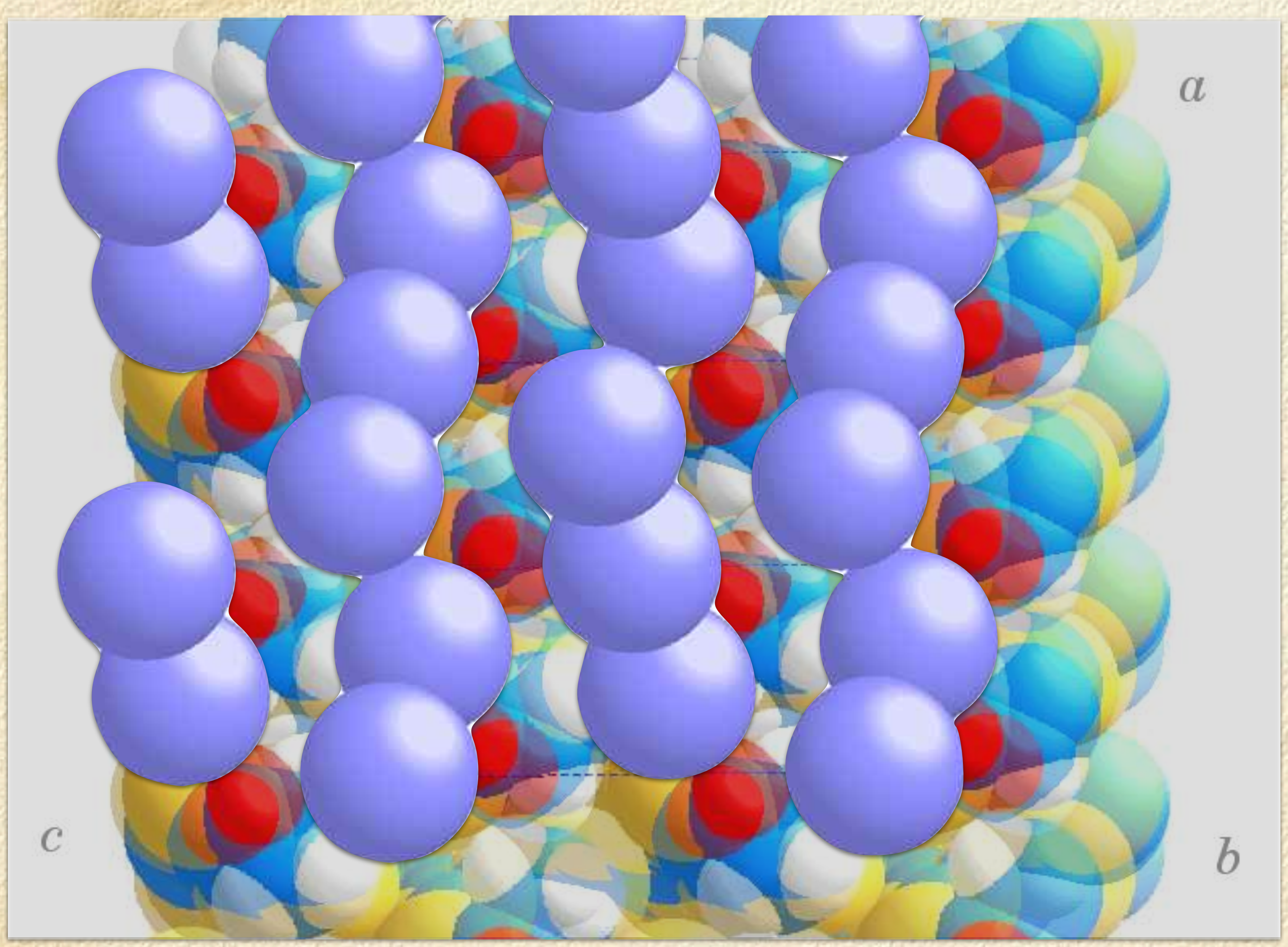
B–A–B type

horizontal stripe?


a
c
b




a
c
b


a
c
b

Summary

1. α-ET_2I_3の表面層に**横ストライプ電荷秩序（室温）**

2. 片側の **I_3** 層の**欠如**が生む表面 **ET_2** 面内**分子配向自由度の付加**

   ＝＞ 表面 **ET_2** シートの**最安定電子状態（電荷秩序）**の実現

3. **析出型層状**結晶に**共通**の現象？