

Люминесценция: не только красиво, но и полезно

Уточникова Валентина Владимировна









WILLEMITE (fl. green)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

CALCITE (fl. blue-white, green)
Quartz Mountain
New York, New York

AGATE
New Agate, SD

OPAL
New Agate, SD

FLUORITE (fl. yellow)
Franklin, NJ

CALCITE (fl. red)
FLUORITE (fl. blue)
Hessenthal, Rhine Region, Hesse
Hesse, Germany

FLUORITE (fl. orange)
Franklin, NJ

WILLEMITE (fl. green)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

AGATE
New Agate, SD

WILLEMITE (fl. orange)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

AGATE (fl. green)
New Agate, SD

CALCITE (fl. red)
Hunan, Cheng Zhou Prov.
China

OPAL
New Agate, SD

PETRIFIED WOOD (fl. white)
Unknown locality

WILLEMITE (fl. green)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

CALCITE (fl. white)
Franklin, NJ

CALCITE (manganese) (fl. red)
Mesa Verde
Colorado

CALCITE (fl. blue-white)
Deming, New Mexico

FLUORITE
Hessenthal, Rhine Region, Hesse
Hesse, Germany

FLUORITE
White Rock Quarry
Clay Center, OH

FLUORITE (fl. red)
Franklin, NJ

WILLEMITE (fl. yellow-orange)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

WILLEMITE (fl. green)
Franklinite (non fl.)
Franklin, Sussex Co., NJ

SEMI OPAL (fl. white)
Peru

ANTHOPHYLLITE (fl. red)
TREMOLITE (fl. orange)
Balmat, New York

SODALITE (fl. green)
Ile-aux-Lacs, Greenland

CAVE ONYX (fl. blue-white)
Cave Rock Quarry
Corydon, Indiana

CERUSSITE
Mibladen, Morocco

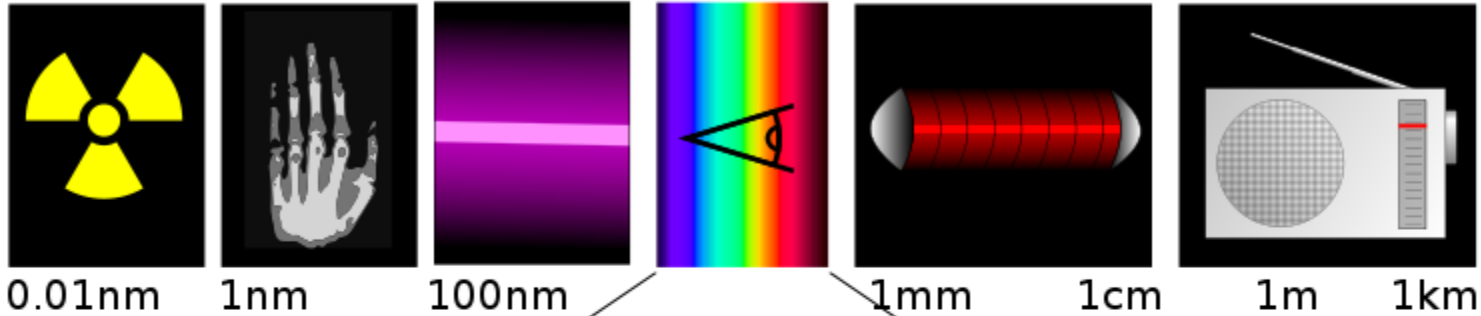
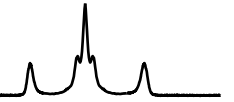
AGRELLITE
Kipawa River,
Temiscaming County,
Quebec, Canada

CALCITE (fl. red)
Hunan, Cheng Zhou Prov.
China

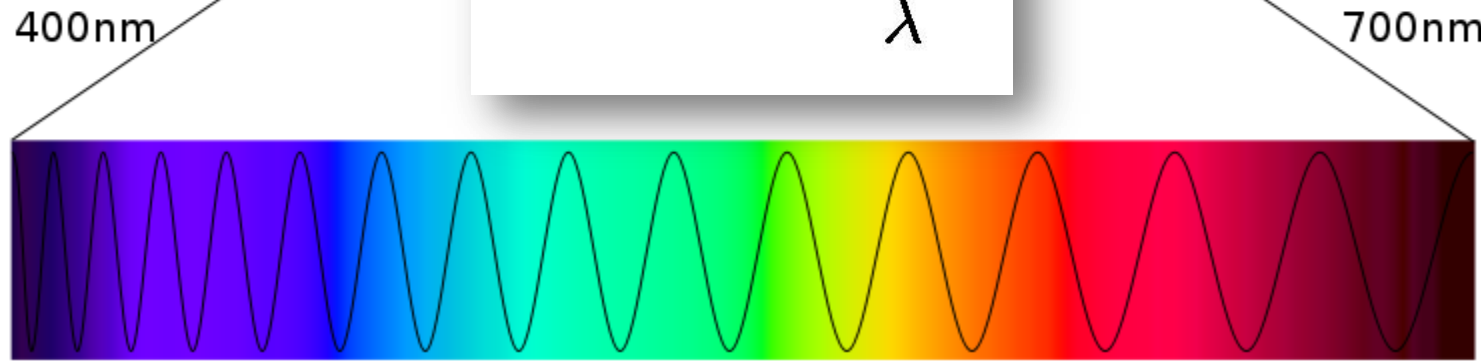
SODALITE (fl. orange)
Mont Saint-Hilaire
Quebec, Canada



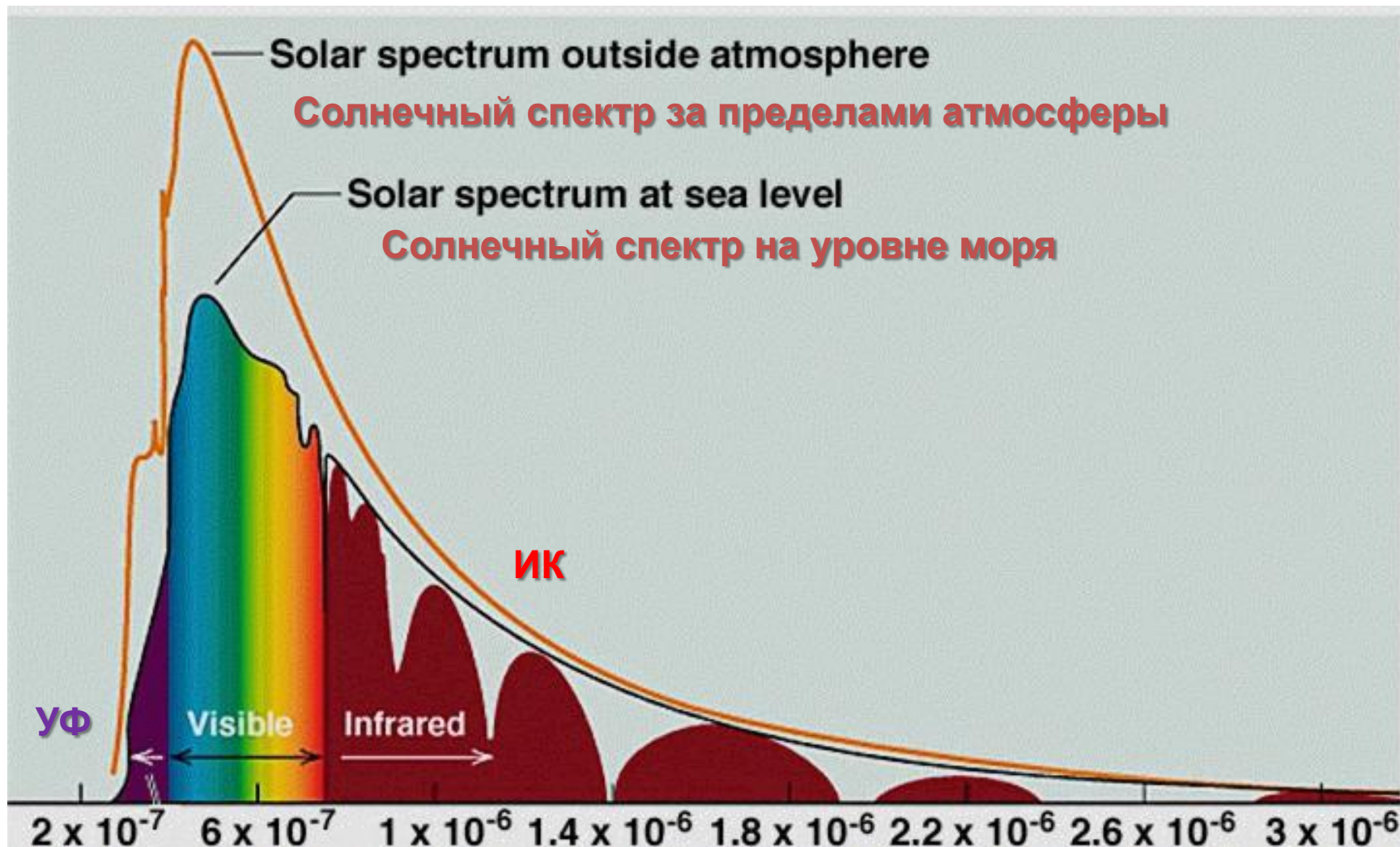
Свет



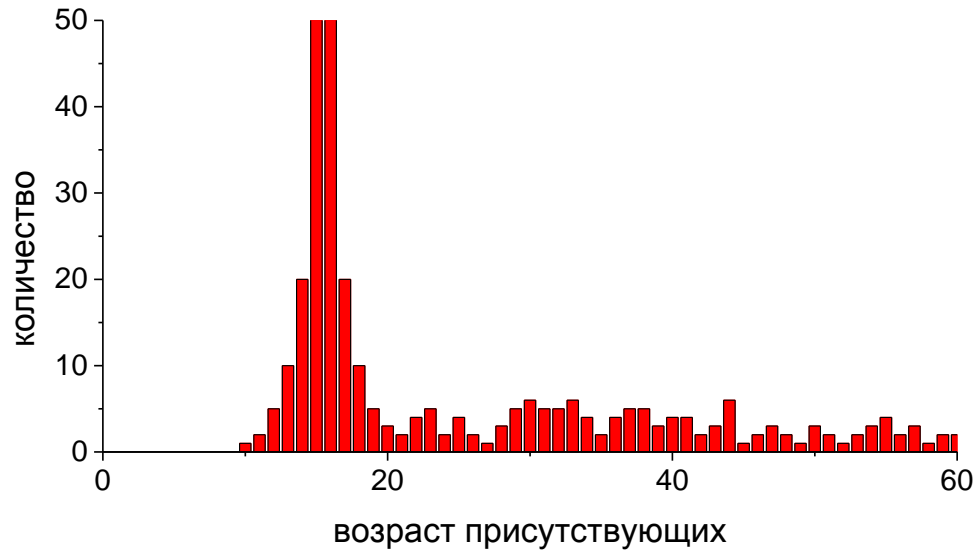
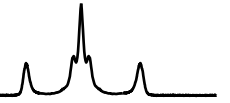
$$E = h\nu = \frac{hc}{\lambda}$$



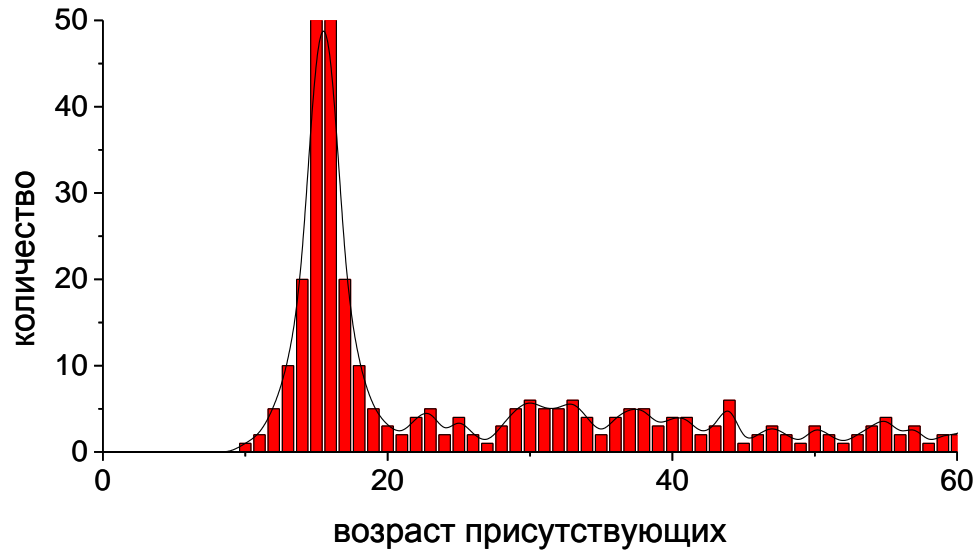
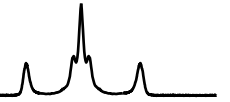
Видимый свет



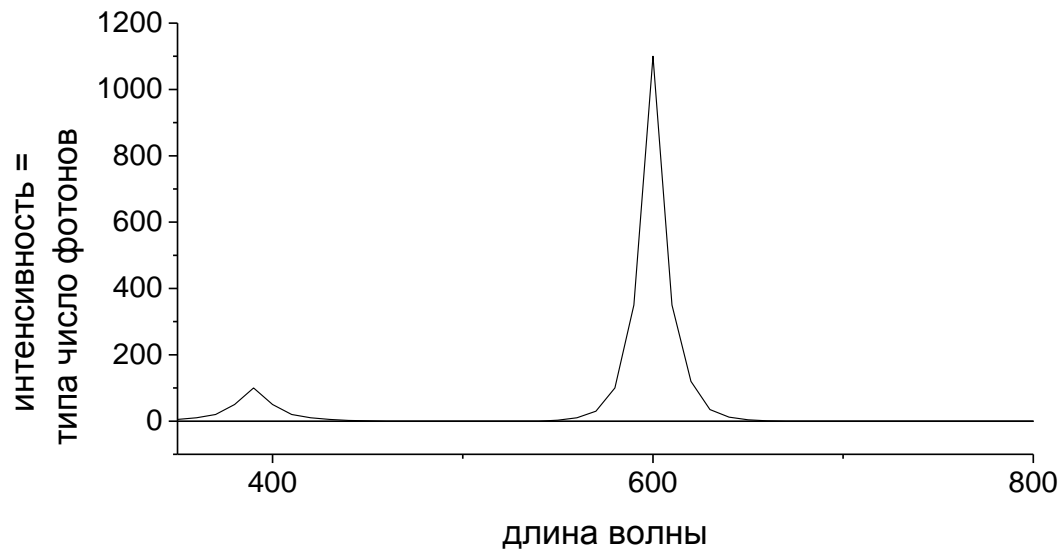
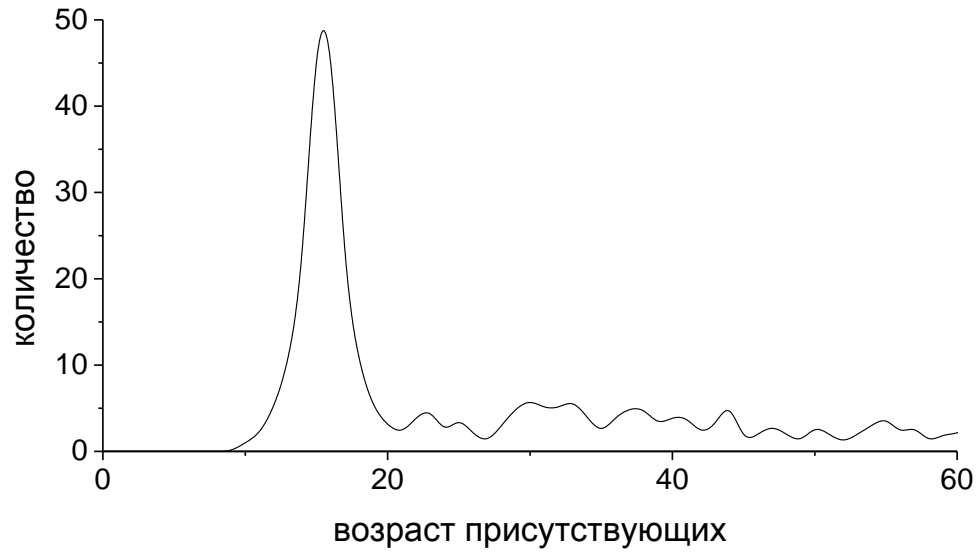
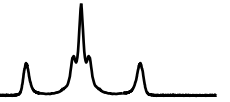
Спектр



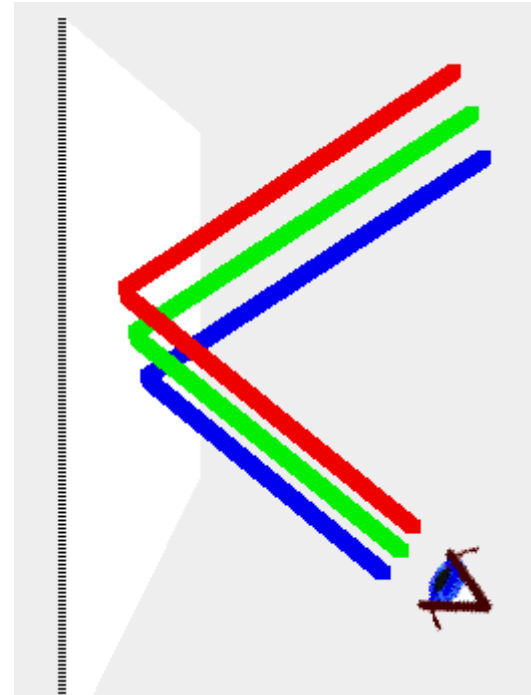
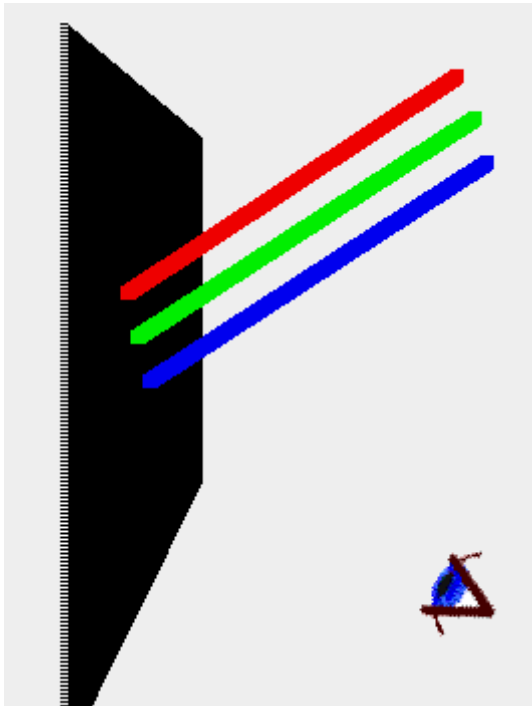
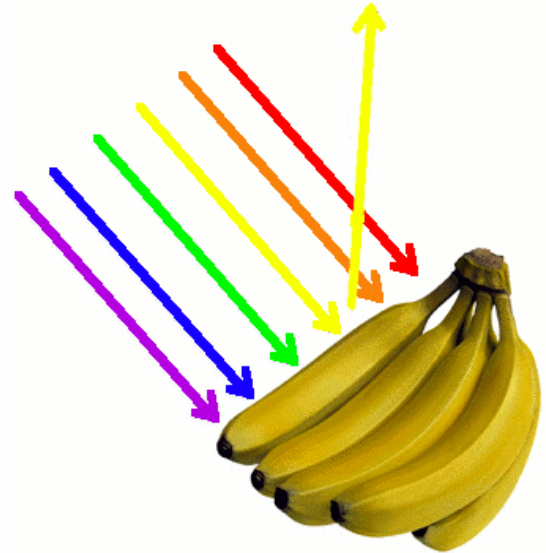
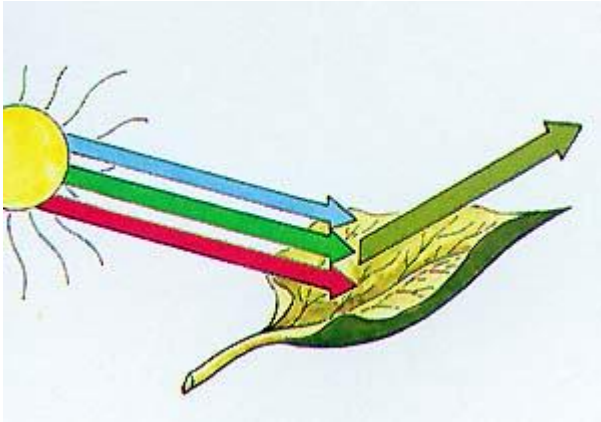
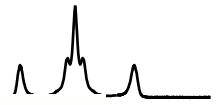
Спектр



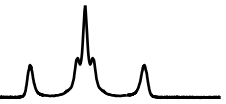
Спектр



Поглощение = окраска



Вещества состоят из атомов



PRODUCED BY THE FOUNDATION FOR EDUCATION, SCIENCE AND TECHNOLOGY FOR NATIONAL SET WEEK 2003

PERIODIC TABLE of the ELEMENTS



Proudly sponsored by the SHUTTLEWORTH FOUNDATION

VIII A 18
He
Helium 2
4.00

IA 1
H
Hydrogen 1
1.01

IIA 2
Li
Lithium 3
6.94

Be
Beryllium 4
9.01

III A 13
B
Boron 5
10.81

Mg
Magnesium 12
24.31

H
Hydrogen 1.01

Legend:
 ALKALI METALS
 ALKALI EARTH METALS
 TRANSITION METALS
 OTHER METALS
 OTHER NONMETALS
 HALOGENS
 NOBLE GASES
 DIATOMIC MOLECULES
 DIATOMIC GASES
 DIATOMIC LIQUIDS
 DIATOMIC SOLIDS

At room temperature the element is:
 Gas
 Liquid
 Natural solid
 Man-made solid (synthetic)

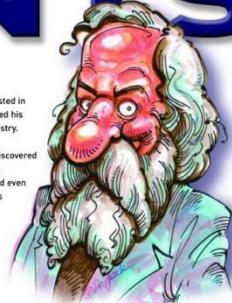
Symbol
 Element name
 Atomic number
 Atomic mass

DMITRI MENDELEYEV (1834 - 1907)

The Russian chemist, Dmitri Mendeleev, was the first to observe that if elements were listed in order of atomic mass, they showed regular (periodical) repeating properties. He formulated his discovery in a periodic table of elements, now regarded as the backbone of modern chemistry.

The crowning achievement of Mendeleev's periodic table lay in his prophecy of then, undiscovered elements. In 1869, the year he published his periodic classification, the elements gallium, germanium and scandium were unknown. Mendeleev left spaces for them in his table and even predicted their atomic masses and other chemical properties. Six years later, gallium was discovered and his predictions were found to be accurate. Other discoveries followed and their chemical behaviour matched that predicted by Mendeleev.

This remarkable man, the youngest in a family of 17 children, has left the scientific community with a classification system so powerful that it became the cornerstone in chemistry teaching and the prediction of new elements ever since. In 1955, element 101 was named after him: Md, Mendeleevium.



IVA 14
C
Carbon 6
12.01

N
Nitrogen 7
14.01

O
Oxygen 8
16.00

F
Fluorine 9
19.00

Al
Aluminum 13
26.98

Si
Silicon 14
28.09

P
Phosphorus 15
30.97

S
Sulphur 16
32.06

Cl
Chlorine 17
35.45

Neon
Ne
Neon 10
20.18

IV B 4
Ti
Titanium 22
47.88

Sc
Scandium 21
44.96

V
Vanadium 23
50.94

Cr
Chromium 24
52.00

Mn
Manganese 25
54.94

Fe
Iron 26
55.85

Co
Cobalt 27
58.93

Ni
Nickel 28
58.69

Cu
Copper 29
63.55

Zn
Zinc 30
65.39

Ga
Gallium 31
69.72

Ge
Germanium 32
72.61

As
Arsenic 33
74.92

Se
Selenium 34
78.96

Br
Bromine 35
79.90

Kr
Krypton 36
83.80

VB 5
Zr
Zirconium 40
91.22

Y
Yttrium 39
88.91

Nb
Niobium 41
92.91

Mo
Molybdenum 42
95.94

Tc
Technetium 43
(98)

Ru
Ruthenium 44
101.07

Rh
Rhodium 45
102.91

Pd
Palladium 46
106.42

Ag
Silver 47
107.87

Cd
Cadmium 48
112.41

In
Indium 49
114.82

Sn
Tin 50
118.71

Sb
Antimony 51
121.76

Te
Tellurium 52
127.60

I
Iodine 53
126.90

Xe
Xenon 54
131.29

VI B 6
Hf
Hafnium 72
178.49

Ba
Barium 56
137.33

Lanthanide Series

Ta
Tantalum 73
180.95

W
Tungsten 74
183.85

Re
Rhenium 75
186.21

Os
Osmium 76
190.23

Ir
Iridium 77
192.22

Pt
Platinum 78
195.08

Au
Gold 79
196.97

Hg
Mercury 80
200.59

Tl
Thallium 81
204.38

Pb
Lead 82
207.20

Bi
Bismuth 83
208.98

Po
Polonium 84
(209)

At
Astatine 85
(210)

Rn
Radon 86
(222)

VII B 7
Fr
Francium 87
(223)

Ra
Radium 88
(226)

Actinide Series

Rf
Rutherfordium 104
(261)

Db
Dubnium 105
(262)

Sg
Seaborgium 106
(263)

Bh
Bohrium 107
(262)

Hs
Hassium 108
(265)

Mt
Meitnerium 109
(266)

La
Lanthanum 57
138.91

Ce
Cerium 58
140.12

Pr
Praseodymium 59
140.91

Nd
Neodymium 60
144.24

Pm
Promethium 61
(145)

Sm
Samarium 62
150.36

Eu
Europium 63
151.96

Gd
Gadolinium 64
157.25

Tb
Terbium 65
158.93

Dy
Dysprosium 66
162.50

Ho
Holmium 67
164.93

Er
Erbium 68
167.26

Tm
Thulium 69
168.93

Yb
Ytterbium 70
173.04

Lu
Lutetium 71
174.96

Ac
Actinium 89
227.03

Th
Thorium 90
232.04

Pa
Protactinium 91
231.04

U
Uranium 92
238.03

Np
Neptunium 93
(237)

Pu
Plutonium 94
(244)

Am
Americium 95
(243)

Cm
Curium 96
(247)

Bk
Berkelium 97
(247)

Cf
Californium 98
(251)

Es
Einsteinium 99
(252)

Fm
Fermium 100
(257)

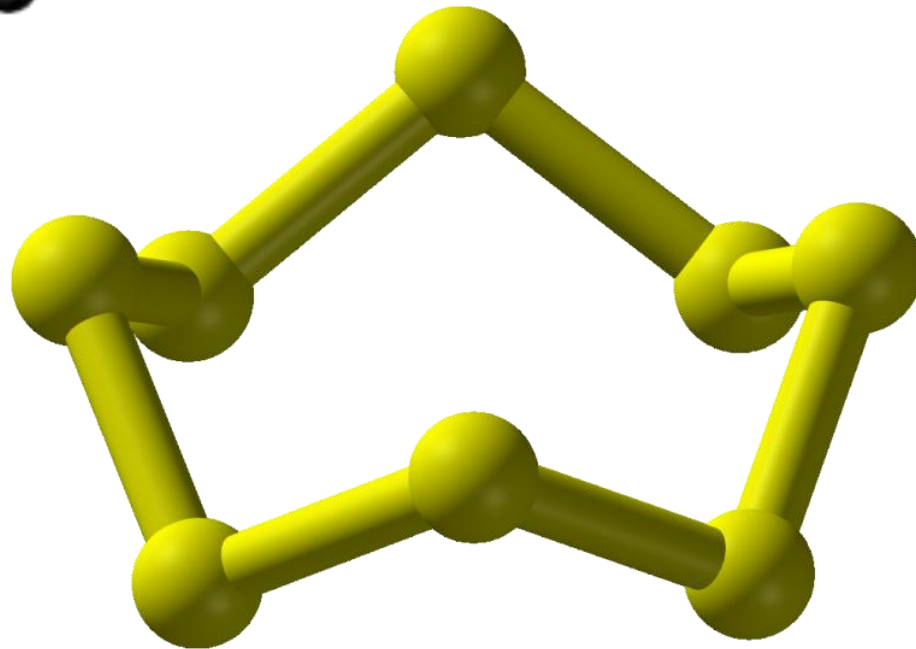
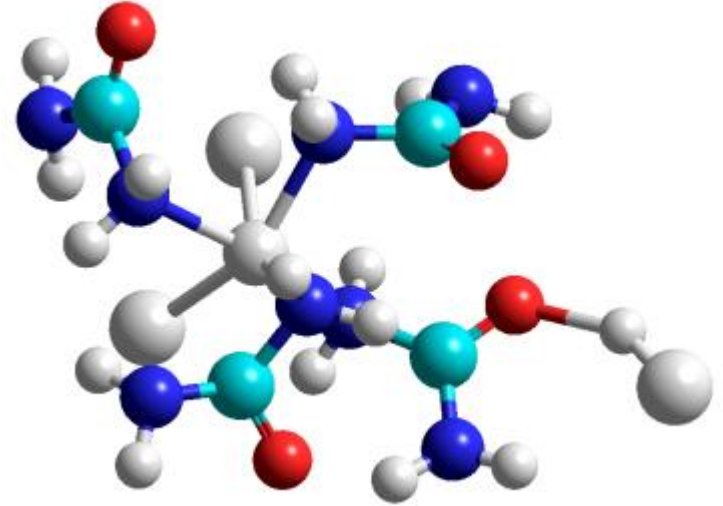
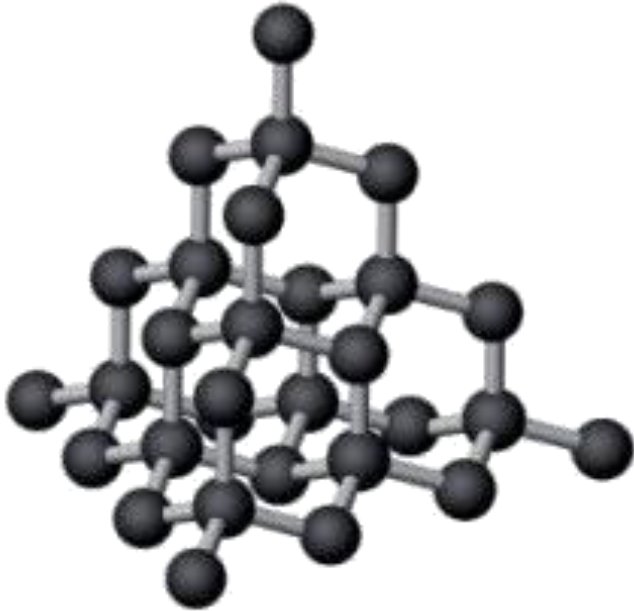
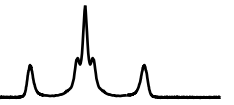
Md
Mendelevium 101
(258)

No
Nobelium 102
(259)

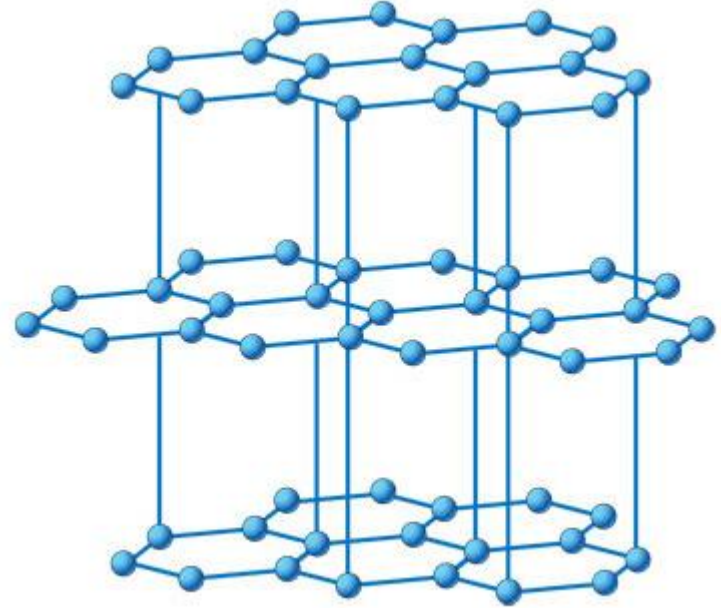
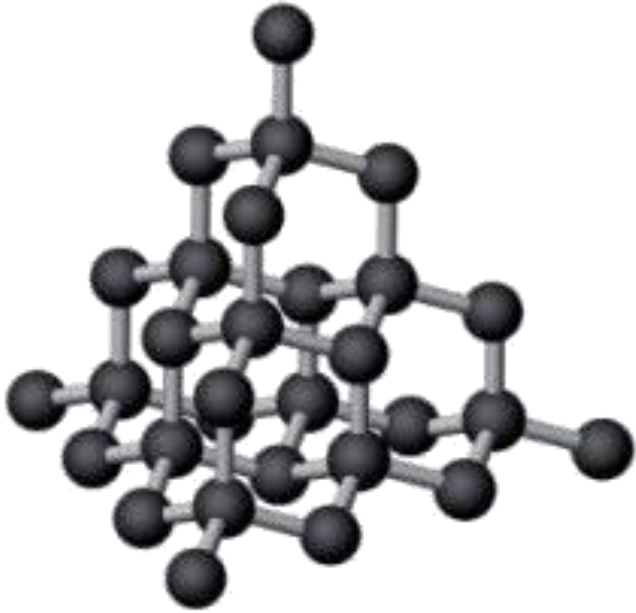
Lr
Lawrencium 103
(260)



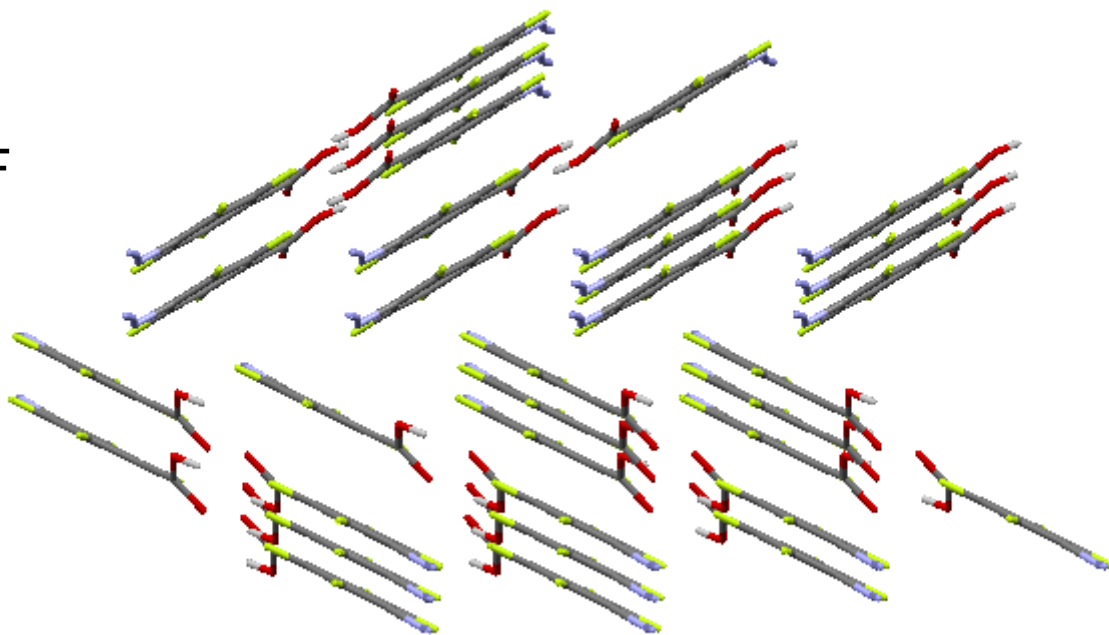
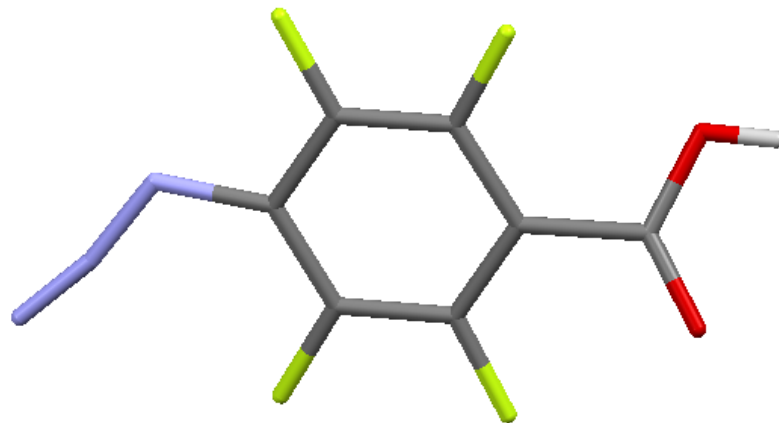
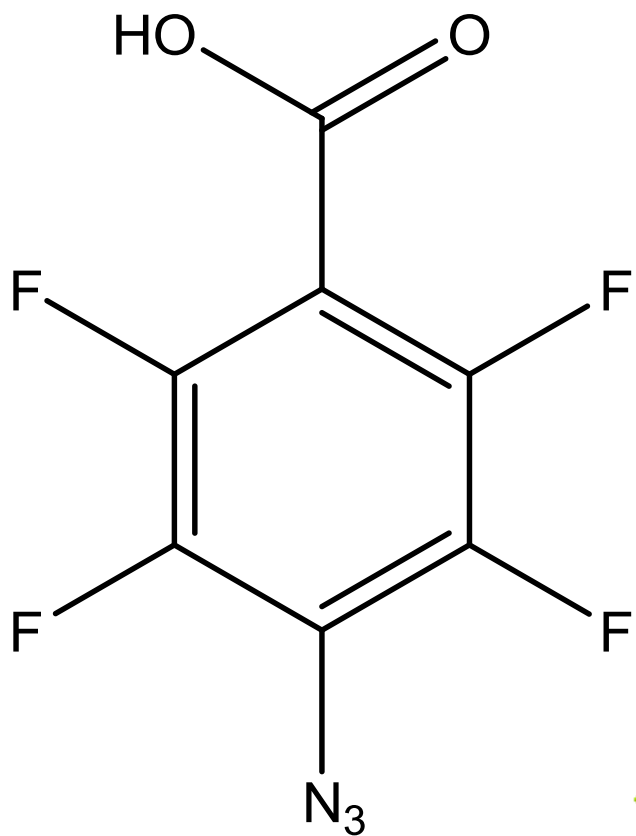
Вещества состоят из атомов



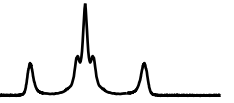
Пространственное расположение



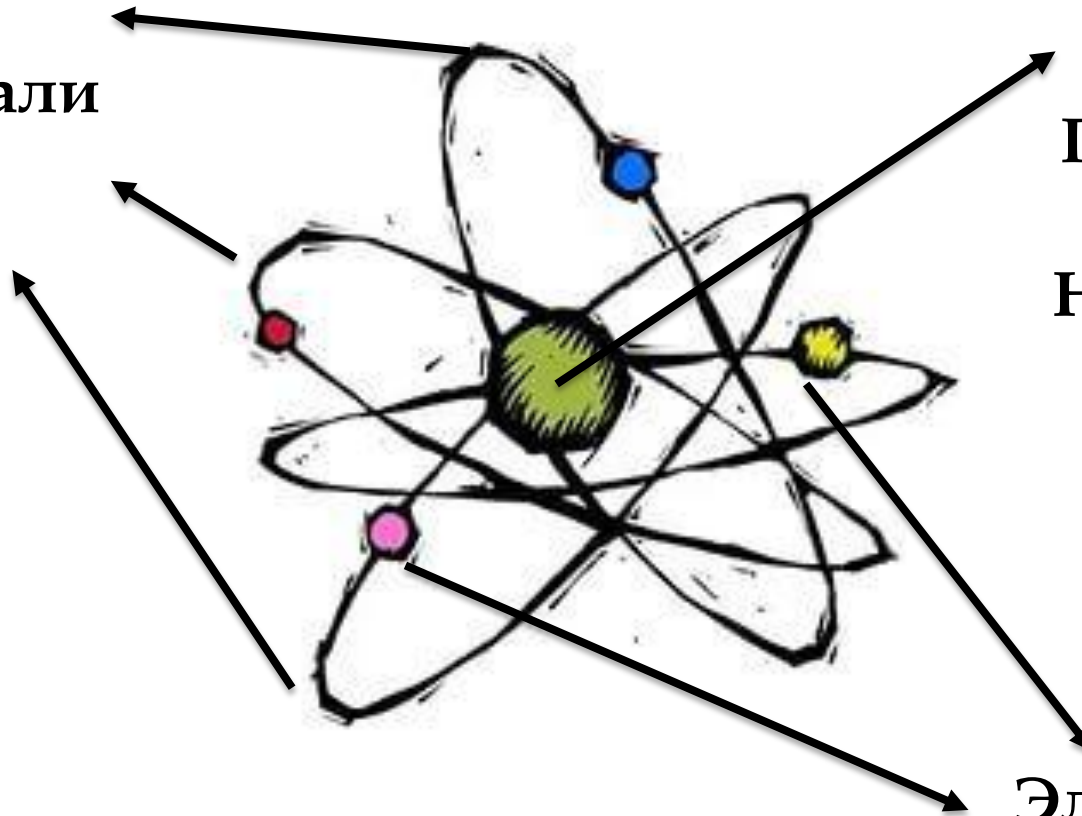
Молекулярные материалы



Обратно к атомам



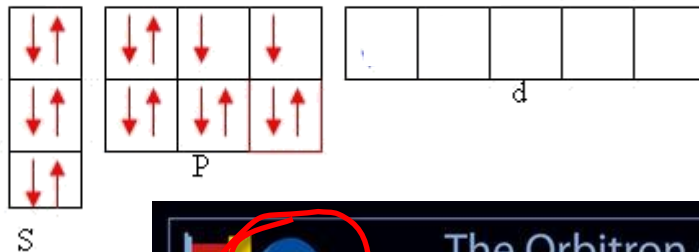
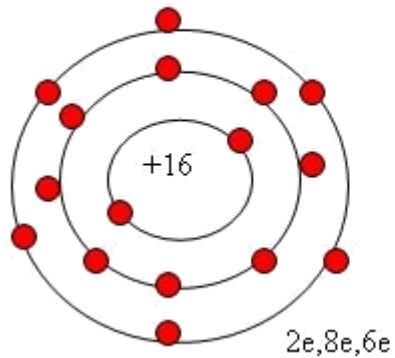
орбитали



Ядро =
Протоны (+)
+
Нейтроны (0)

Электроны (-)

Основное состояние



The Orbitron gallery of atomic orbitals

3s

3p_x 3p_y 3p_z

4s 4d_{z²-y²} 4d_{yz} 4d_{x²-y²} 4d_{xy} 4p_y 4p_z 4p_x

5s 5d_{z²-y²} 5d_{yz} 5d_{x²-y²} 5d_{xy} 6p_y 6p_z 6p_x

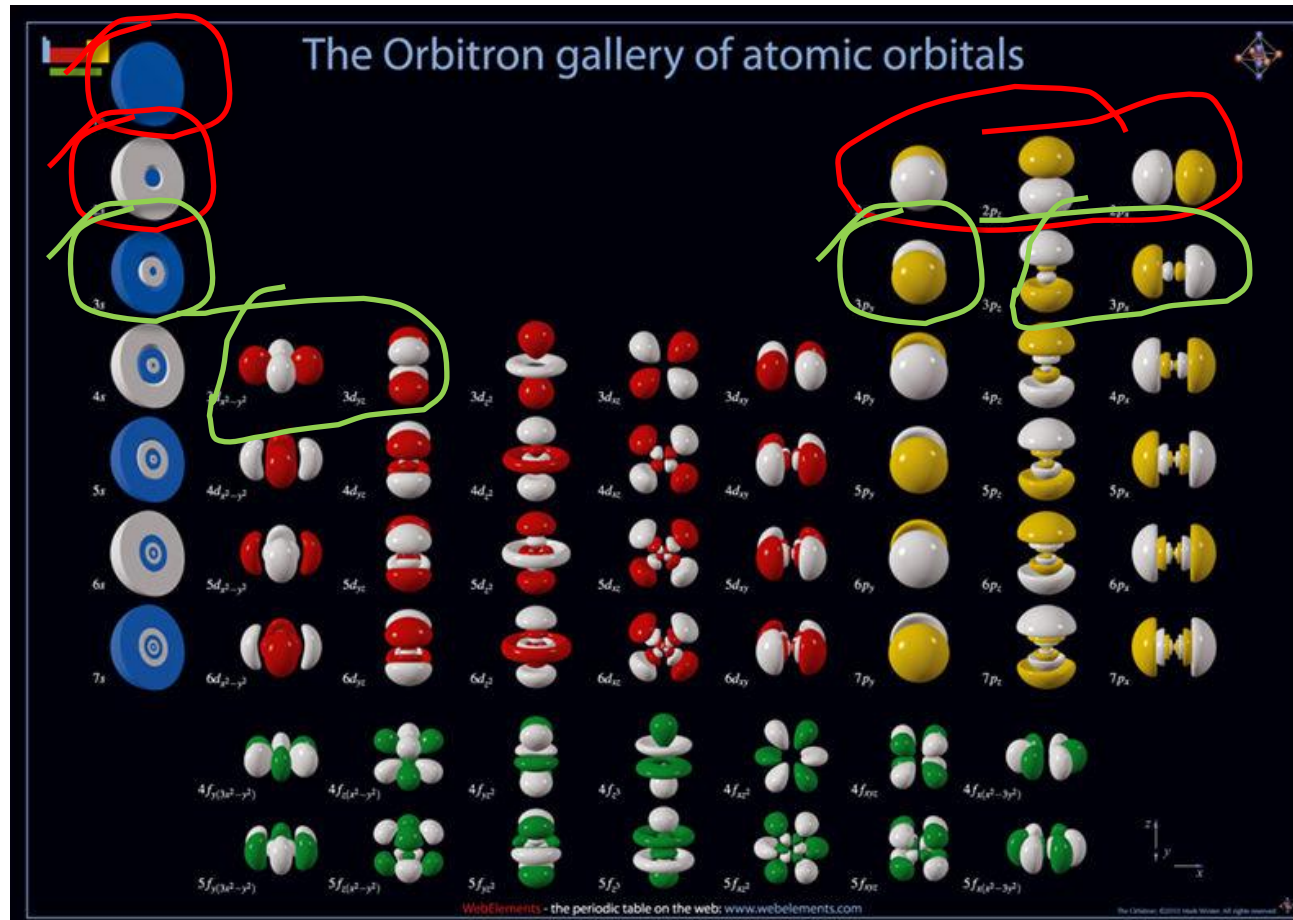
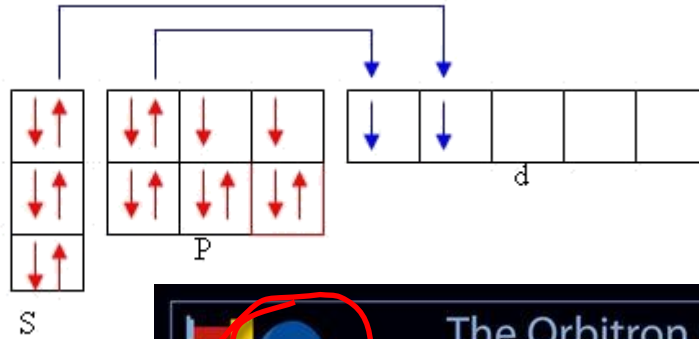
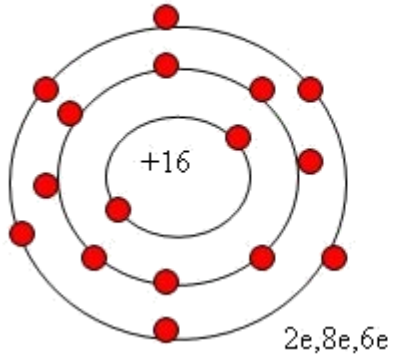
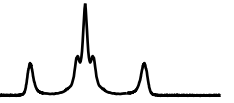
7s 7p_y 7p_z 7p_x

4f_(3z²-r²) 4f_(x²-y²) 4f_{yz} 4f_z 4f_{x²-z²} 4f_{xy} 4f_(x²-3y²)

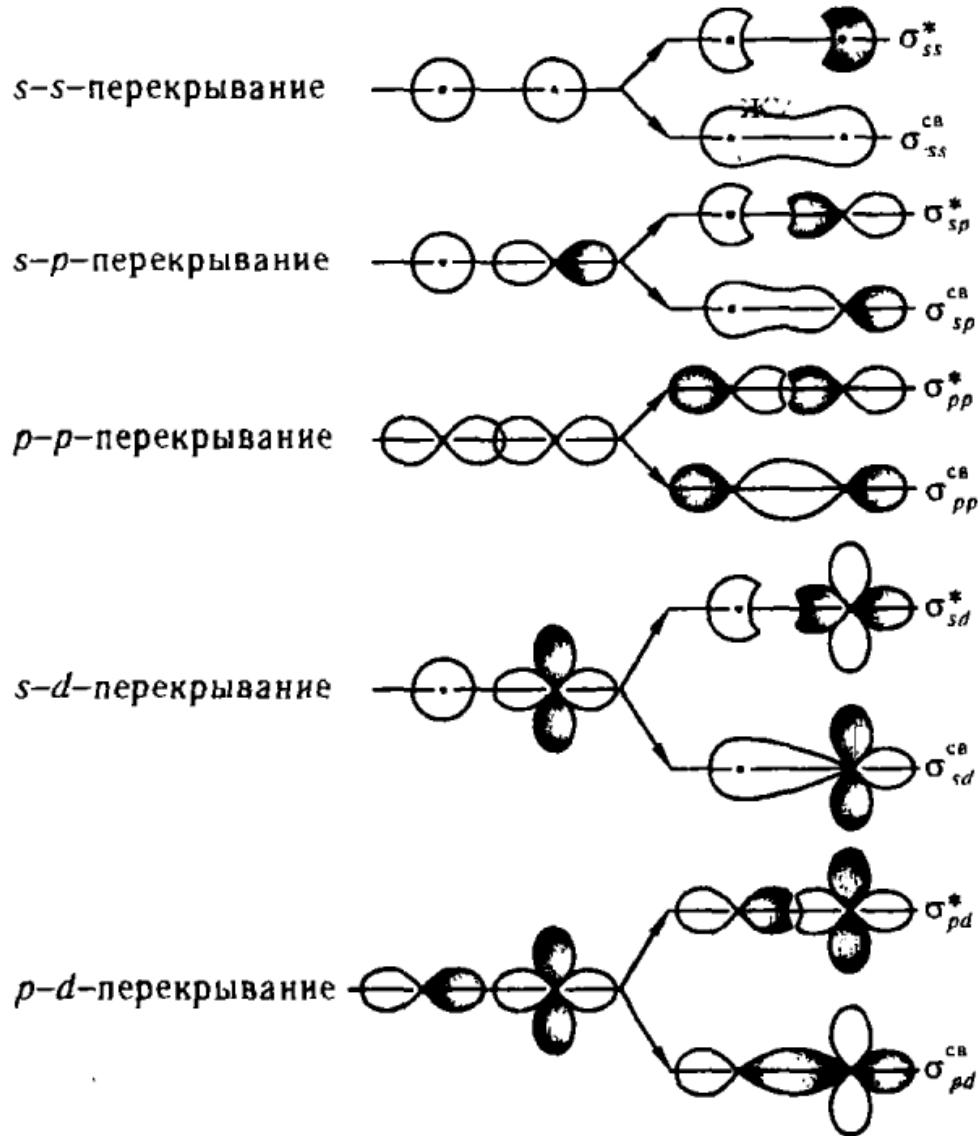
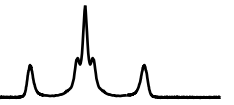
5f_(3z²-r²) 5f_(x²-y²) 5f_{yz} 5f_z 5f_{x²-z²} 5f_{xy} 5f_(x²-3y²)

WebElements - the periodic table on the web: www.webelements.com

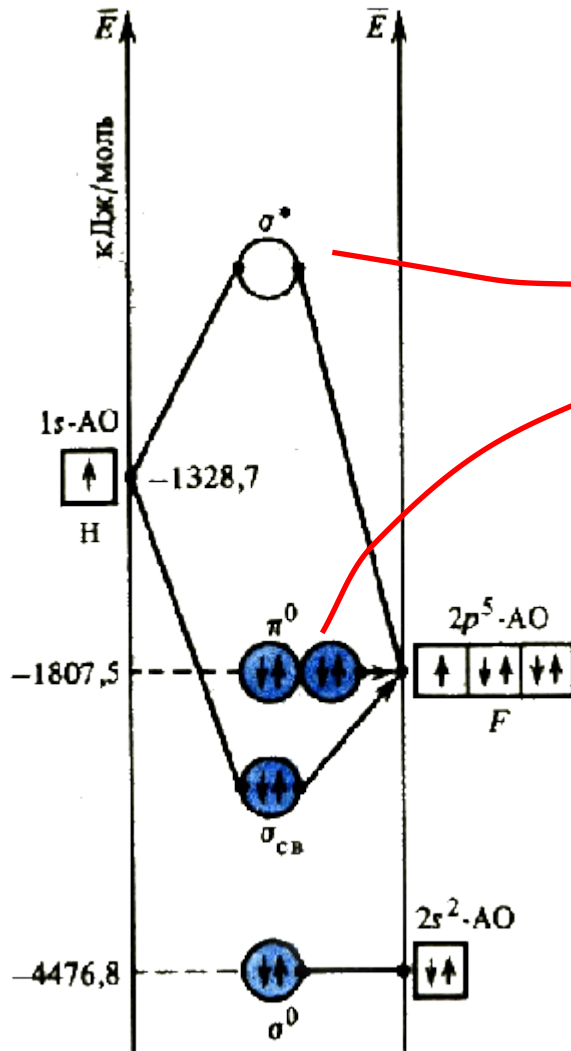
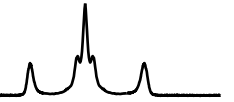
Возбужденное состояние



Молекулярные орбитали



Вспомнили энергию



Низшая свободная
молекулярная орбиталь

НСМО

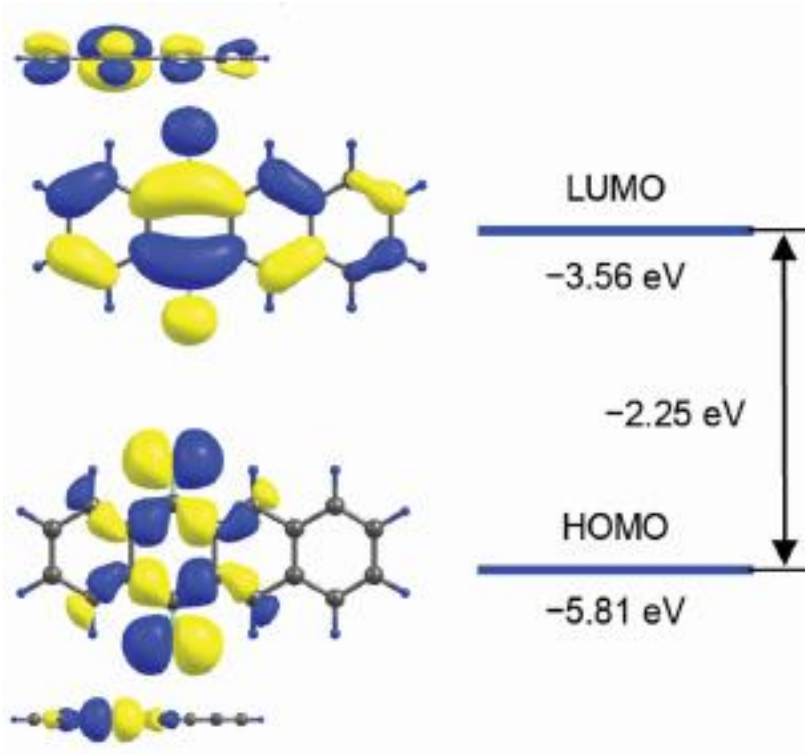
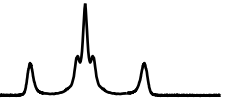
LUMO

Высшая занятая
молекулярная орбиталь

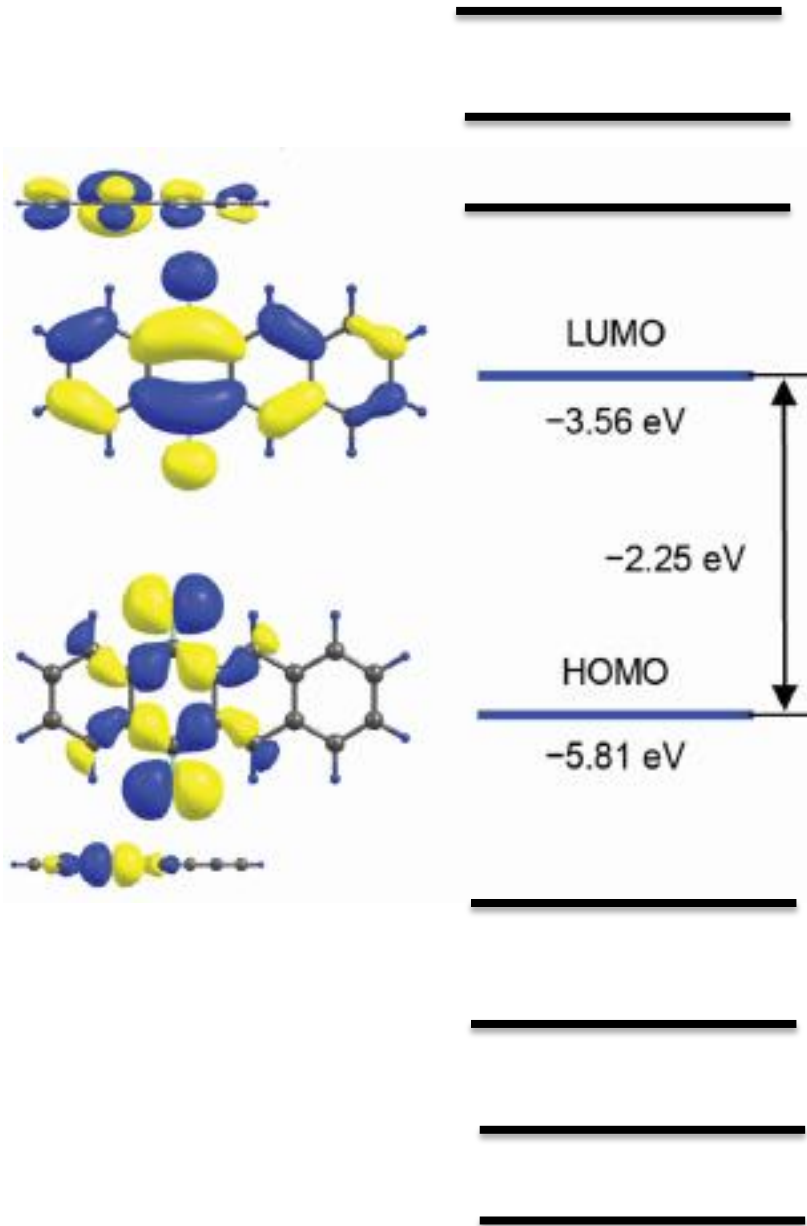
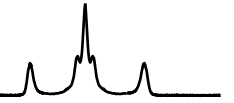
ВЗМО

НОМО

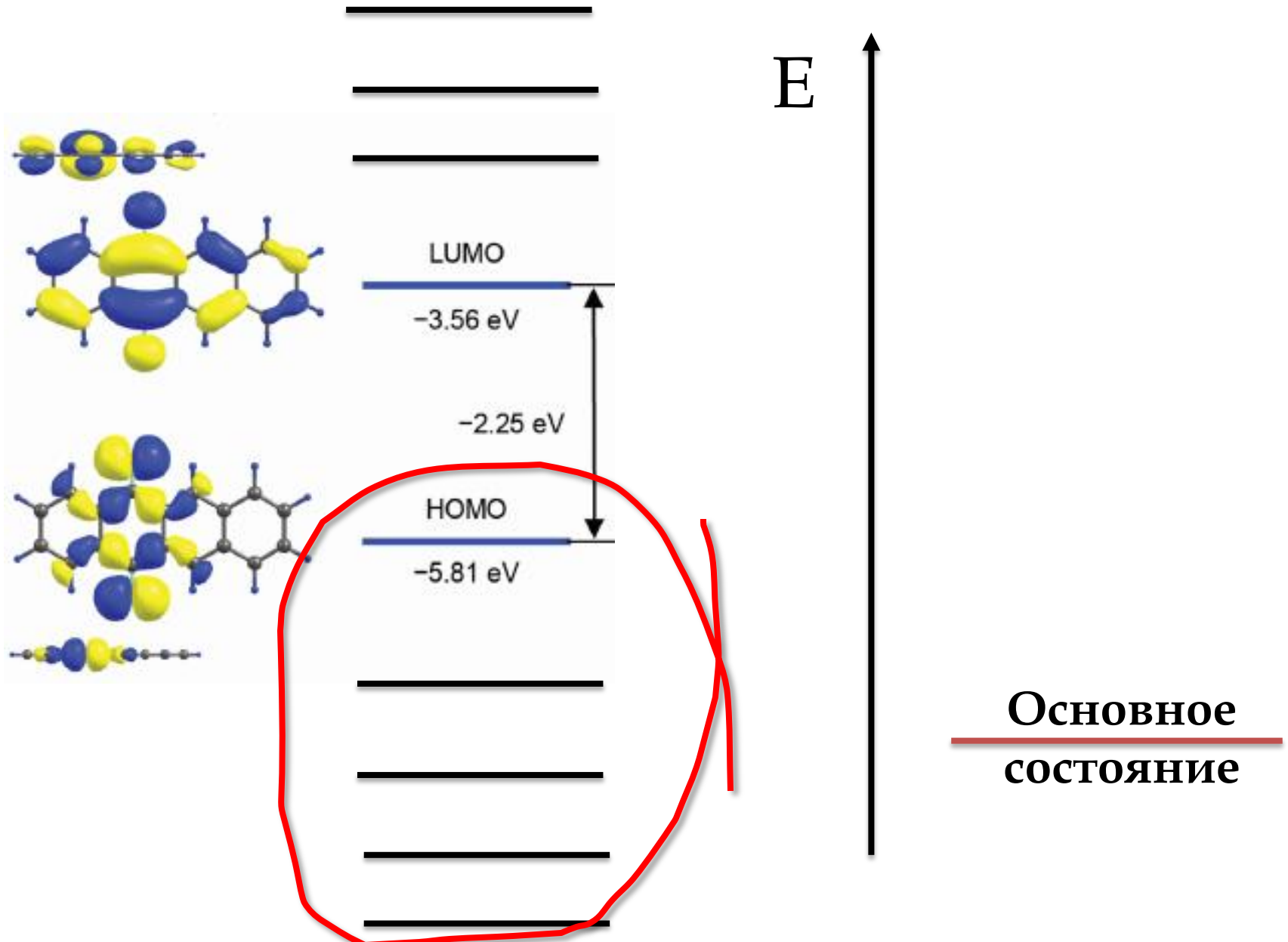
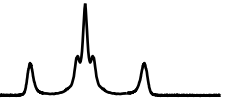
Настоящая молекула



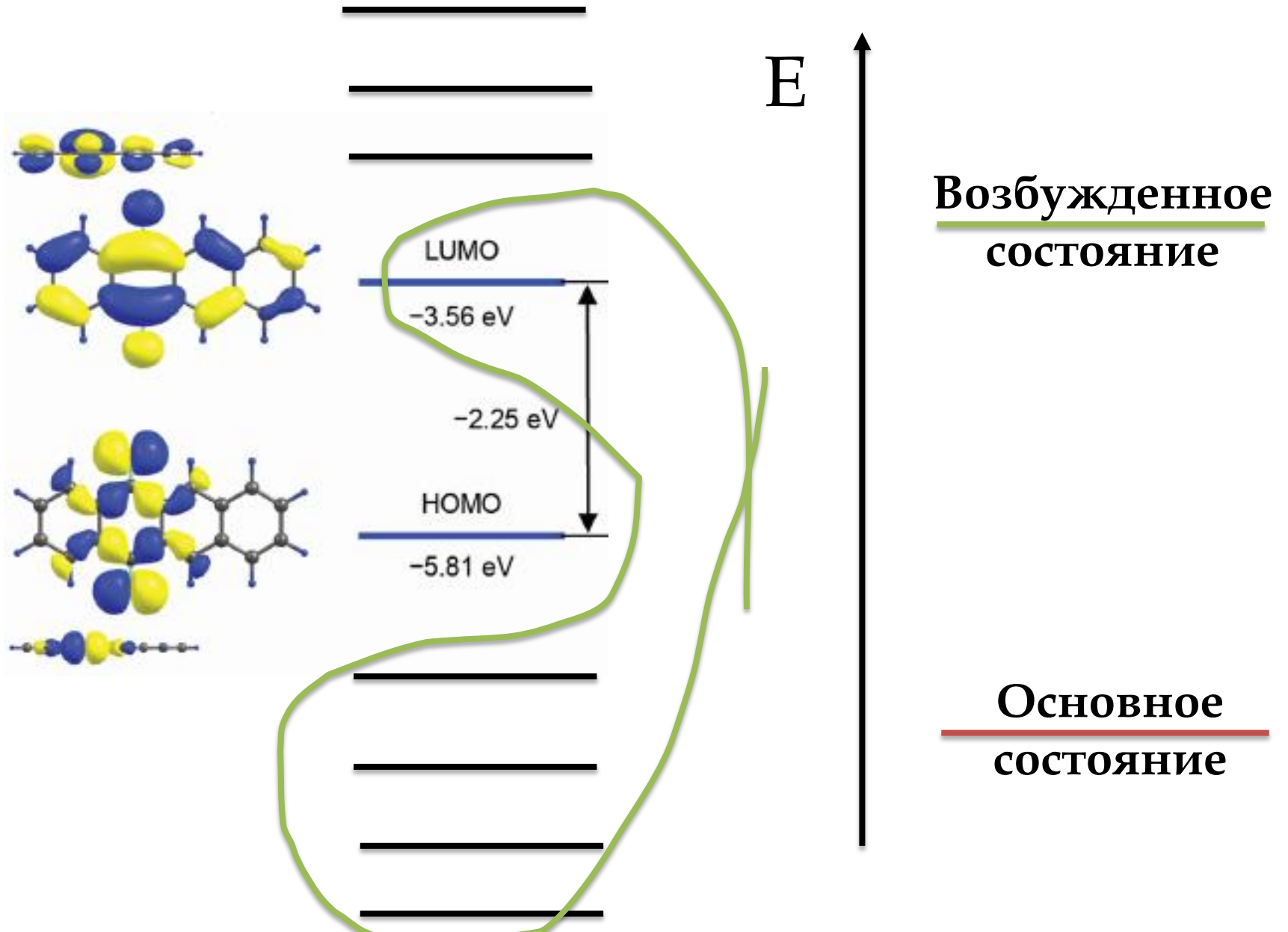
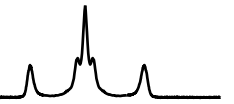
Настоящая молекула



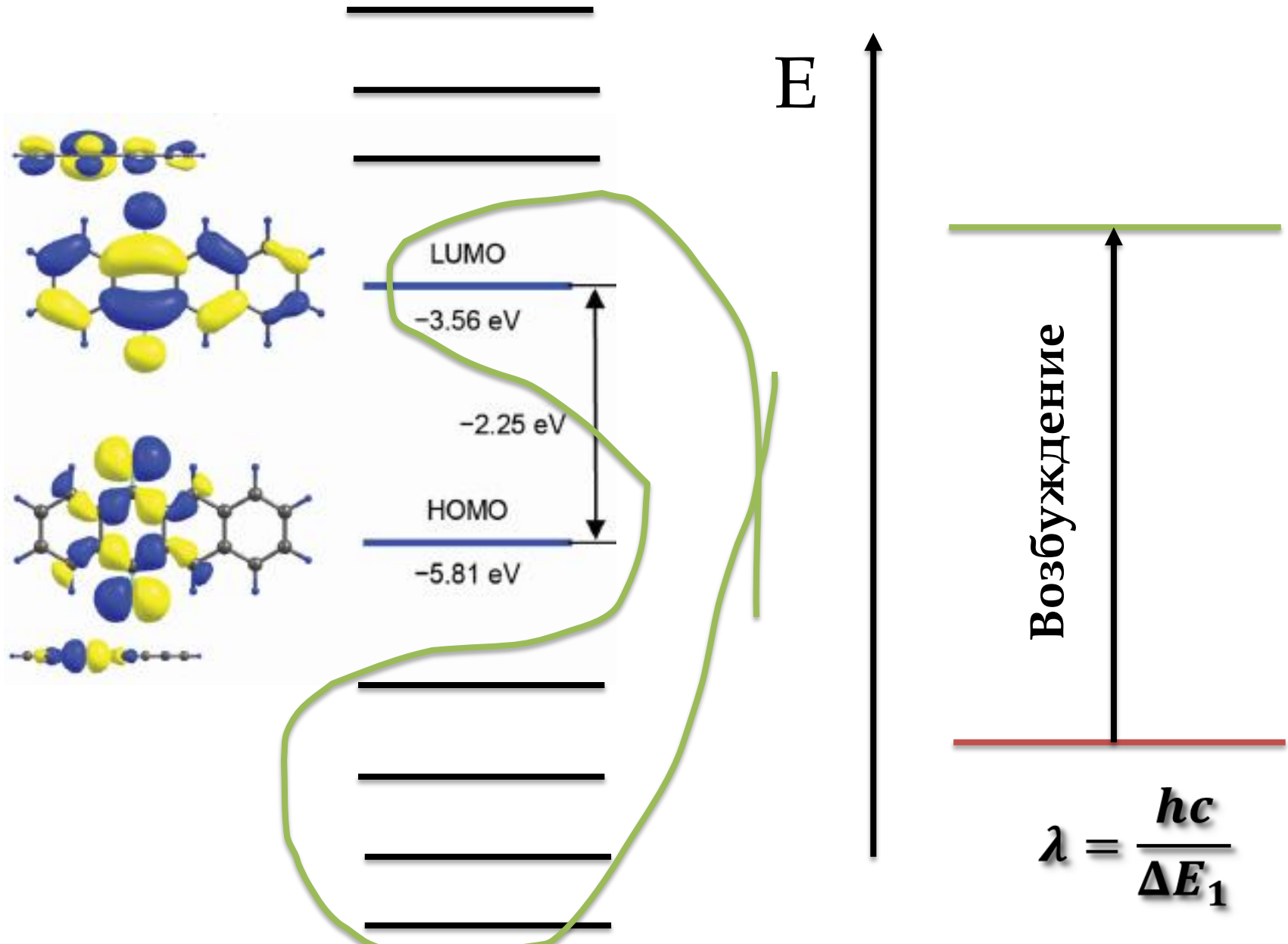
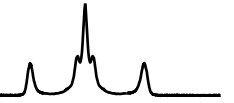
Настоящая молекула



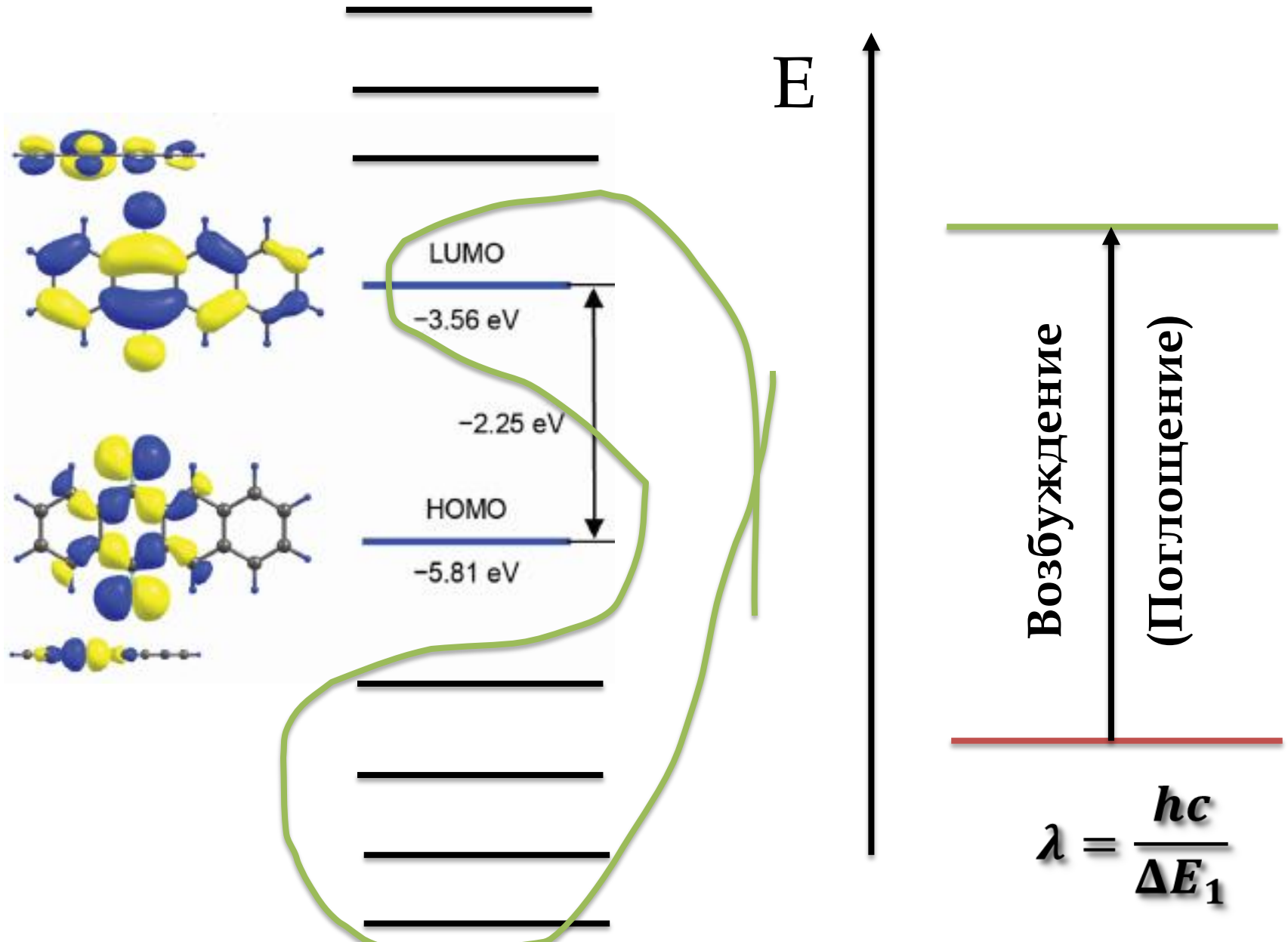
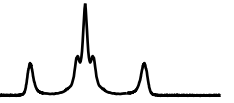
Настоящая молекула



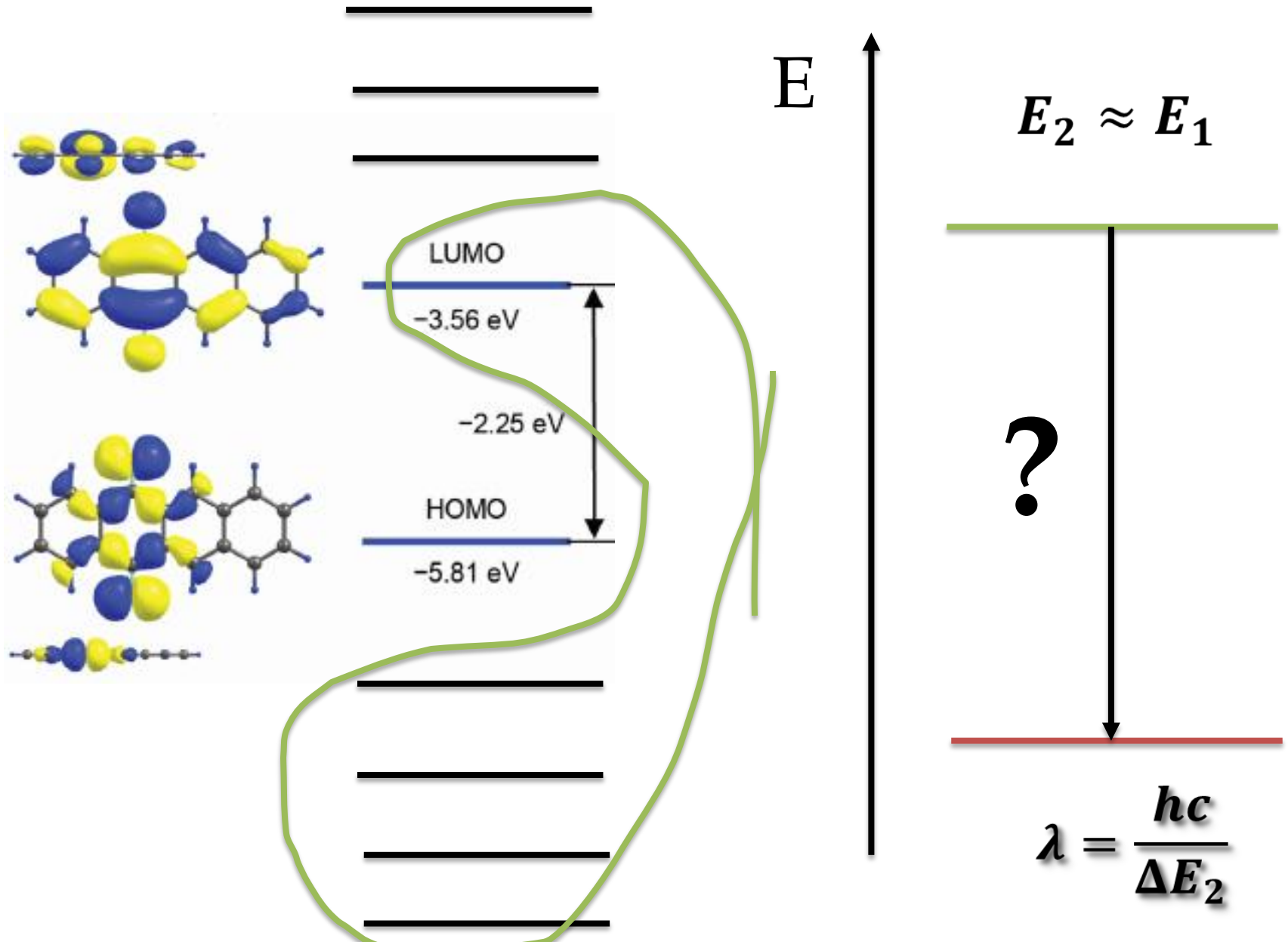
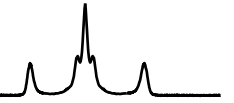
Настоящая молекула

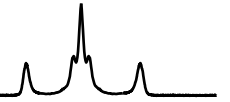


Настоящая молекула



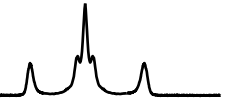
Настоящая молекула





**Переход молекулы из
возбужденного состояния в
основное (= релаксация), при
котором выделившаяся энергия
расходуется на рождение фотона
(= кванта света), называется
люминесценцией.**

Люминесценция

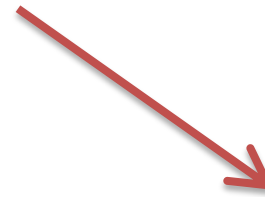


«Будем называть люминесценцией **избыток над температурным излучением** тела в том случае, если это избыточное излучение обладает конечной **длительностью примерно 10^{-10} секунд и больше**»

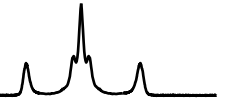
С. И. Вавилов, 1948 г.



НЕ тепловое излучение



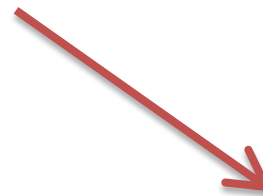
НЕ рассеяние, НЕ отражение, НЕ комбинационное рассеяния и т.д.:
длительность меньше колебания световой волны (которая $<10^{-10}$ с)



Переход молекулы из возбужденного состояния в основное (= релаксация), при котором выделившаяся энергия расходуется на рождение фотона (= кванта света), называется **люминесценцией**.



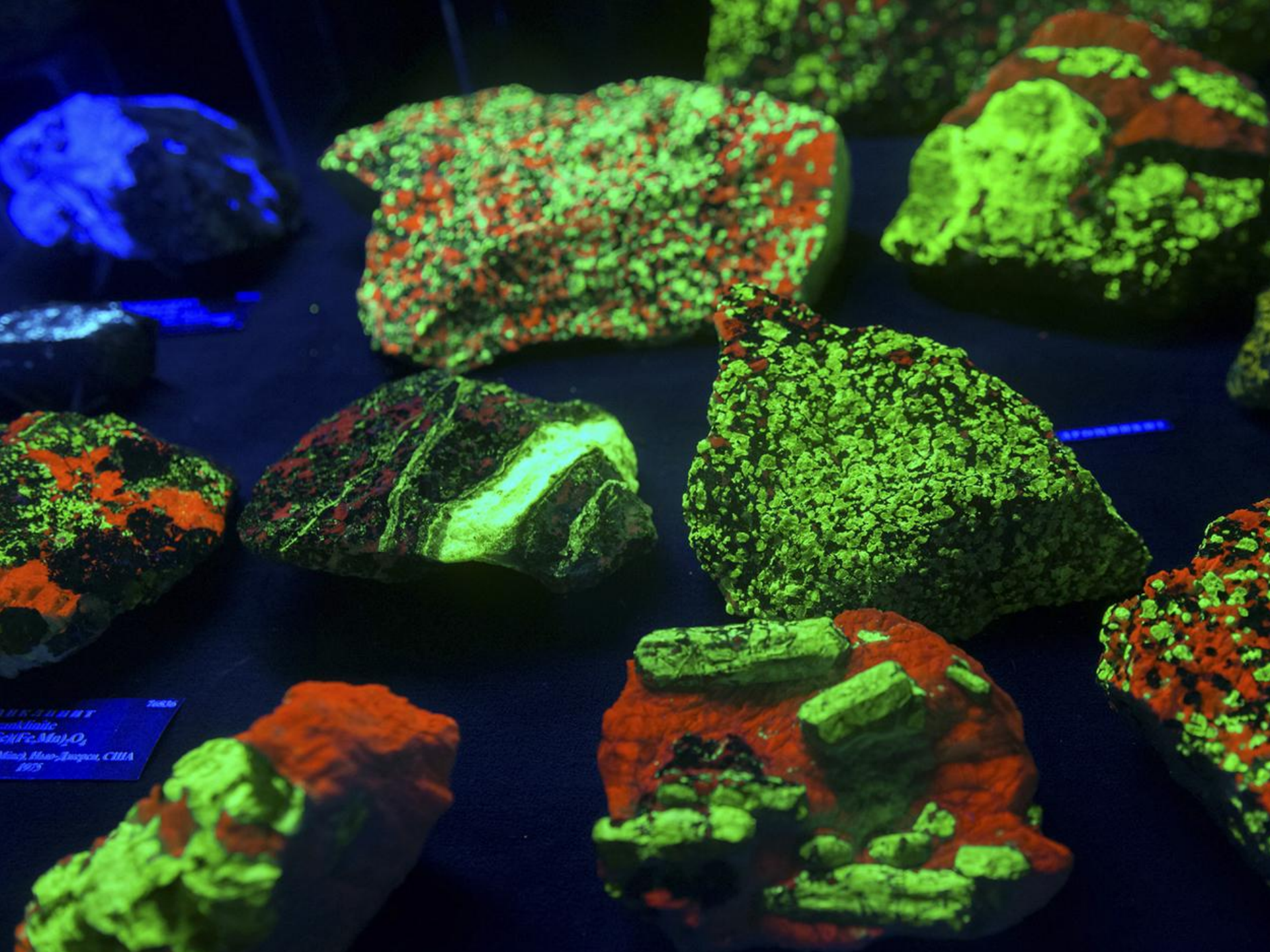
Как перевести молекулу в возбужденное состояние



Как заставить ее релаксировать излучательно



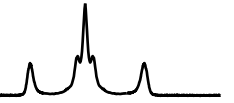
76826
Sankhinite
 $(\text{Fe}, \text{Mn})_2\text{O}_3$
Ming, Hunan, China, CMA
1975





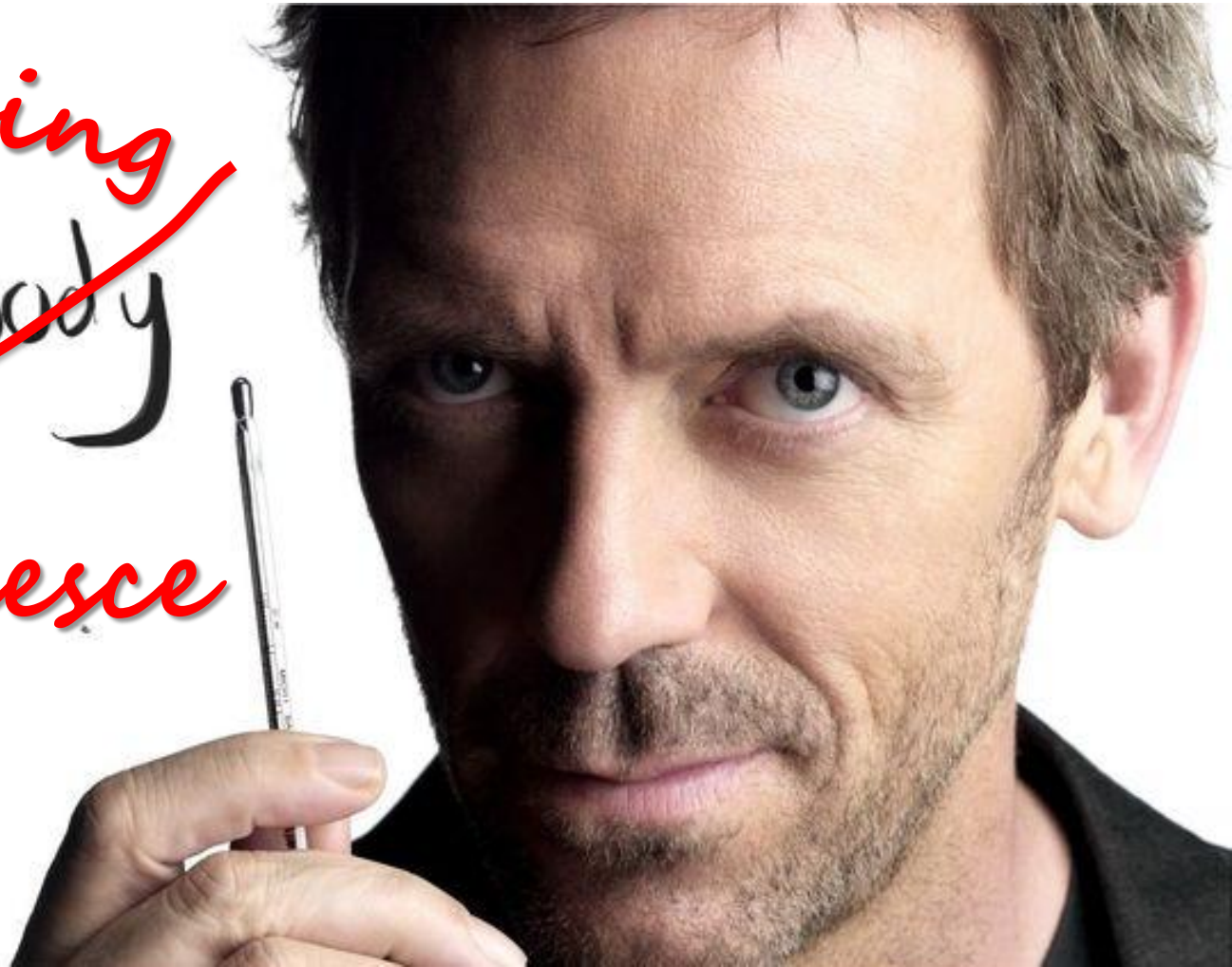
Все люминесцирует.

(Кроме того, что не люминесцирует)



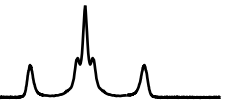
thing
E ~~very body~~

L ~~uminesce~~
~~ies~~

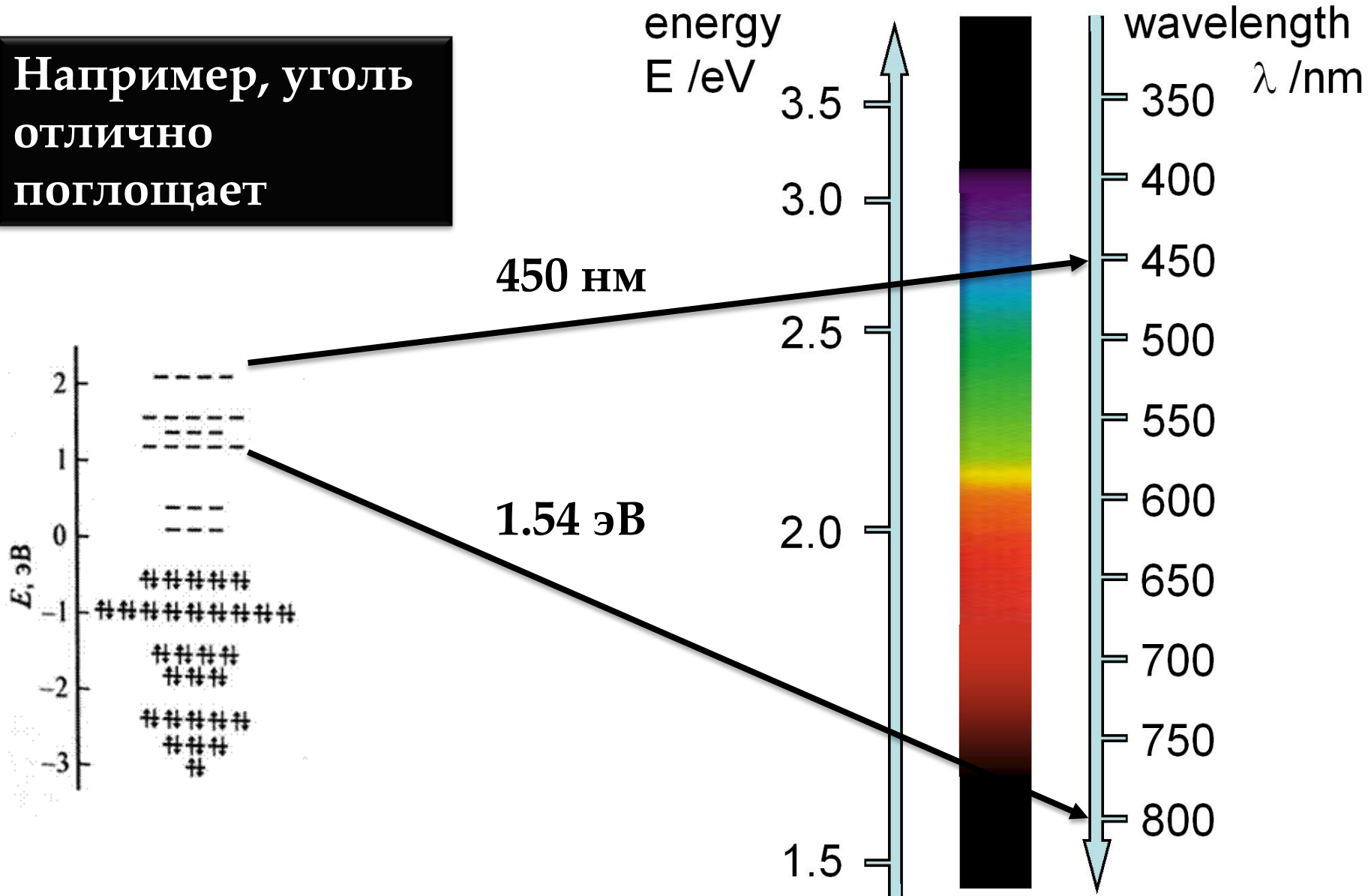


Все люминесцирует.

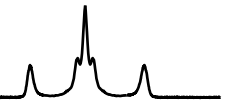
(Кроме того, что не люминесцирует)



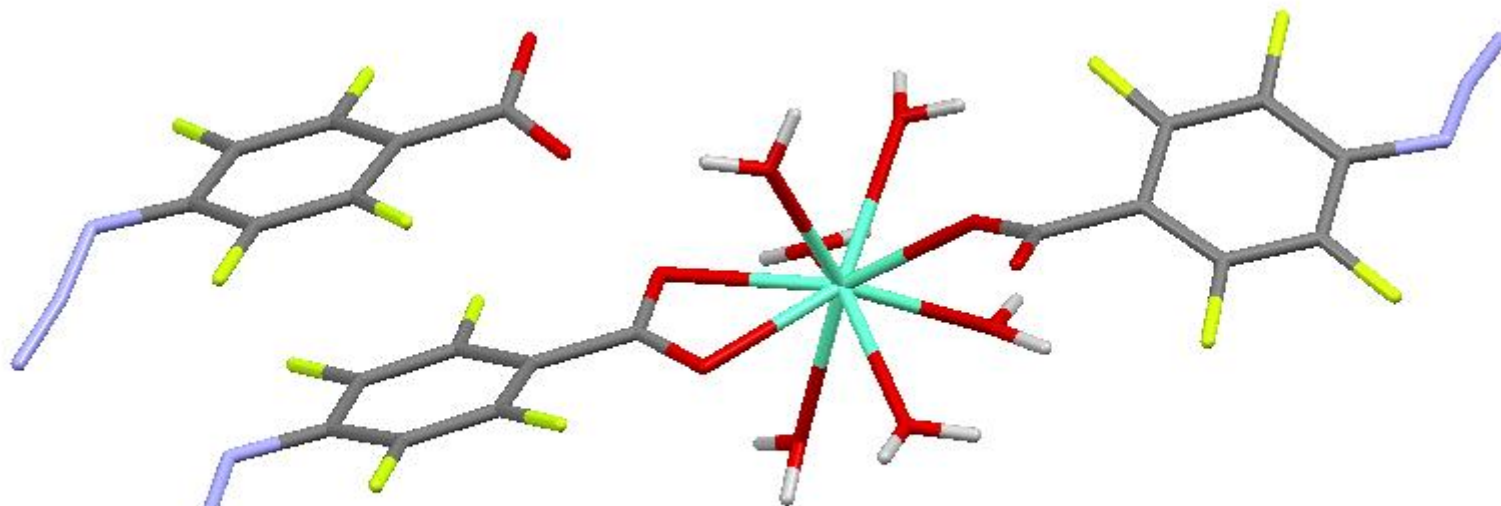
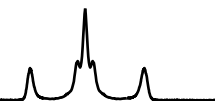
**Например, уголь
отлично
поглощает**



Конкурирующие процессы



Разложение

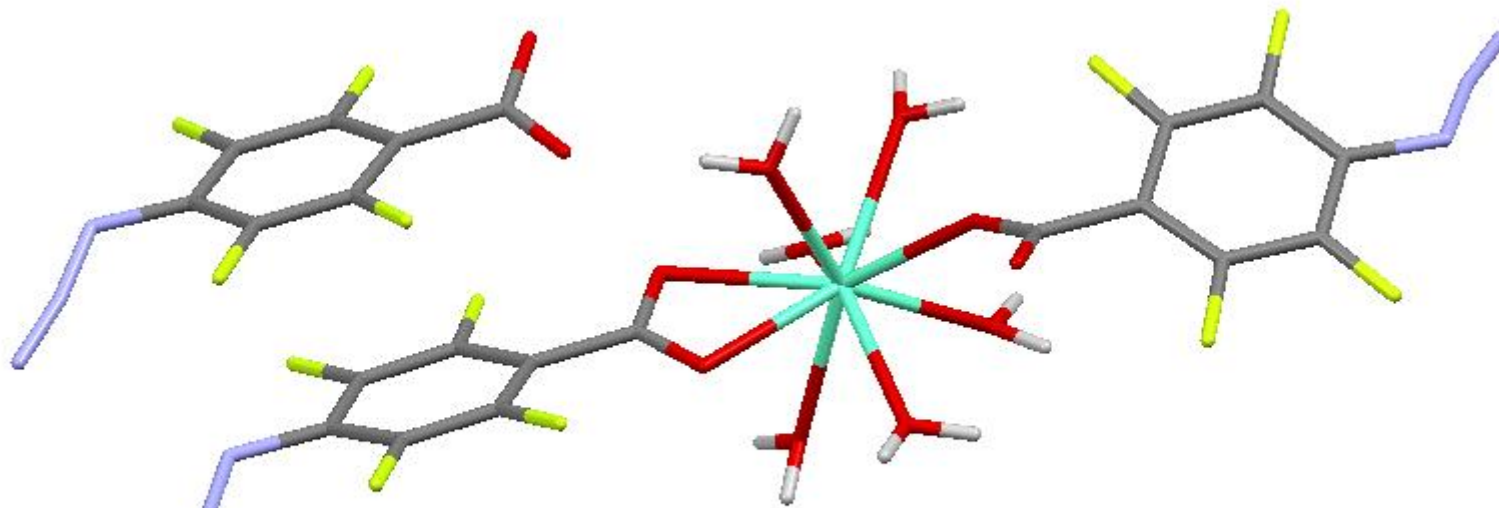


Азотный лазер



БДЫЩ!!!!

Разложение

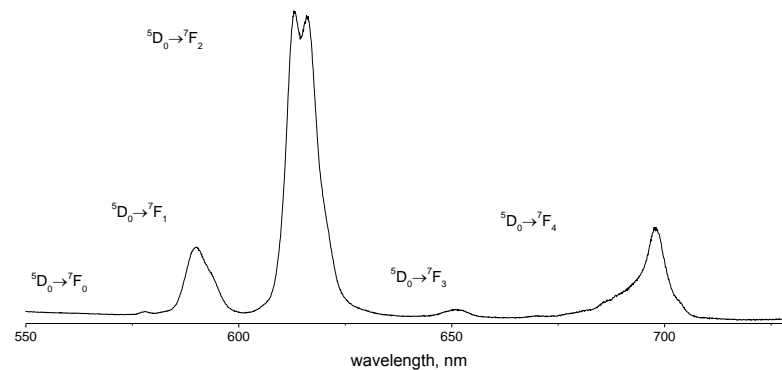


Азотный лазер

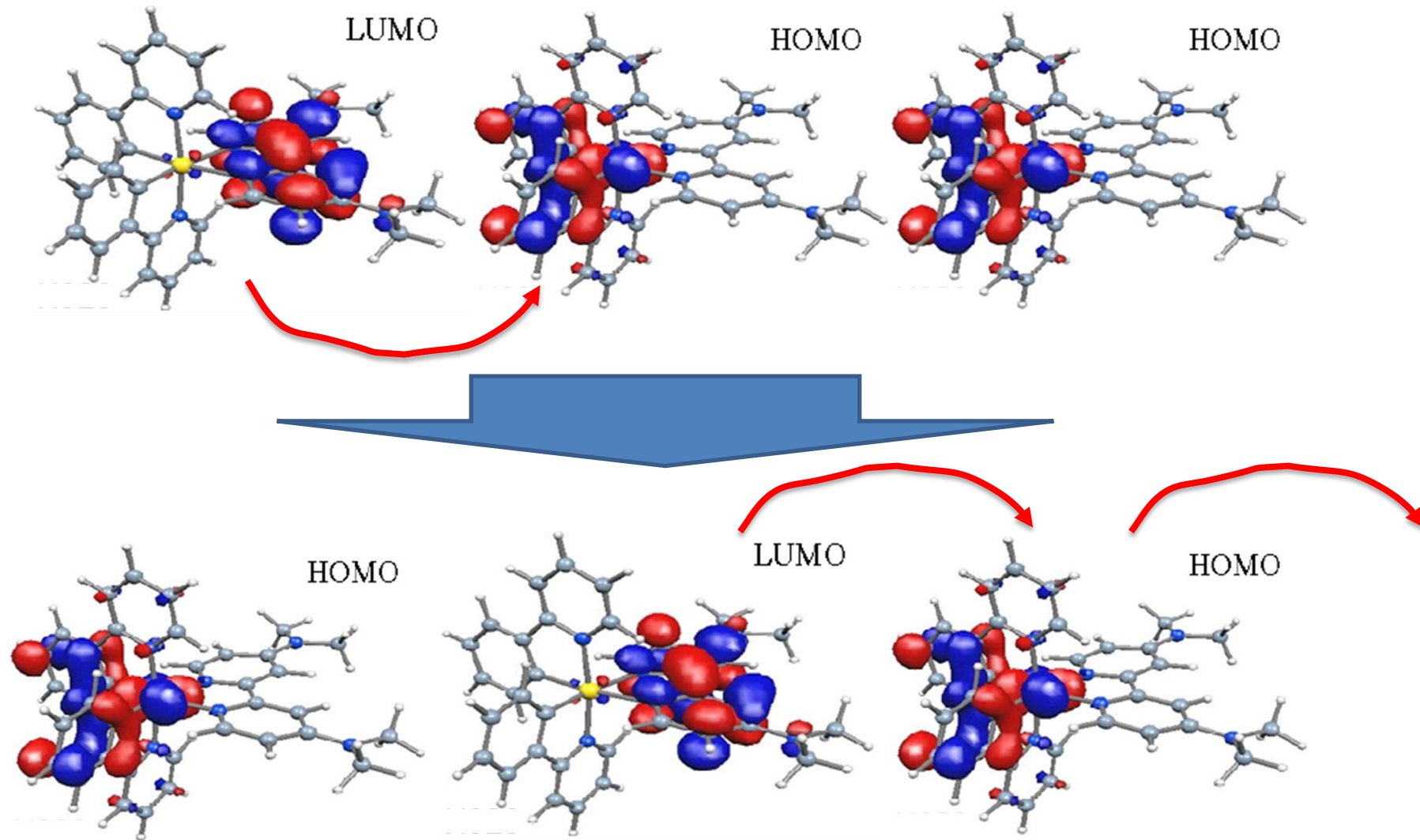
БДЫЩ!!!!



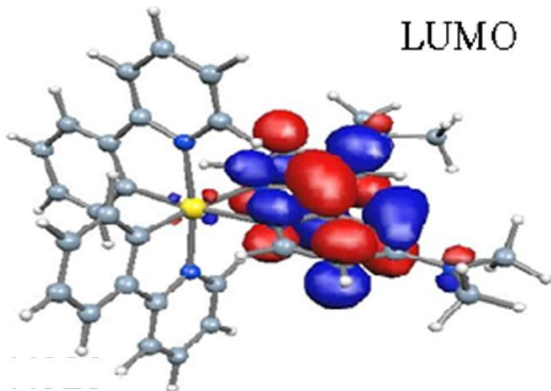
Ксеноновая лампа



Гашение



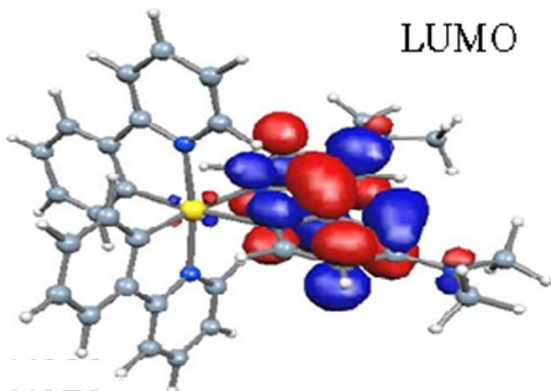
Гашение



Другая
молекула

Другая
молекула

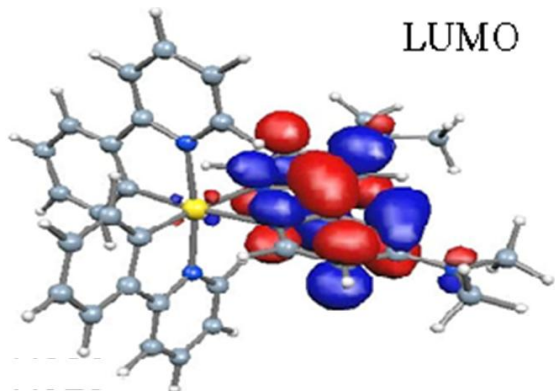
Люминесценция!!!



Другая
молекула

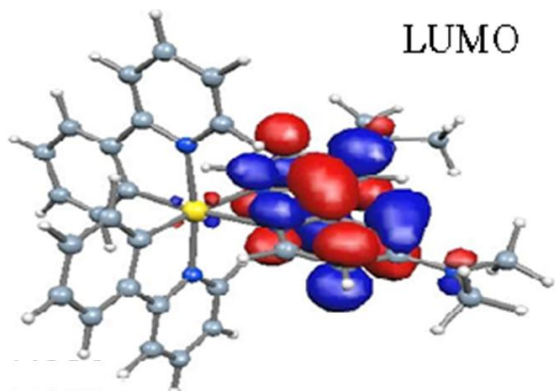
Другая
молекула

Гашение

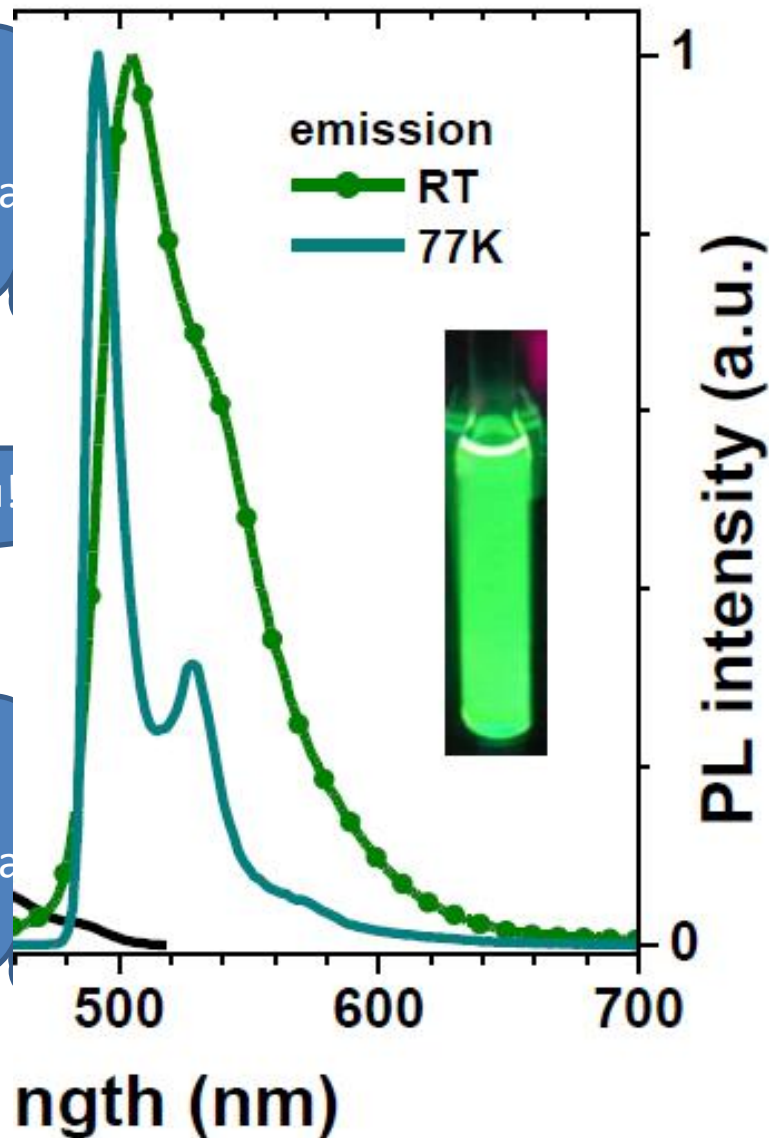


Другая молекула

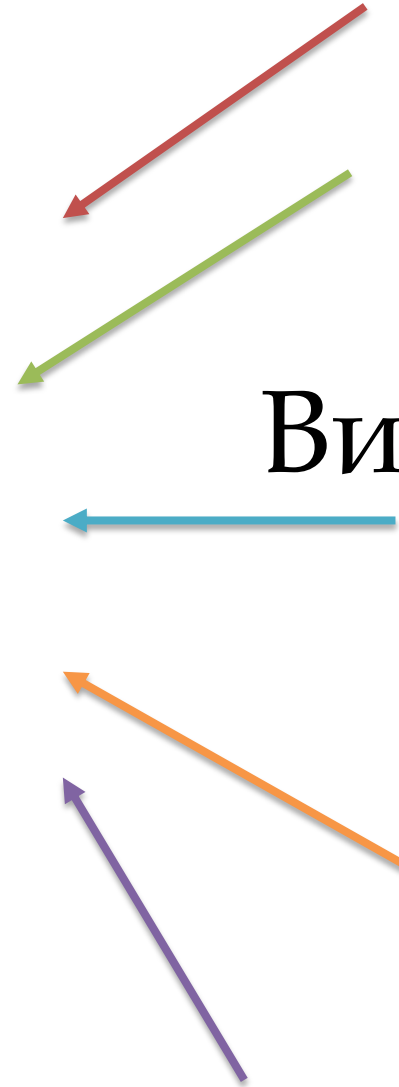
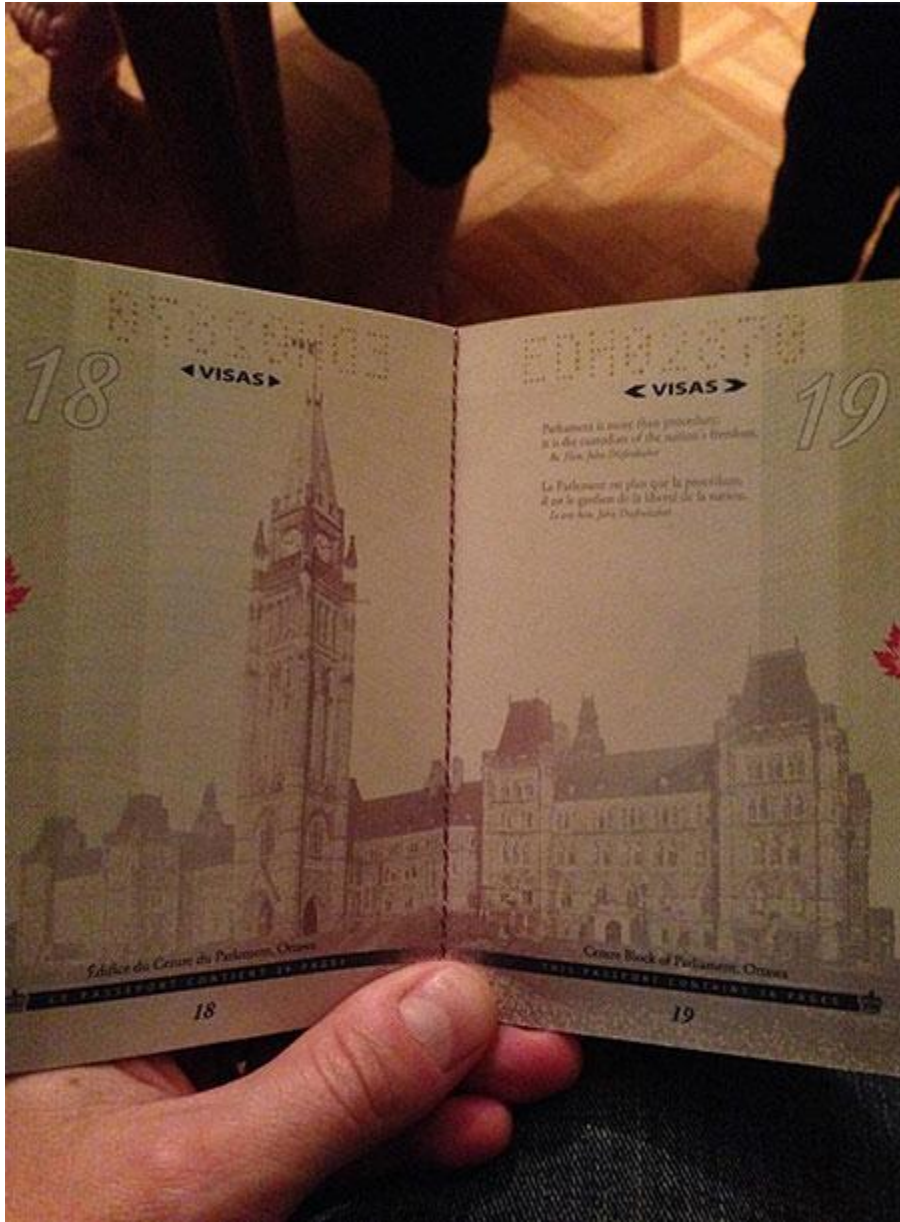
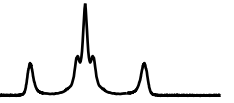
Люминесценция



Другая молекула

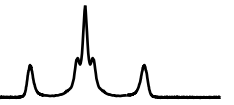


Возбуждение

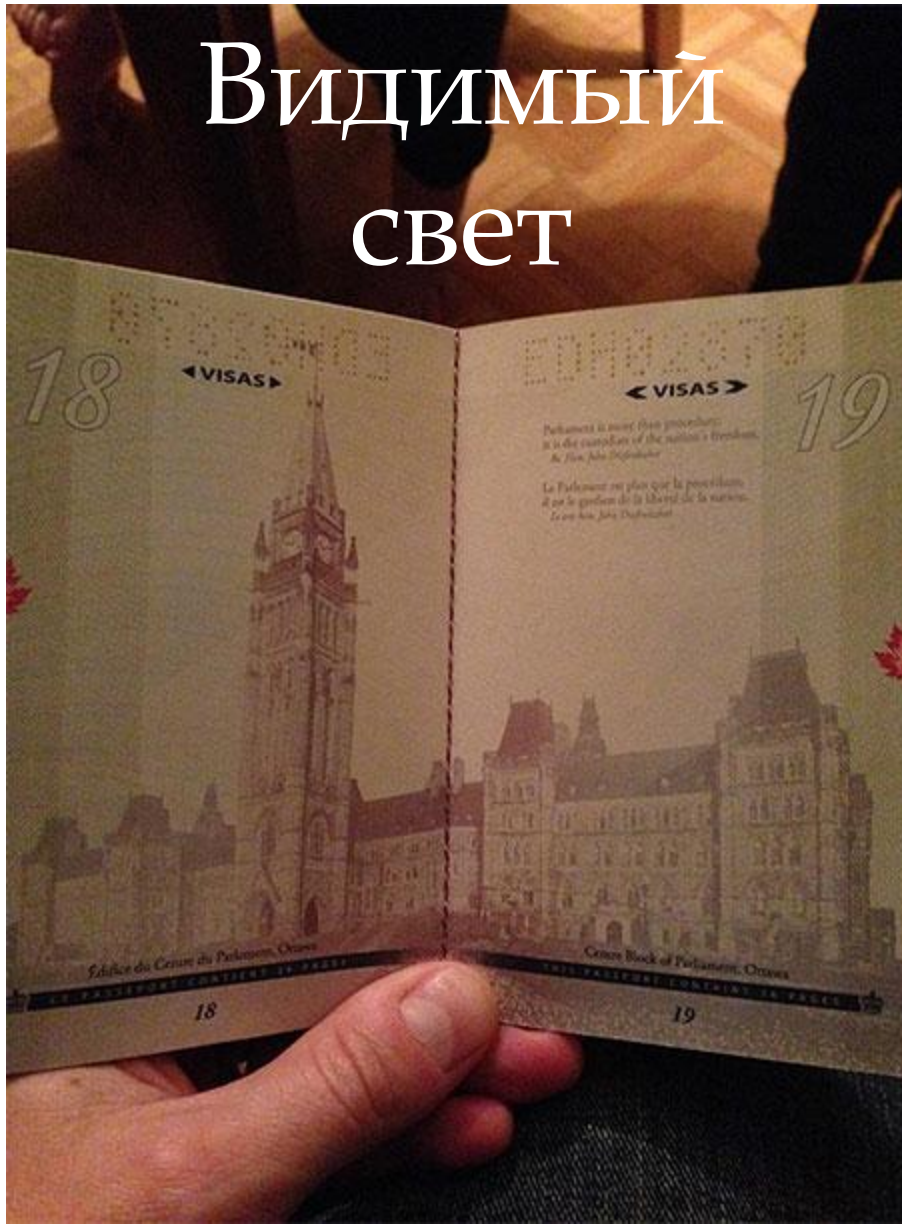


Видимый
свет

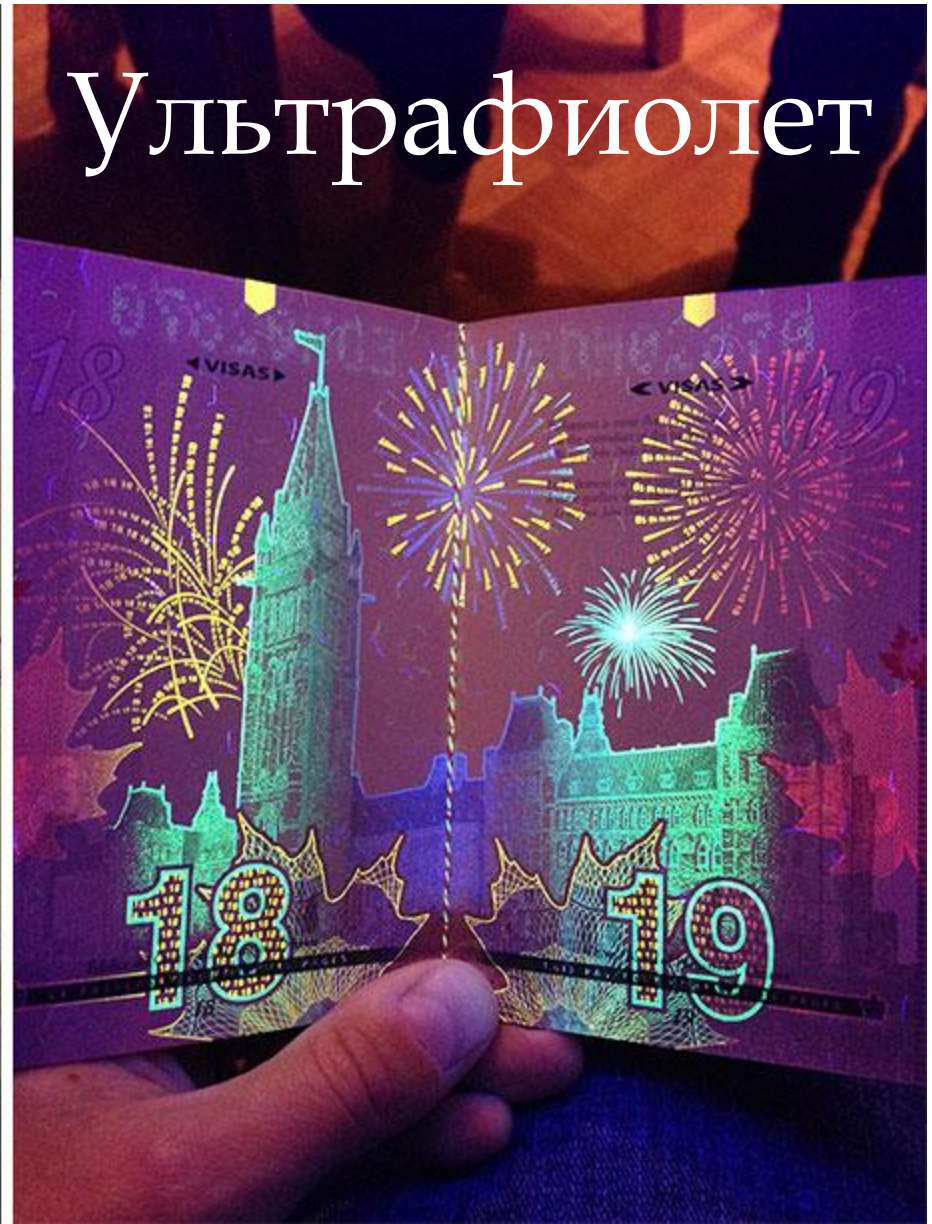
Возбуждение

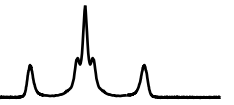


Видимый свет



Ультрафиолет





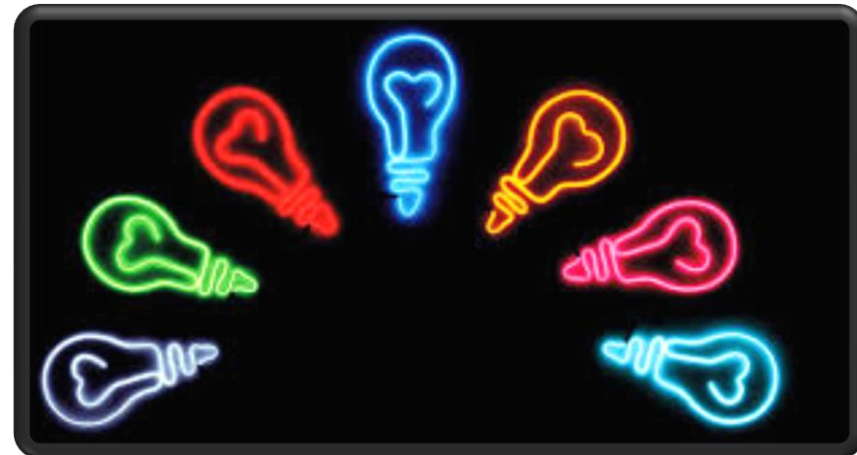
фотолюминесценция –
под действием света



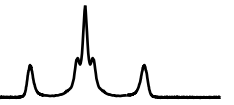
(био)хемилюминесценция –
использует энергию химических
реакций;



электролюминесценция –
при пропускании
электрического тока



Фотолюминесценция



Защитные метки



ЕВРОПИЙ



Eu²⁺

Eu³⁺

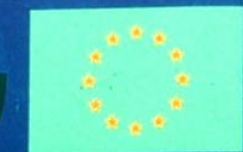
100 EURO

Защитные метки



ЕВРОПИЙ

© BCE ECB EZB EKT EKP 2002



Eu²⁺

Нетоксичность
Нерастворимость
Стабильность

Eu³⁺

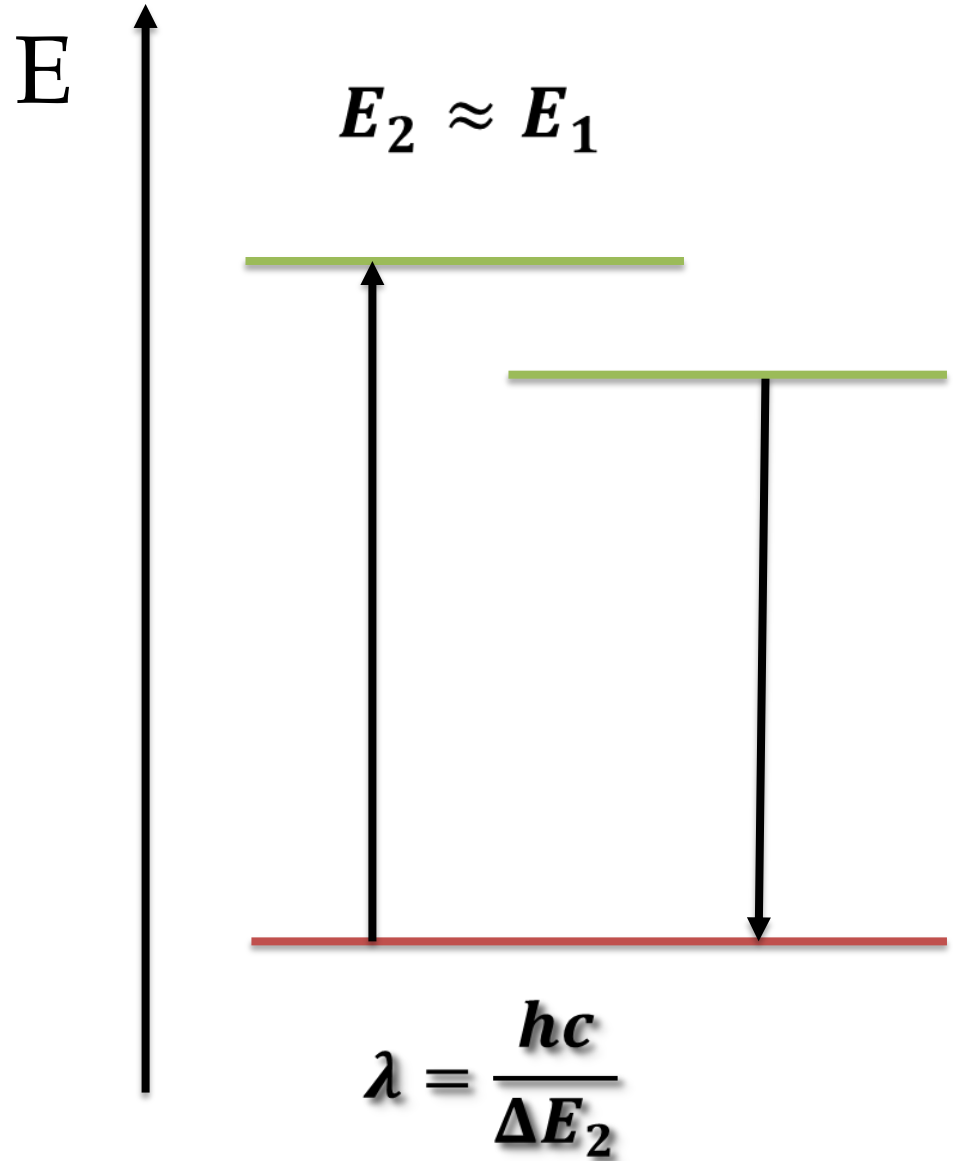
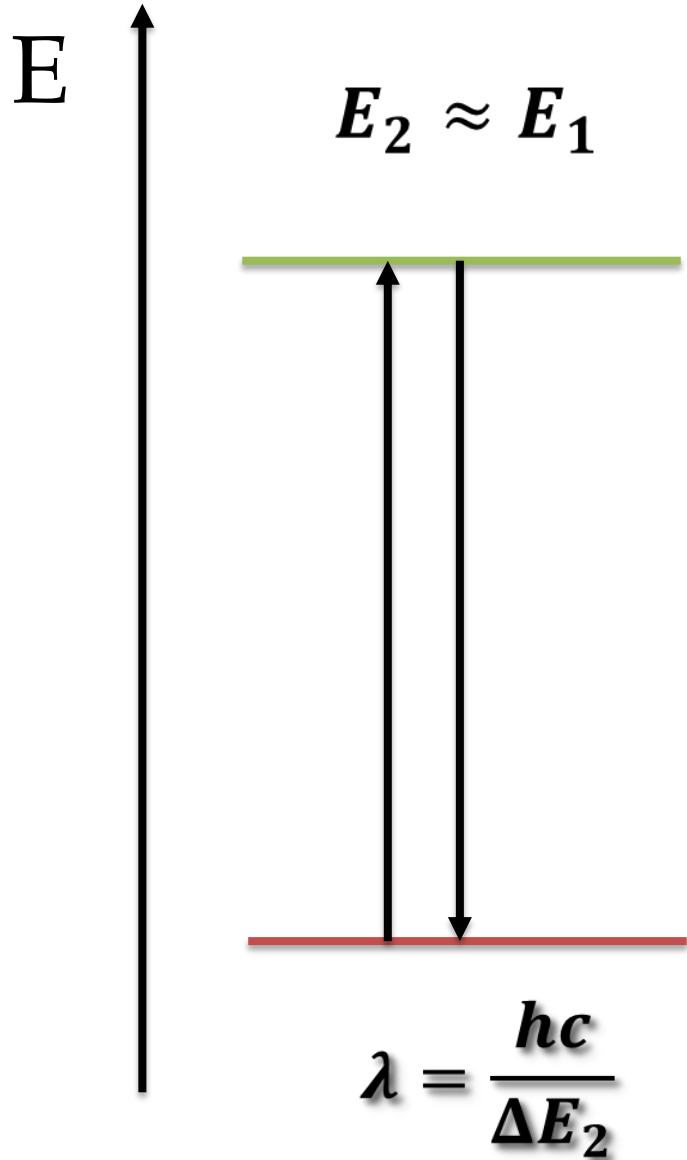
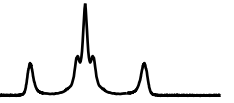
.....
Белый цвет

100 EURO

100



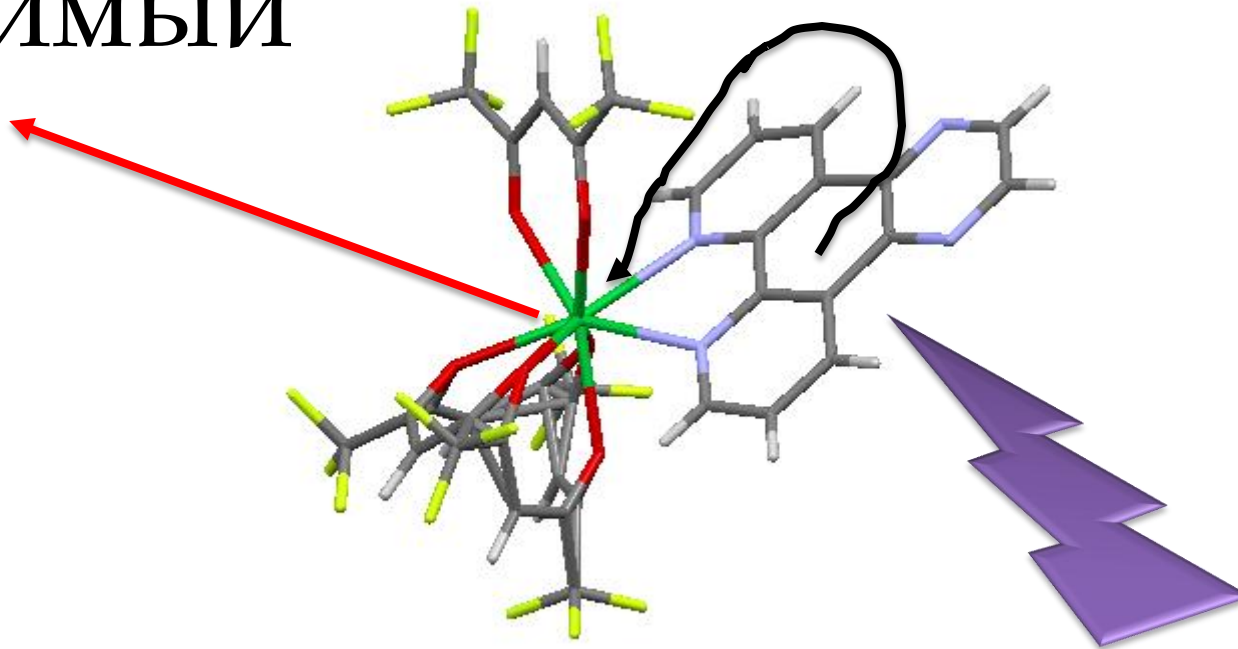
Почему краска невидимая



Это как вообще

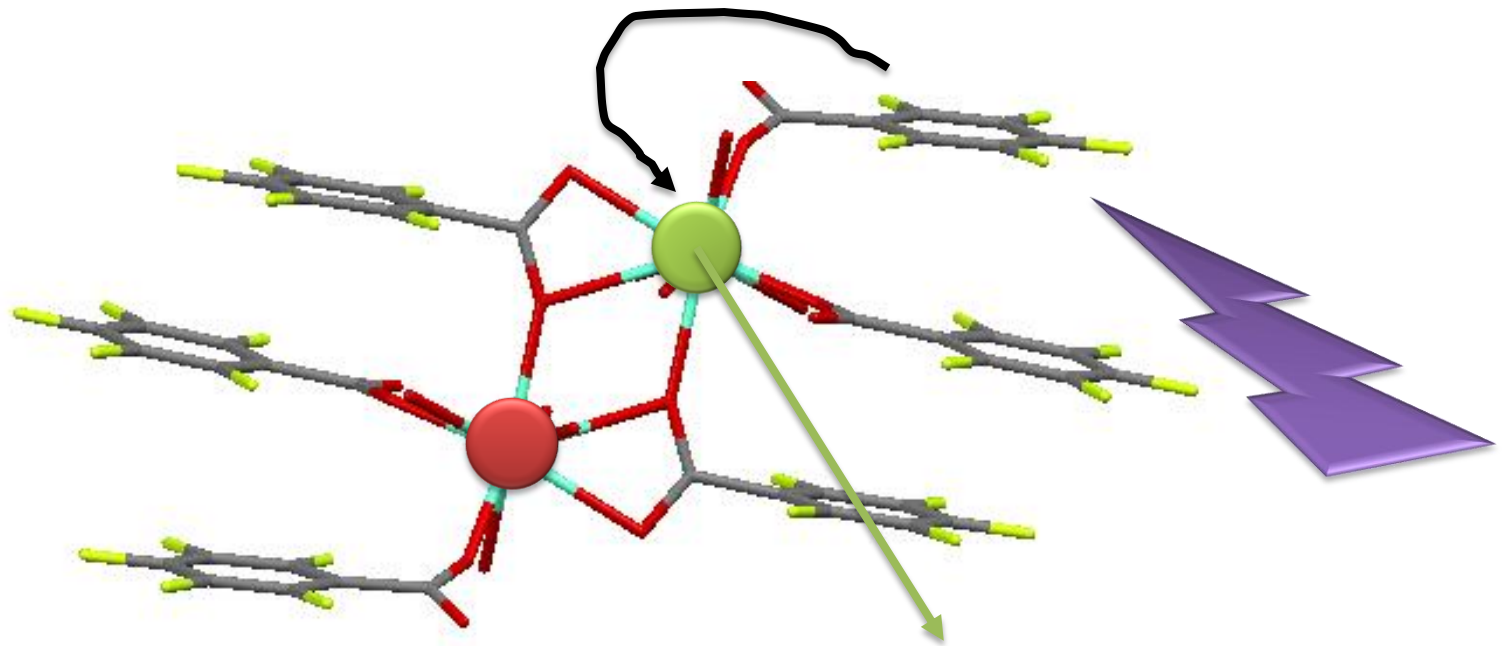
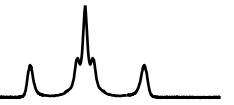


ВИДИМЫЙ

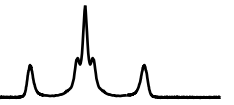


УФ

«Хитрые» метки



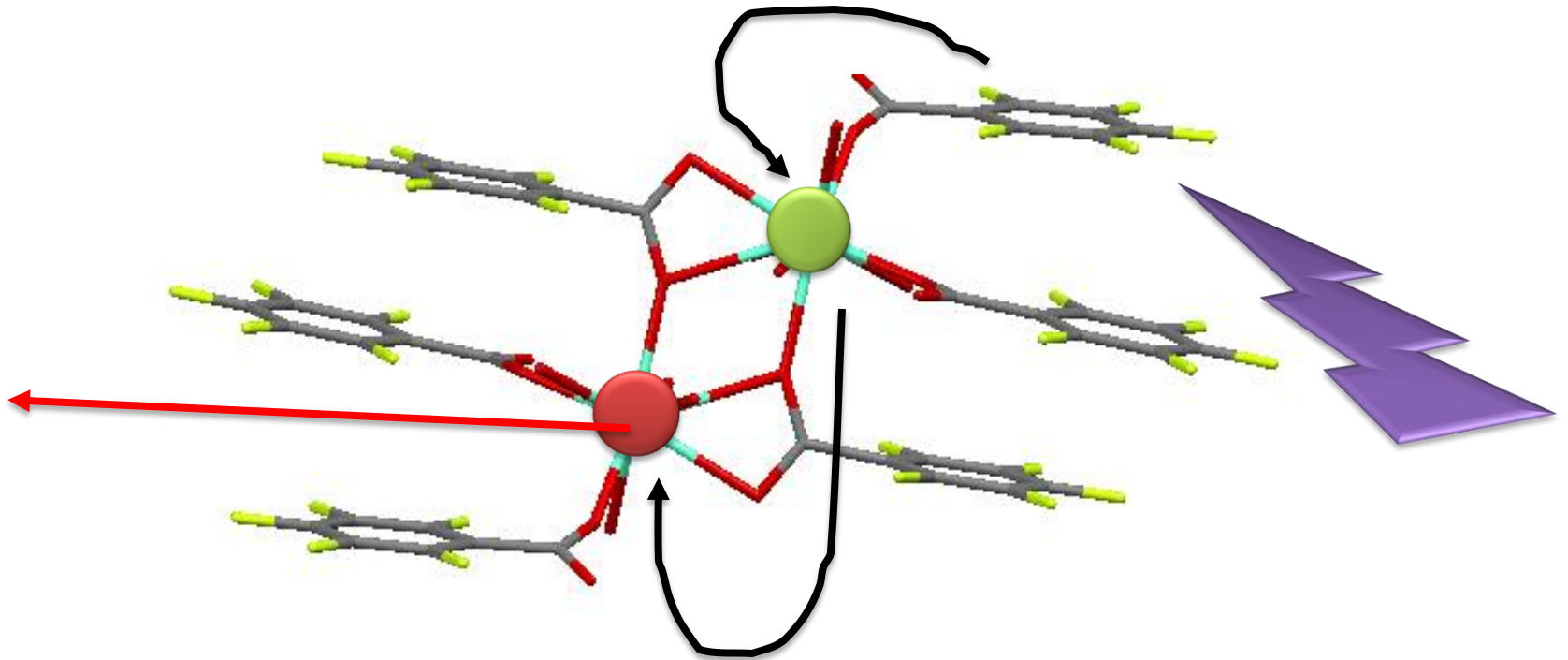
«Хитрые» метки



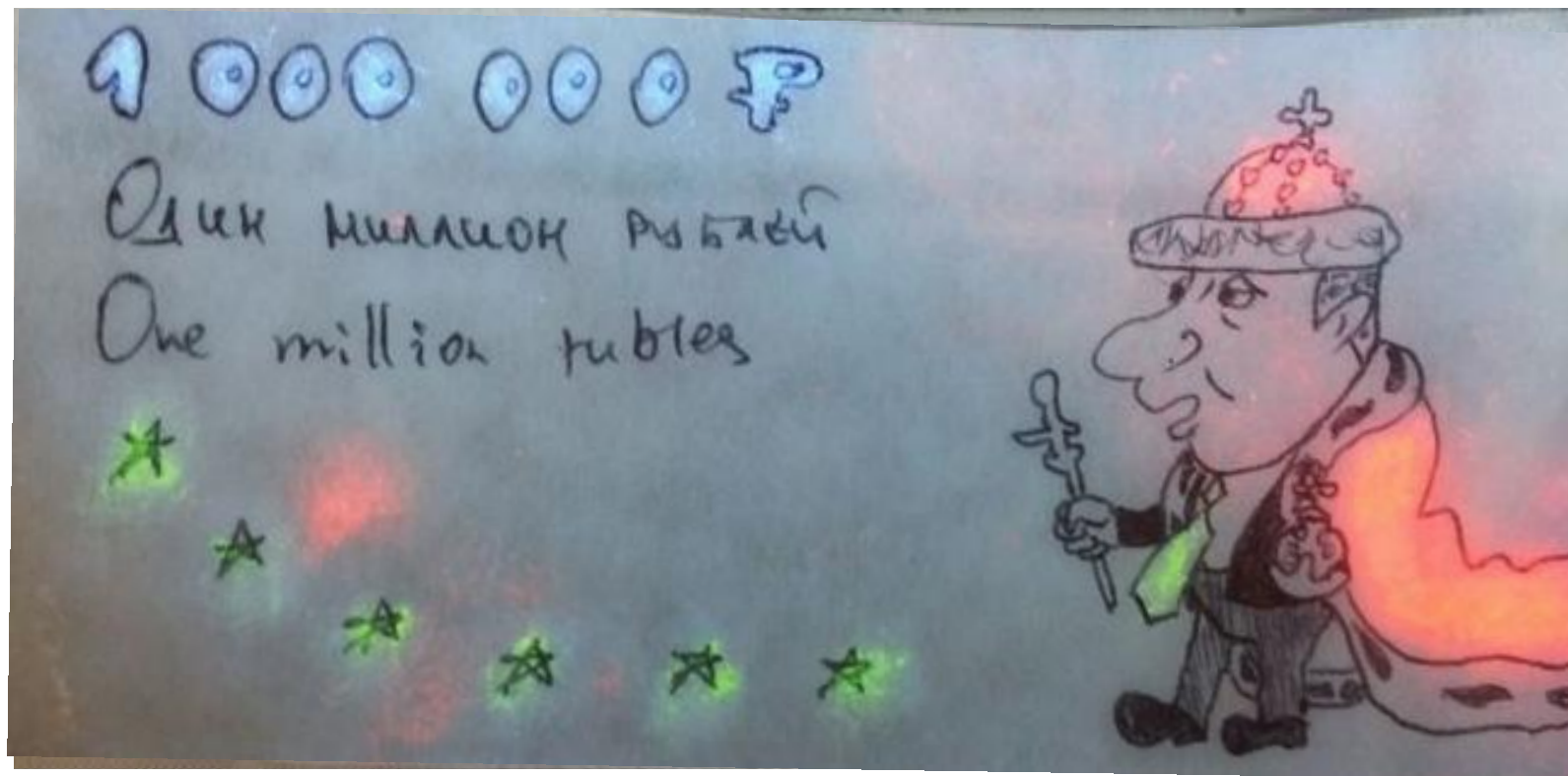
+25 C



-50 C

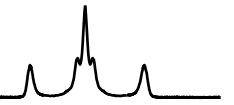


Люминесцентные метки



300 К + УФ

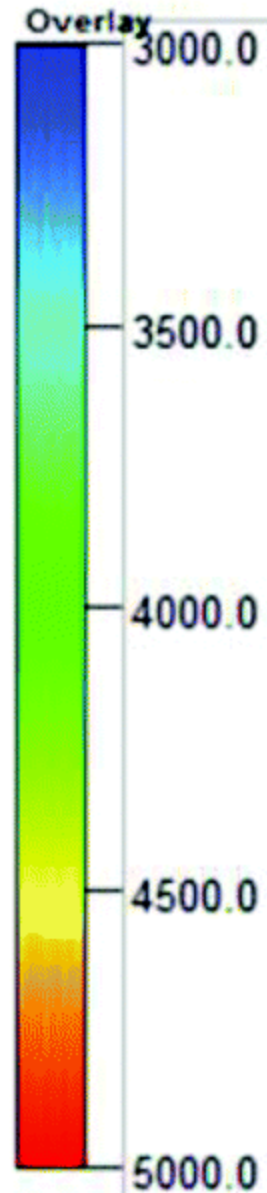
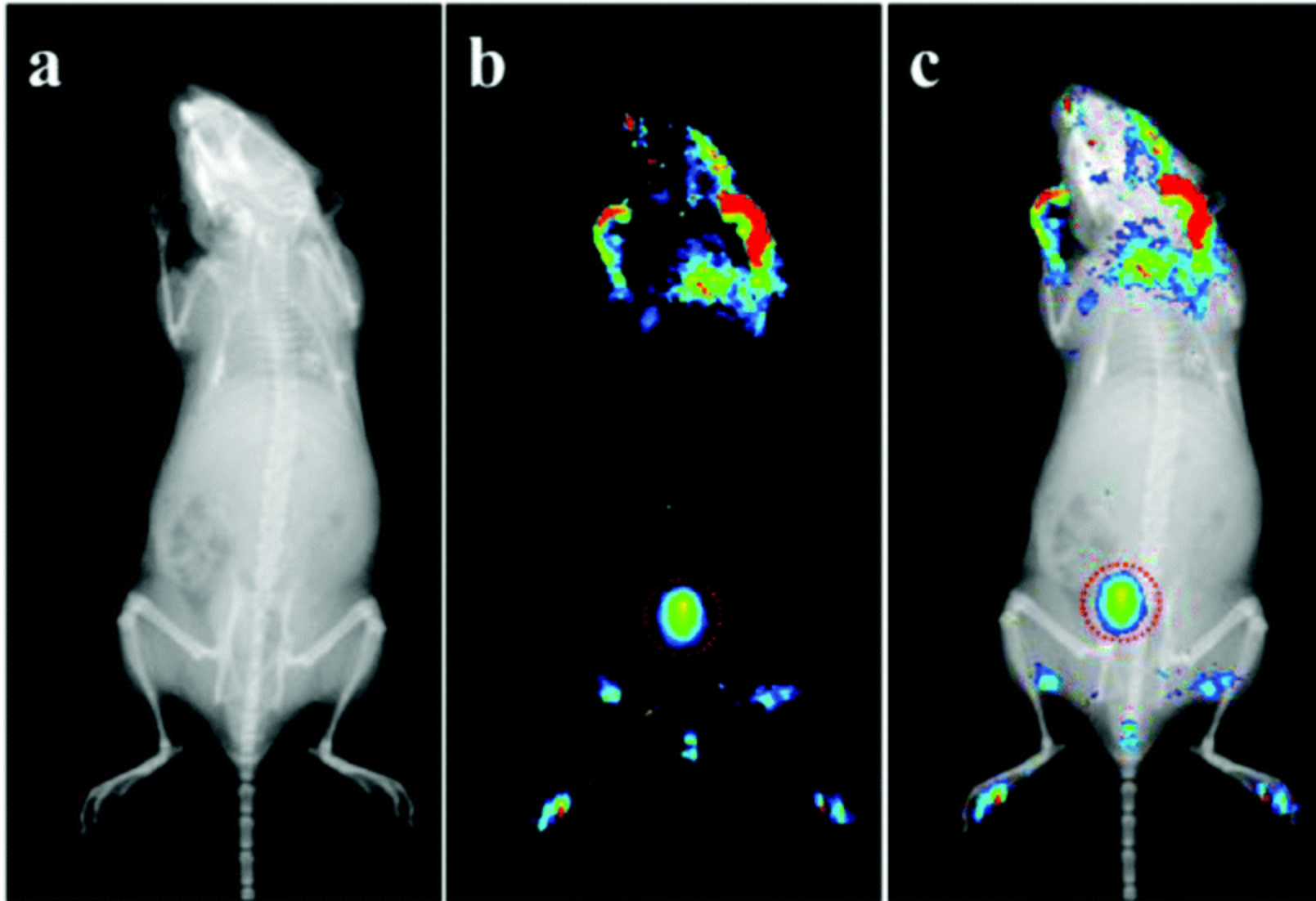
Биовизуализация

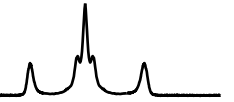


микроскоп

люм. микроскоп

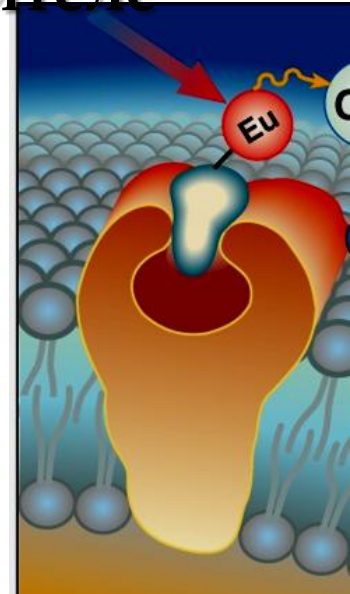
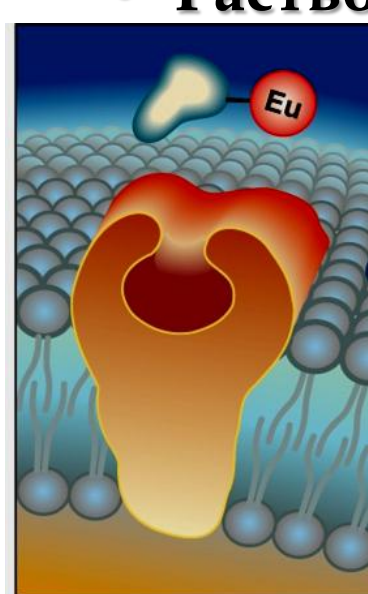
наложение



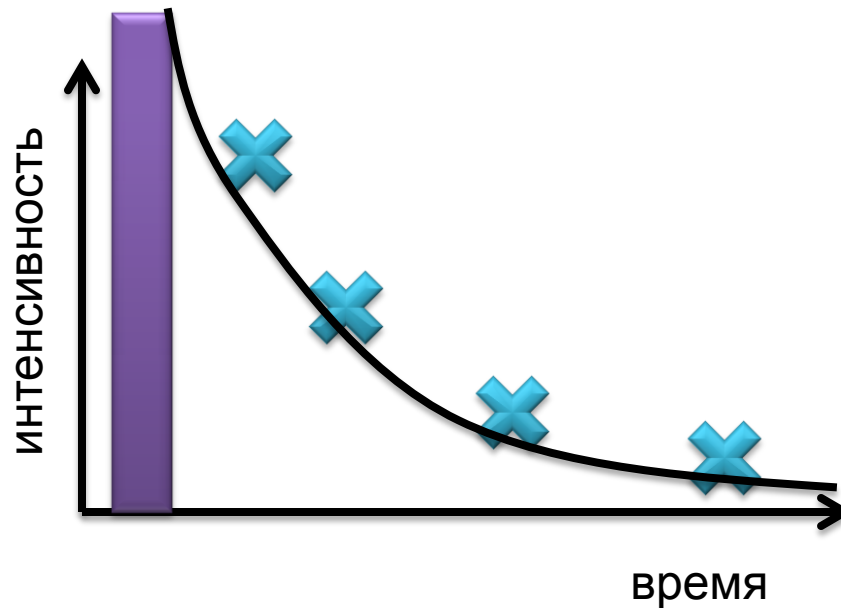
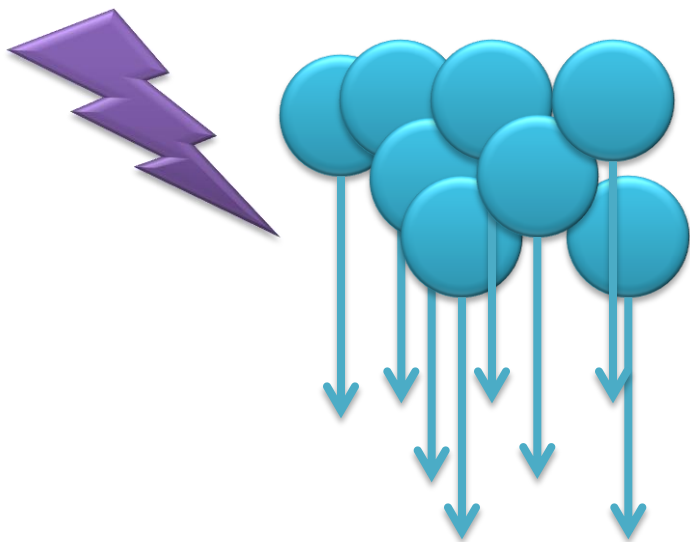


- **Длинные времена жизни: отсекаем автофлуоресценцию**
- **Узкие полосы: эффективный сбор излучения узкощелевыми фильтрами**
- **Большая разница длин волн возбуждения и эмиссии: высокое спектральное разрешение**
- **НЕТОКСИЧНОСТЬ**
- **Растворимость в воде/биоинертном растворителе**

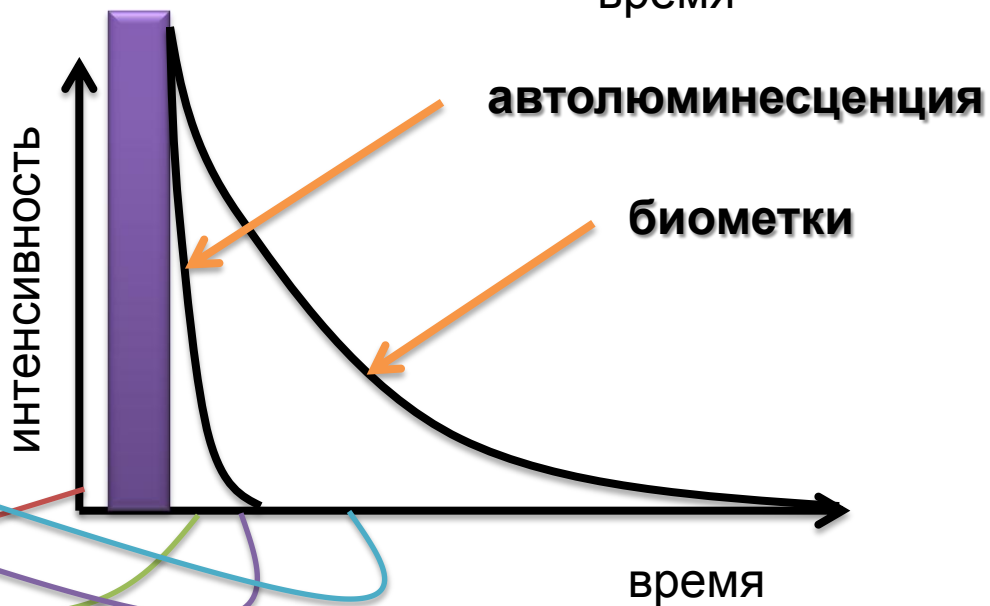
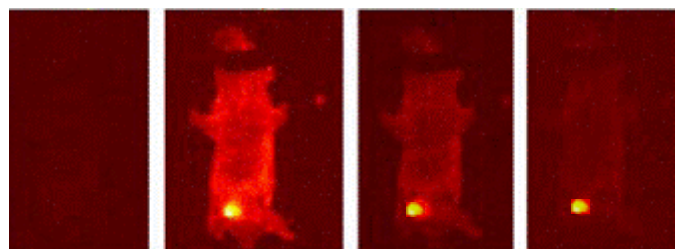
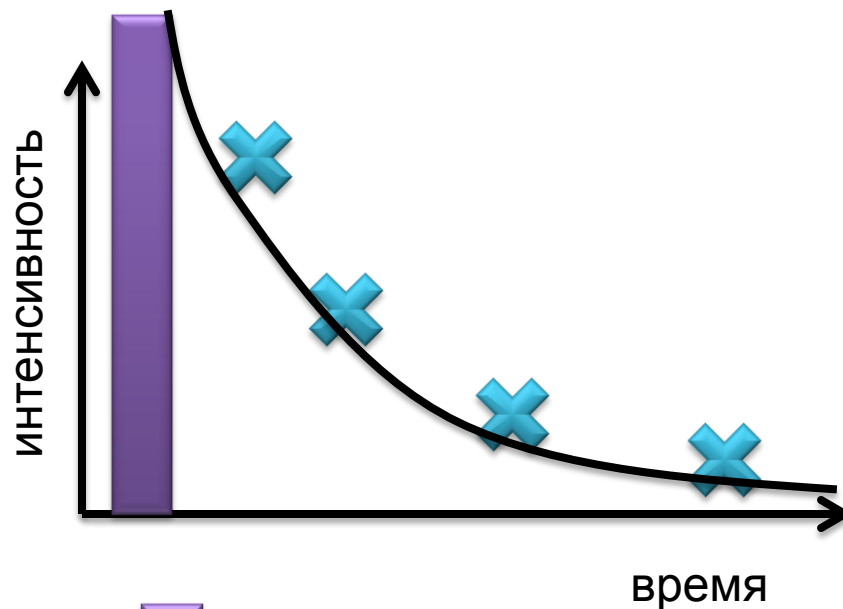
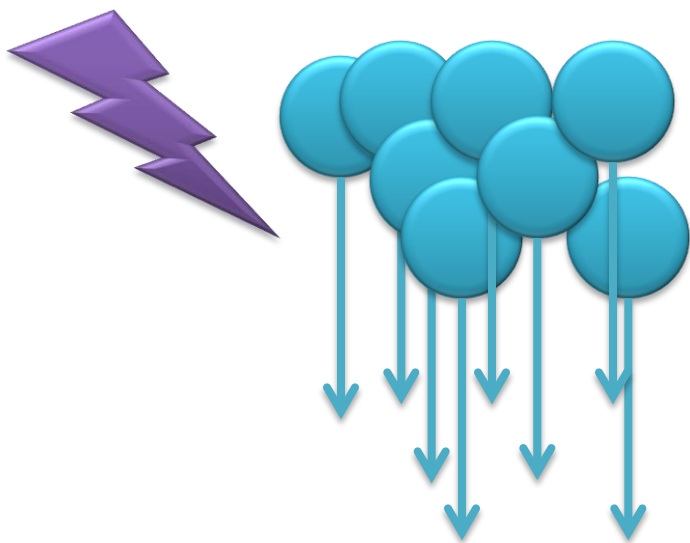
- **Стабильность в (водном) растворе**
- **Высокое поглощение**



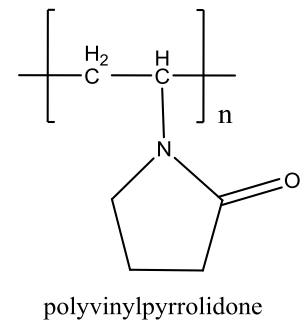
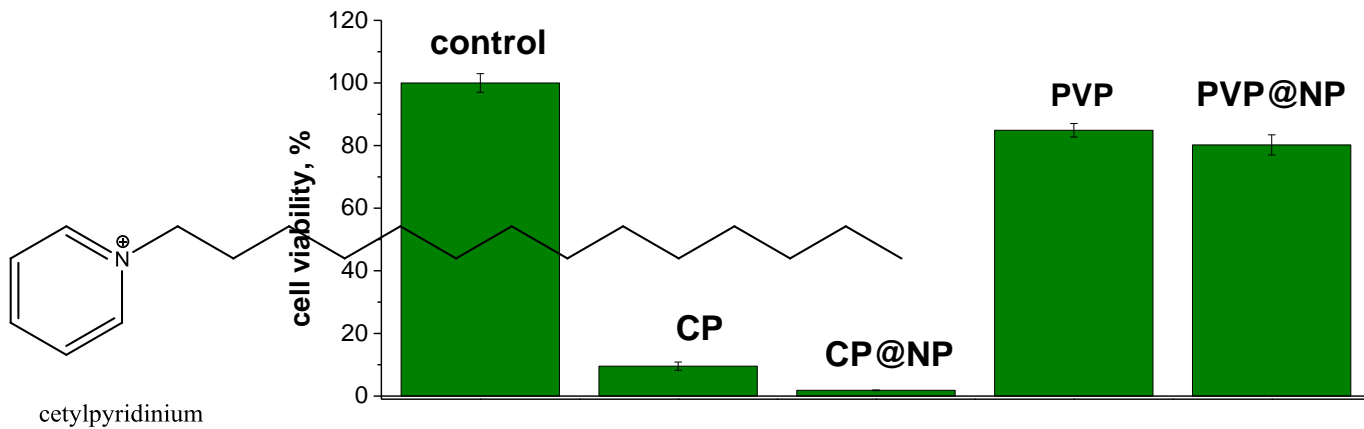
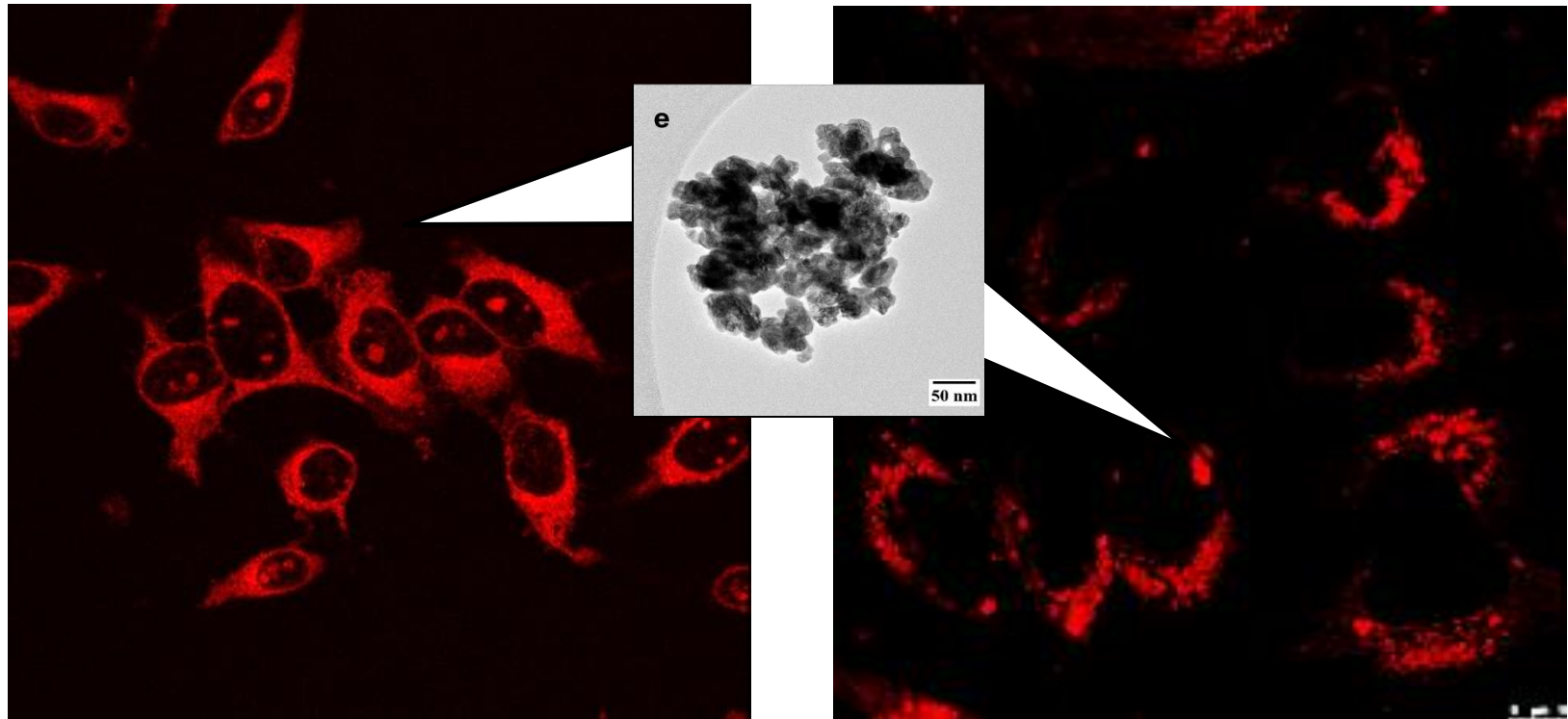
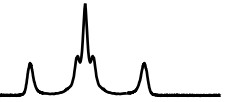
Люминесценция с задержкой



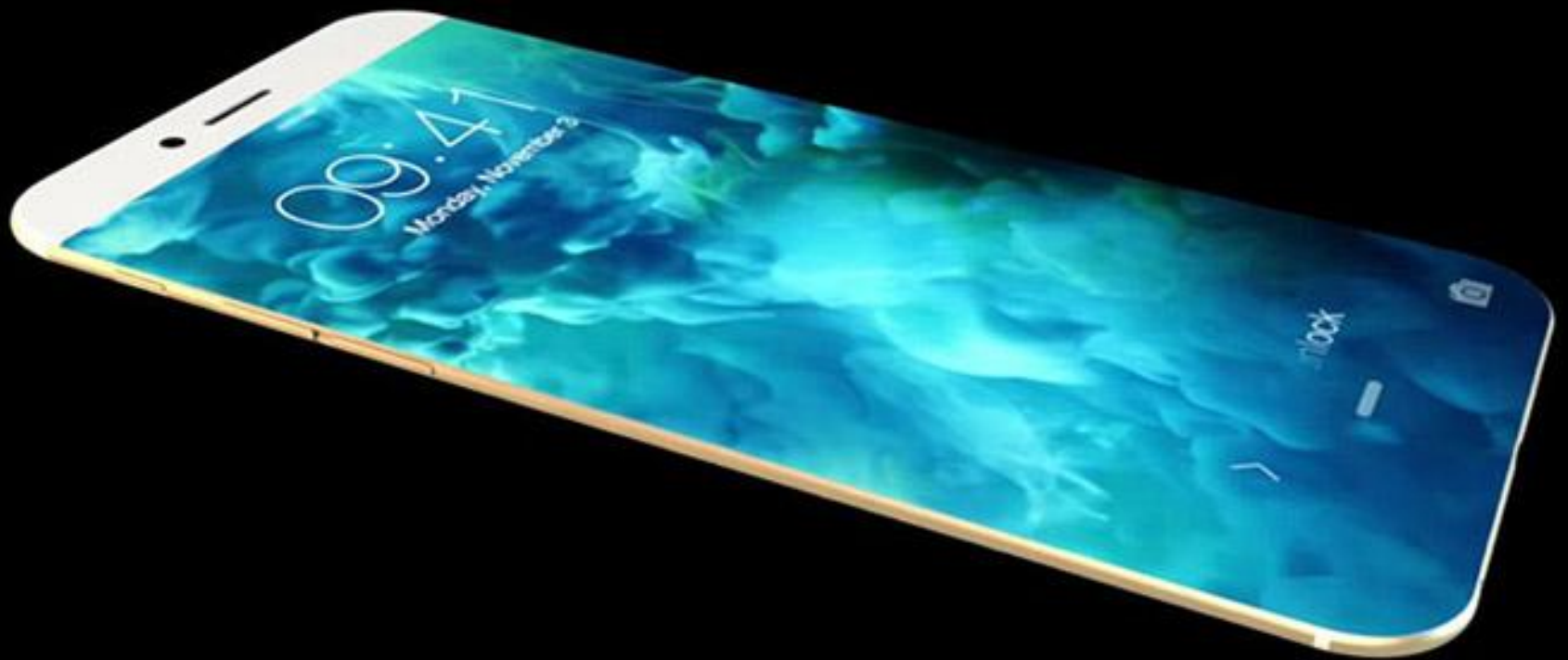
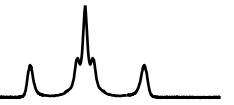
Люминесценция с задержкой



Клеточки



Электролюминесценция

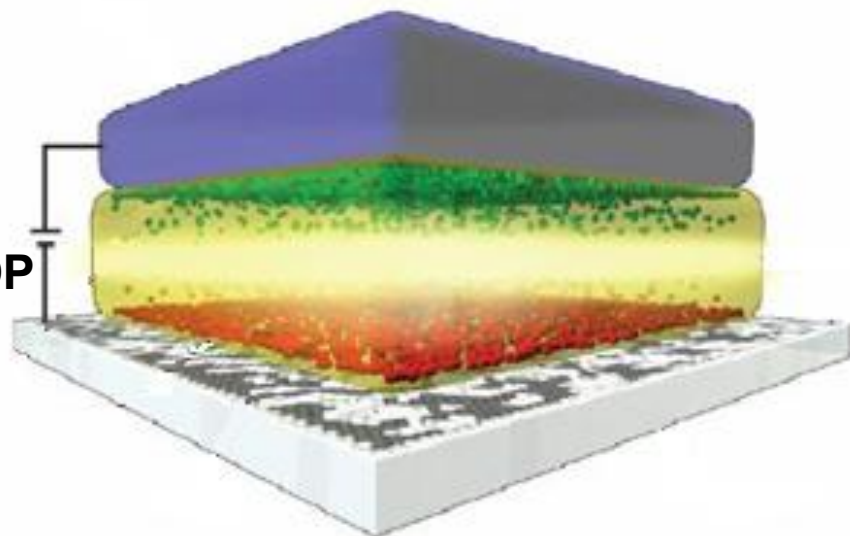


Строение органического светодиода

=59=



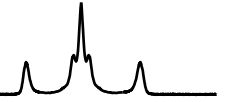
Катод
ETL
ЛЮМИНОФОР
HTL
Анод



ETL – электронпроводящий слой

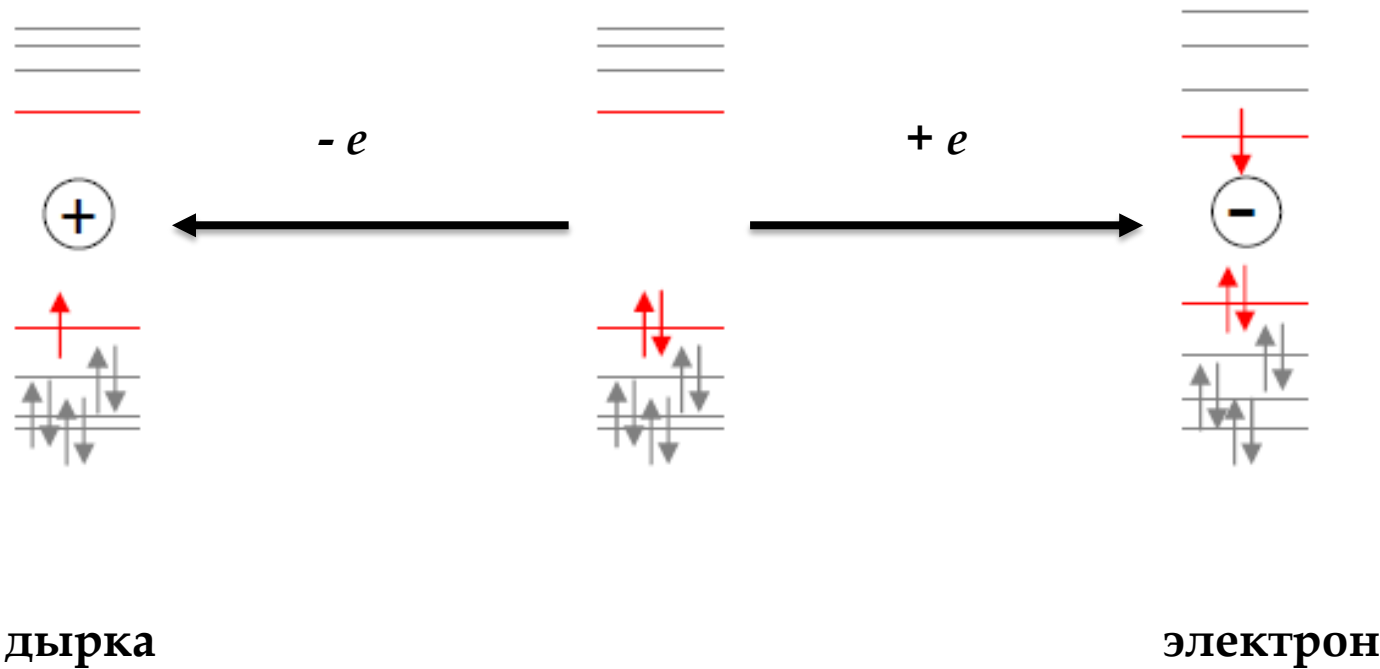
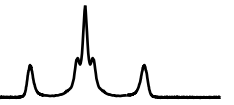
HTL – дыркопроводящий слой

Требования

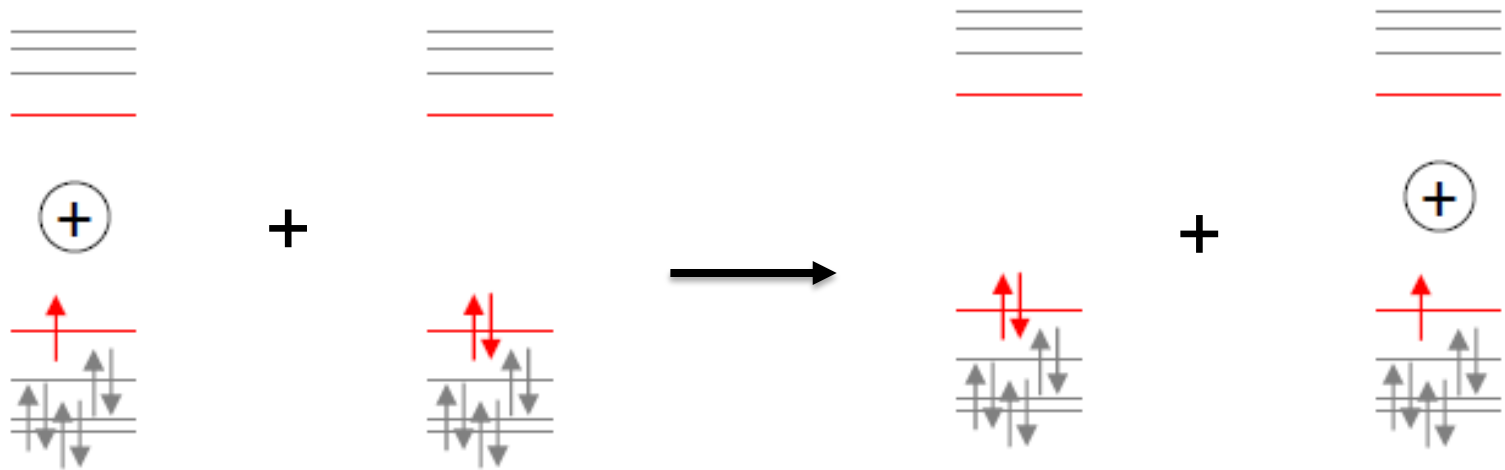
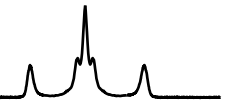


- **Вовлеченность триплетного состояния в процессы переноса**
- **Растворимость в воде/биоинертном пленкообразующем растворителе**
- ~~Высокое поглощение~~ **Высокая подвижность** носителей заряда
- **Термическая стабильность**
- **Оптическая стабильность**

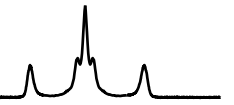
Носители заряда



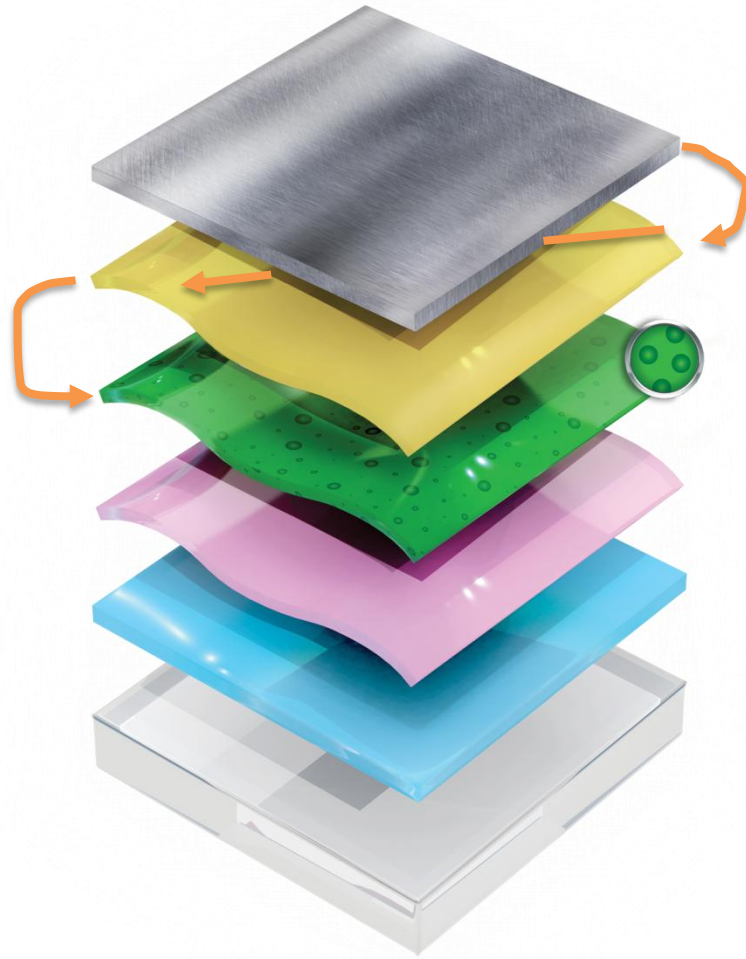
Транспорт заряда



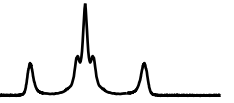
Текут электроны



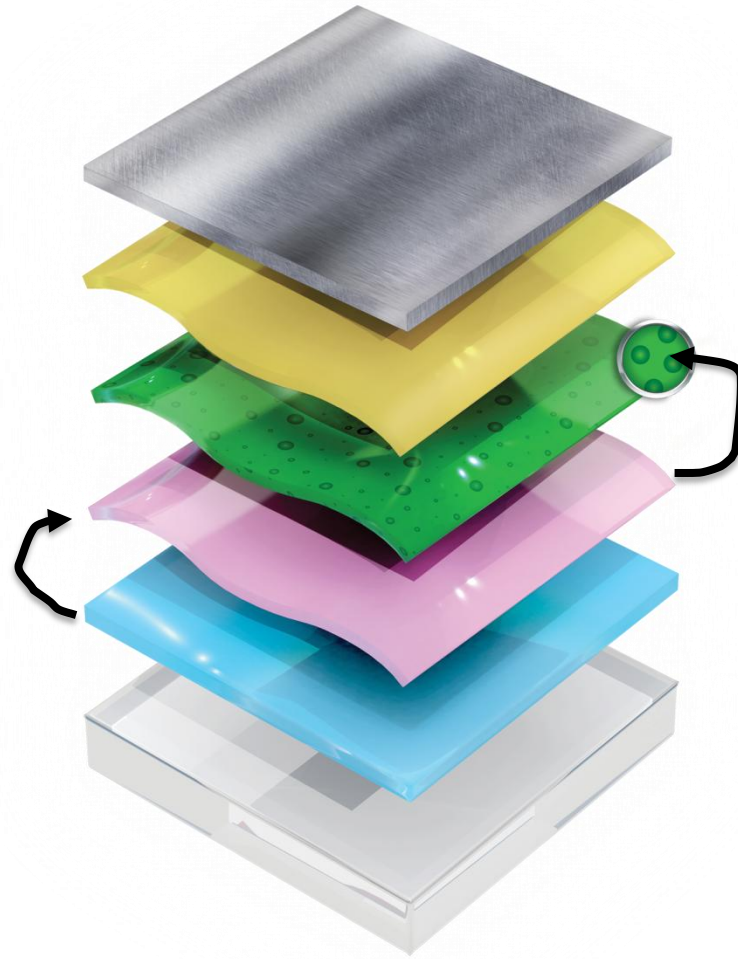
100-200 нм



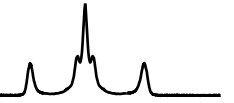
Текут дырки



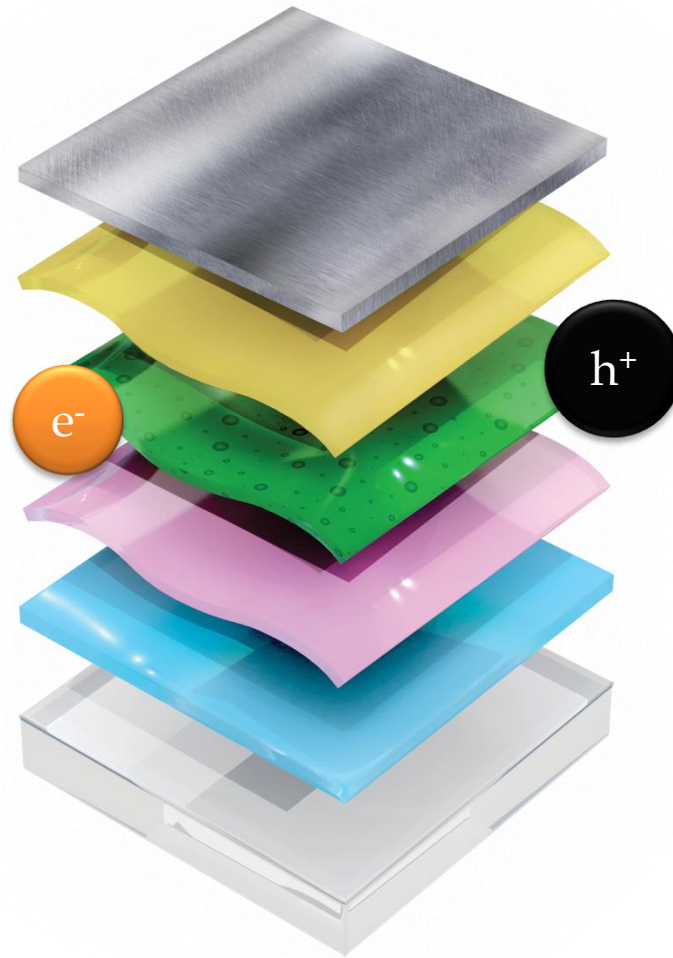
100-200 нм



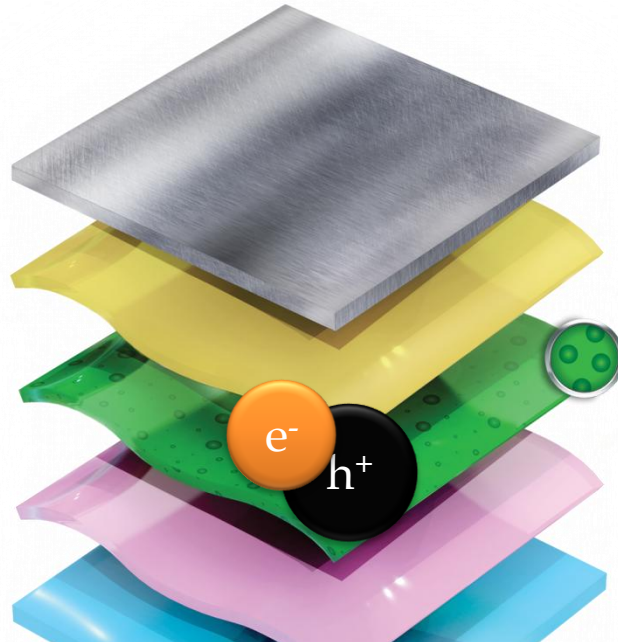
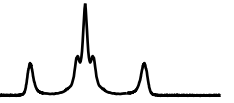
Текут дырки



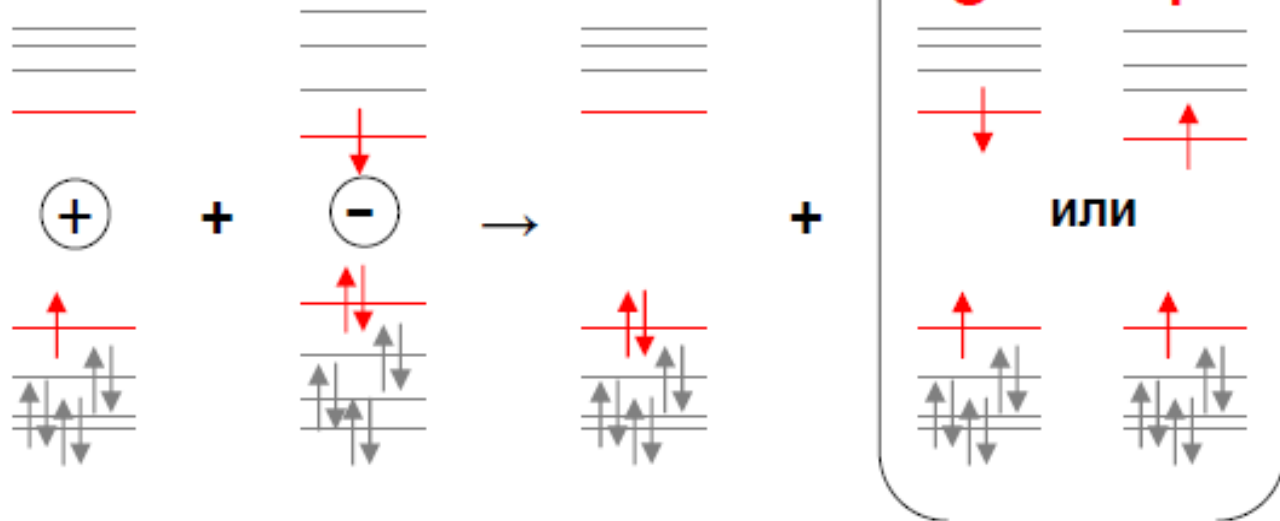
100-200 нм



Текут дырки



1 : 3





Weather

Tampere

5°C

Feels like -4°

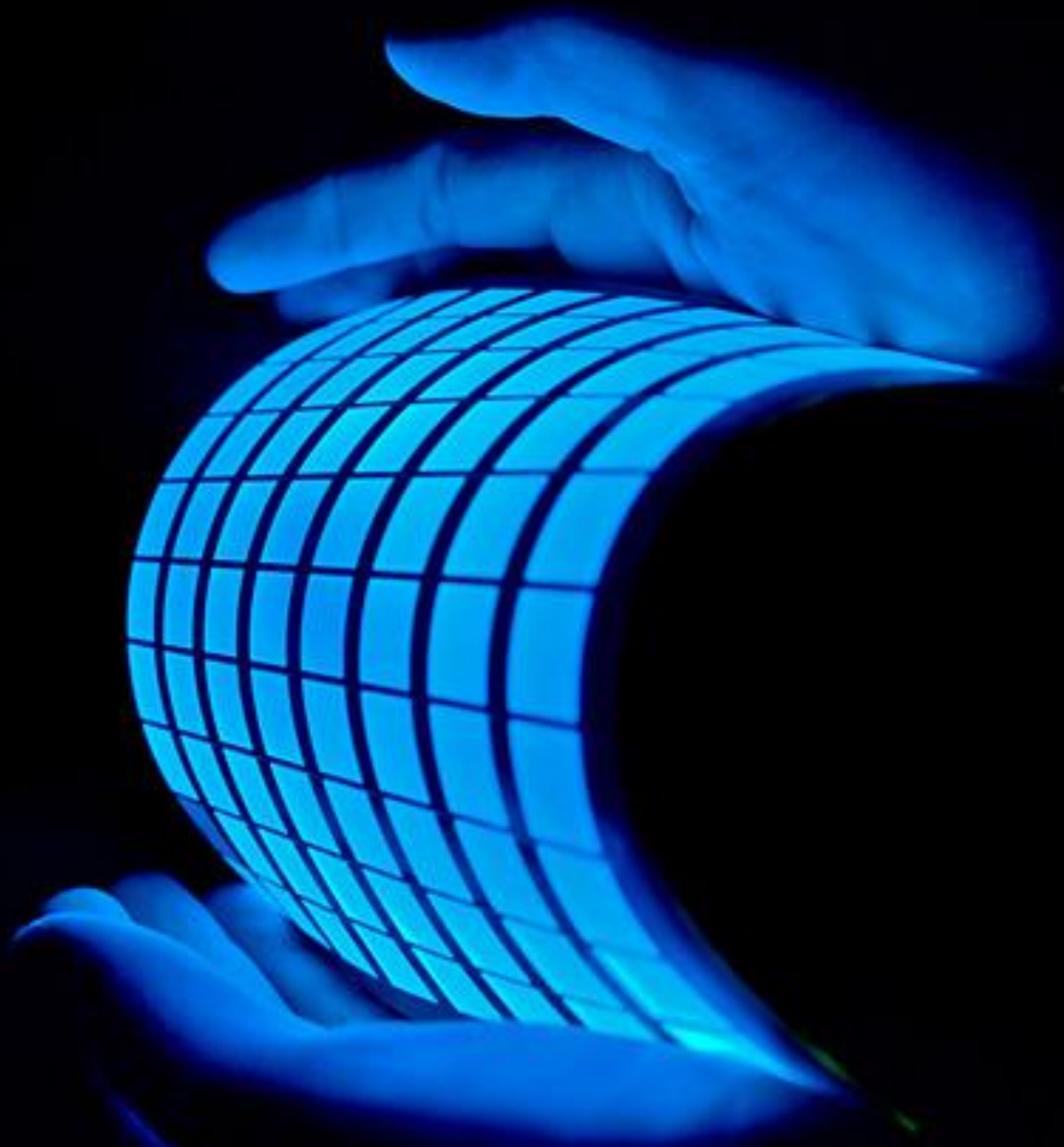
Cold wave

Weekly

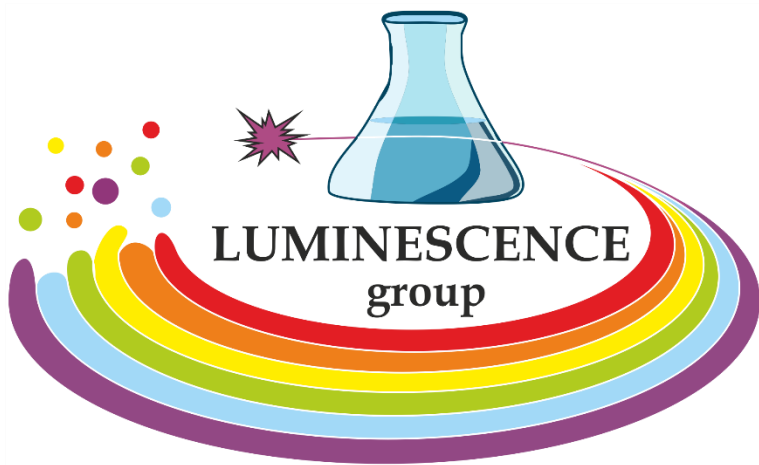
MON

TUE

WED







Спасибо!