

СУПРАМОЛЕКУЛЯРНАЯ ФОТОНИКА

Размер современных сверхбольших интегральных схем, содержащих $\sim 10^6$ схемных элементов (транзисторов, диодов, резисторов), встроенных в поверхностный слой кристалла кремния и функционирующих как единое целое, достигает 1 мкм

"При трехмерной архитектуре применение молекулярных компонентов цепей с промежутками порядка 10- 2 мкм обеспечило бы в миллион раз большую компактность, чем достижимая ныне" [Пиментел Дж., Кунрод Дж. Возможности химии сегодня и завтра. М.: Мир, 1992]

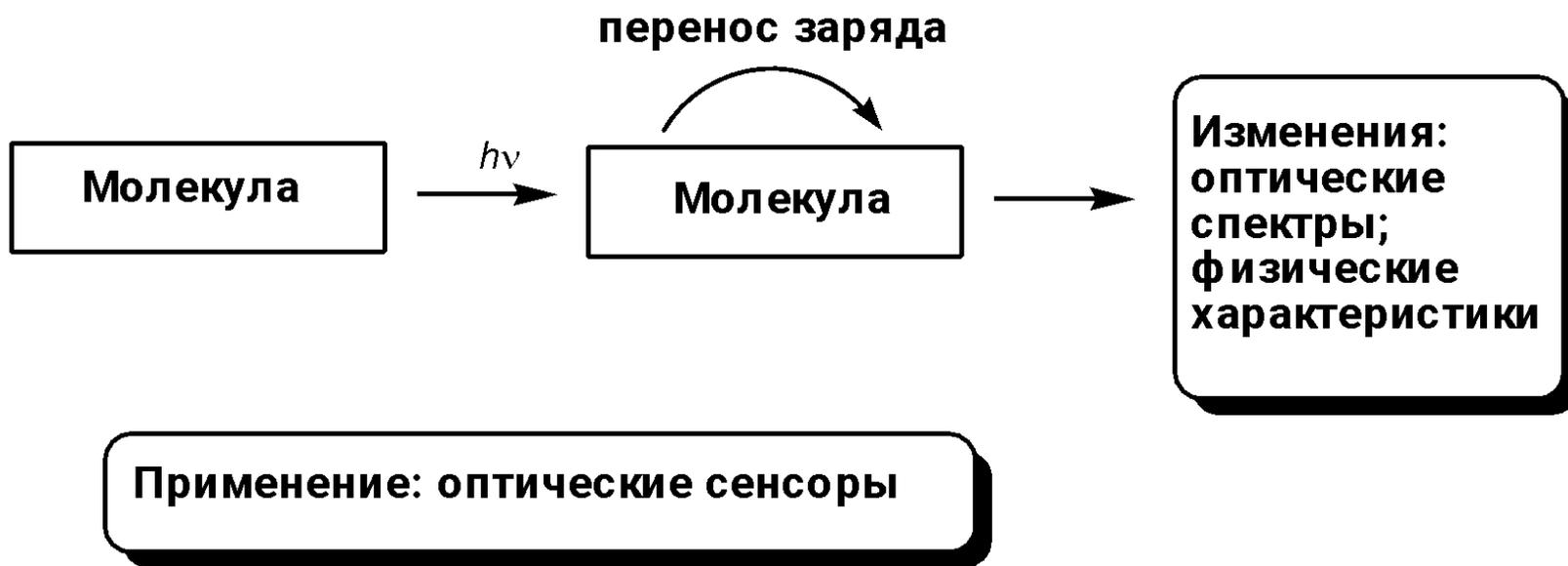
**Супрамолекулы, образованные
за счет связывания компонент
слабыми нековалентными
связями**

**Супрамолекулы, образованные
за счет связывания компонент
ковалентными связями**

Процессы, рассматриваемые супрамолекулярной фотоникой:

- перенос заряда;**
- перенос электрона;**
- перенос энергии;**
- возникновение долгоживущих возбужденных состояний;**
- структурные изменения;**

ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С НАПРАВЛЕННЫМ ПЕРЕНОСОМ ЗАРЯДА



ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С НАПРАВЛЕННЫМ ПЕРЕНОСОМ ЗАРЯДА

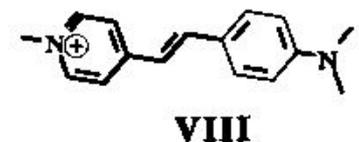
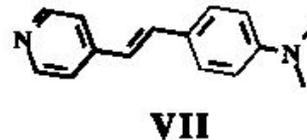
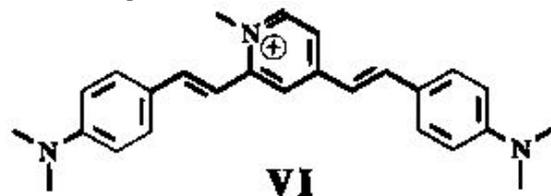
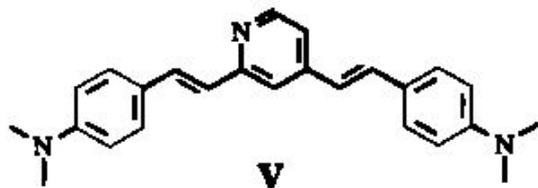
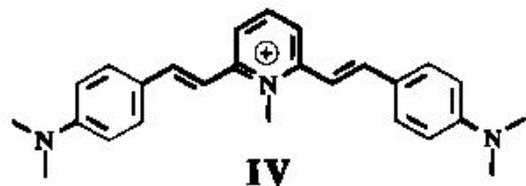
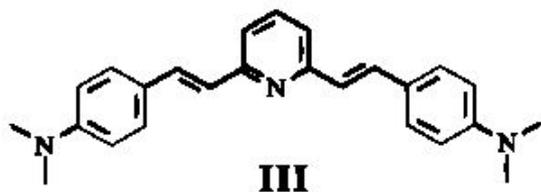
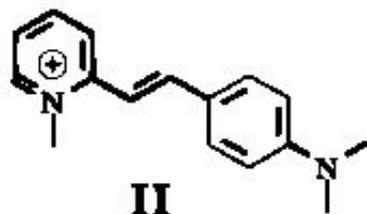
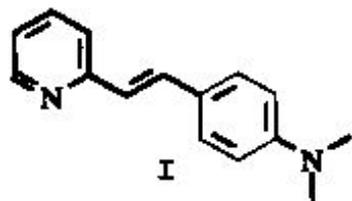


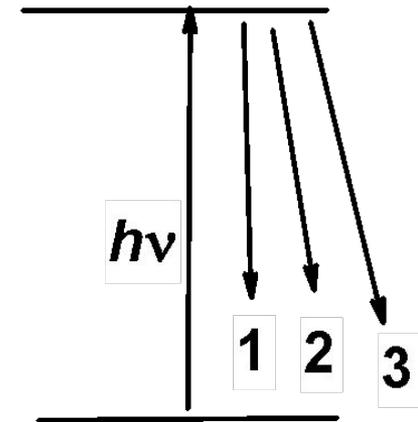
Table 1. Basic Absorption and Emission Properties of Eight Pyridylvinylene Derivatives in Methanol^a

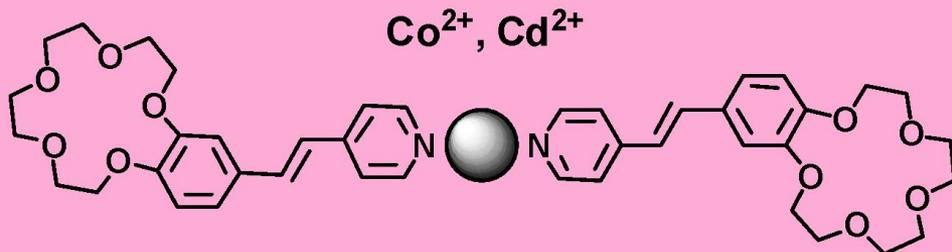
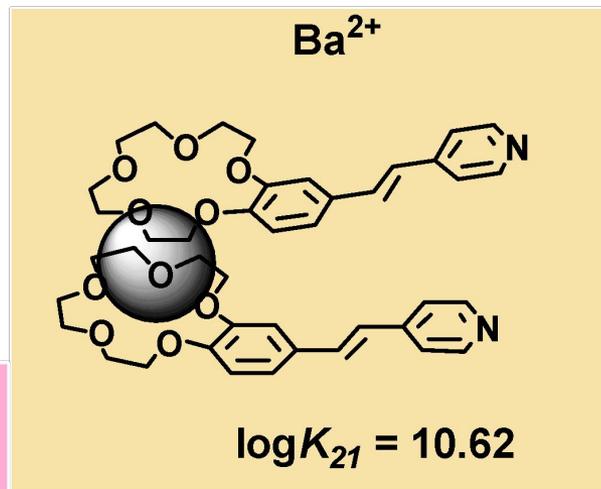
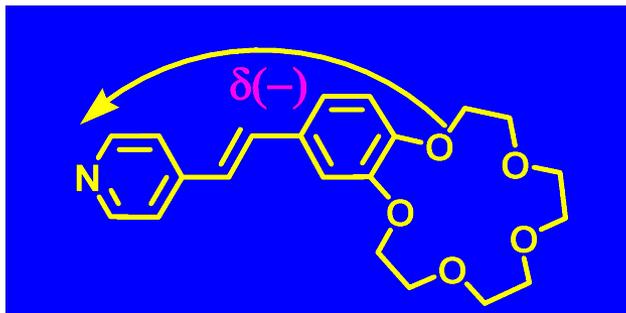
compd	ABS (nm)	FLSC (nm)	Φ_F
I	370	482	0.01
II	463	572	0.003
III	384	476	0.004
III triple-H⁽⁺⁾	364	423	0.01
IV	495	588	0.0004
V	392	518	0.005
VI	508	645	0.002
V mono-H⁽⁺⁾	502	650	0.002
VI double-H⁽⁺⁾	342	425	0.007
V triple-H⁽⁺⁾	345	425	0.009
VII	378	497	0.01
VIII	476	593	0.003

возбужденное состояние молекулы

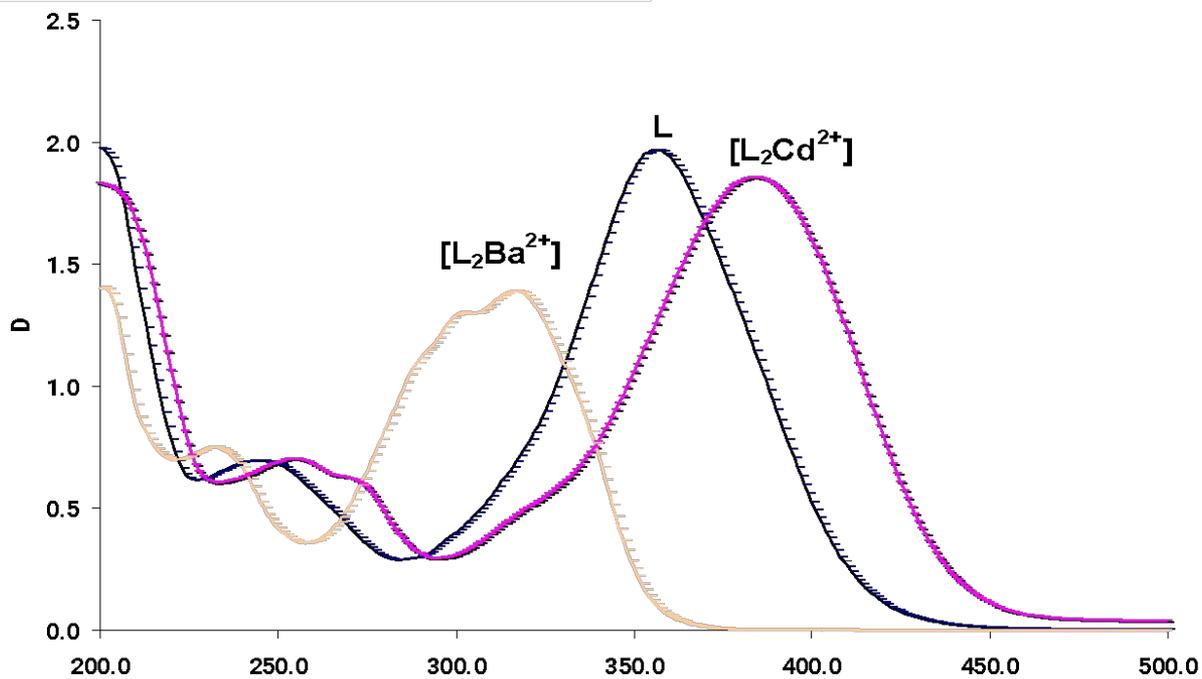
основное состояние молекулы

- 1 - *т* транс-цис-изомеризация ;**
- 2 - флуоресценция ;**
- 3 - перенос заряда**

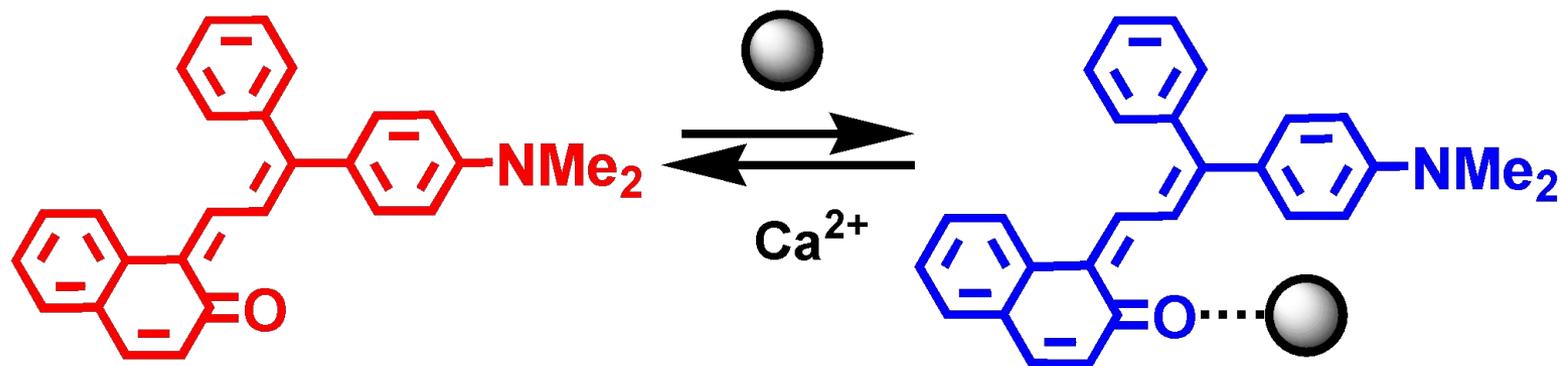




$\log K_{21} = 8.93$



Комплексообразование

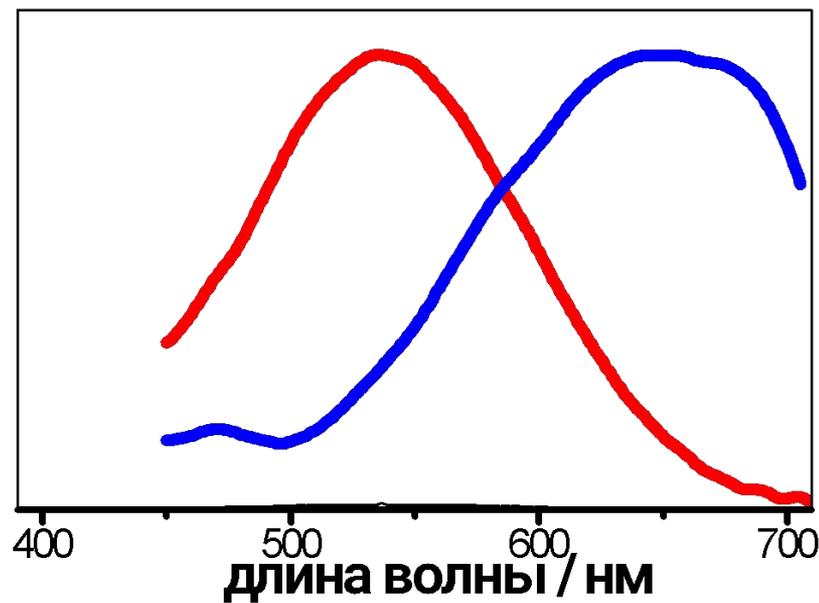


λ_{max}
 $k_{\text{МФ-СФ}}/\text{с}^{-1}$

540nm
0.8

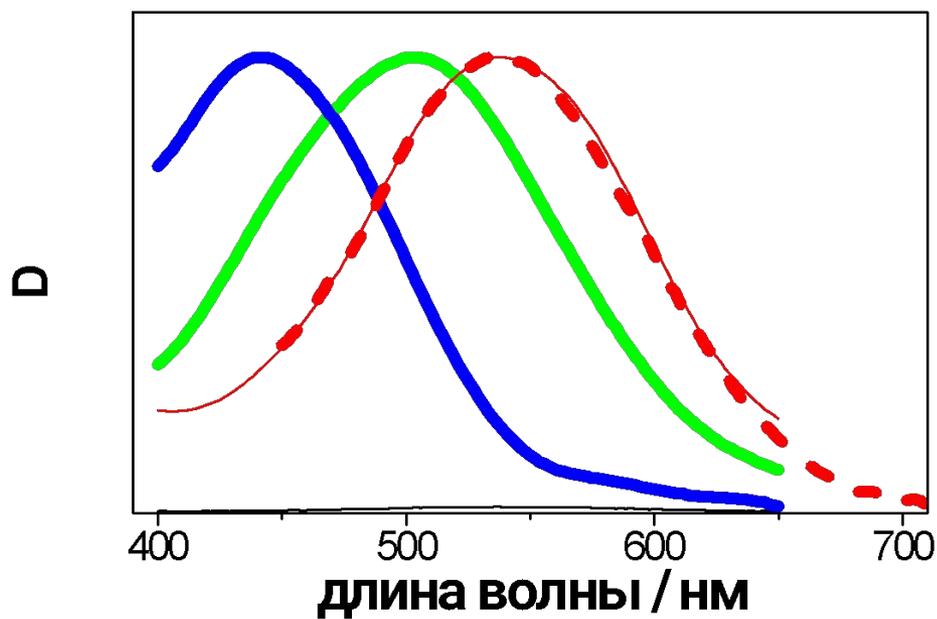
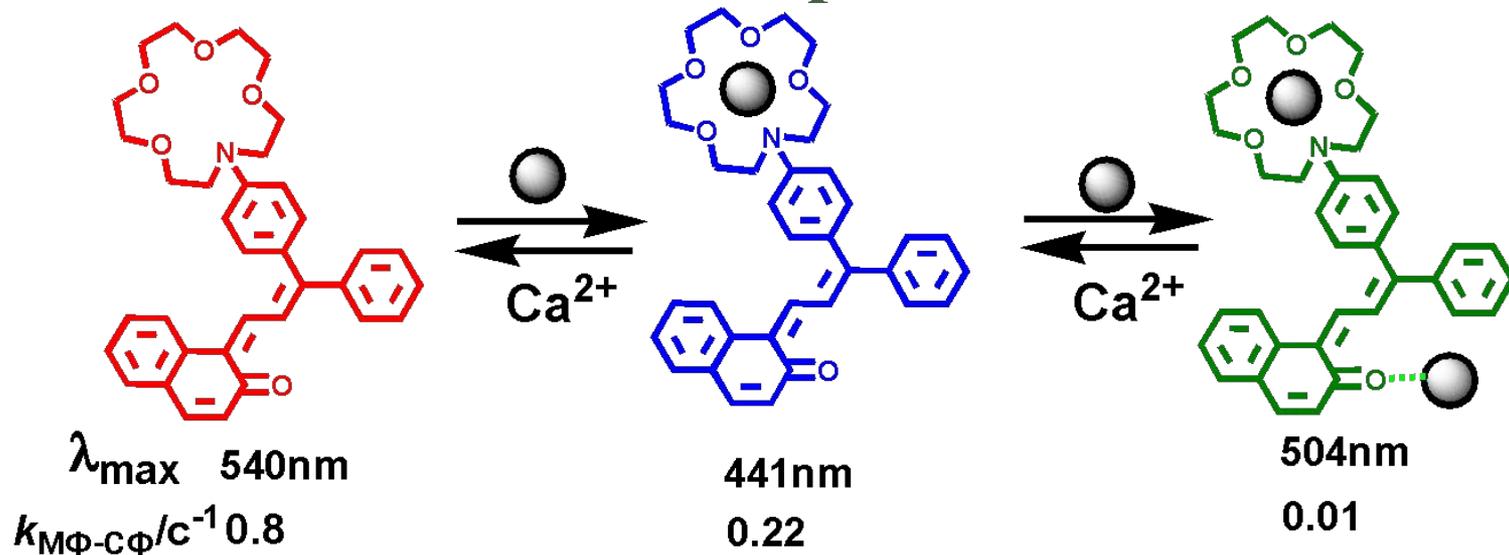
650nm
0.01

D

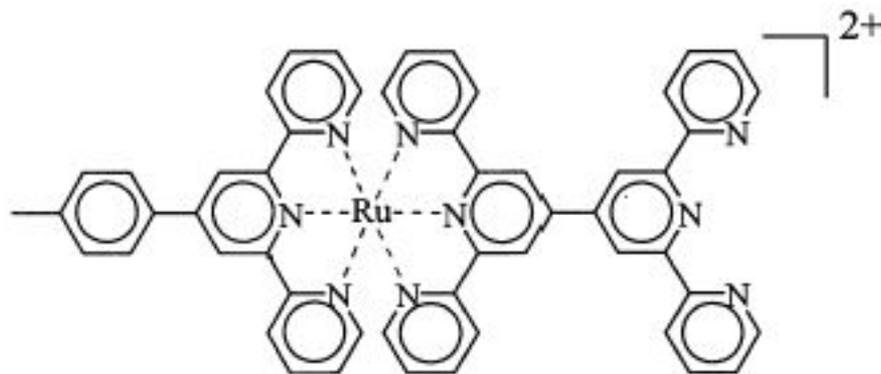


$\log K = 1.6$

Комплексообразование

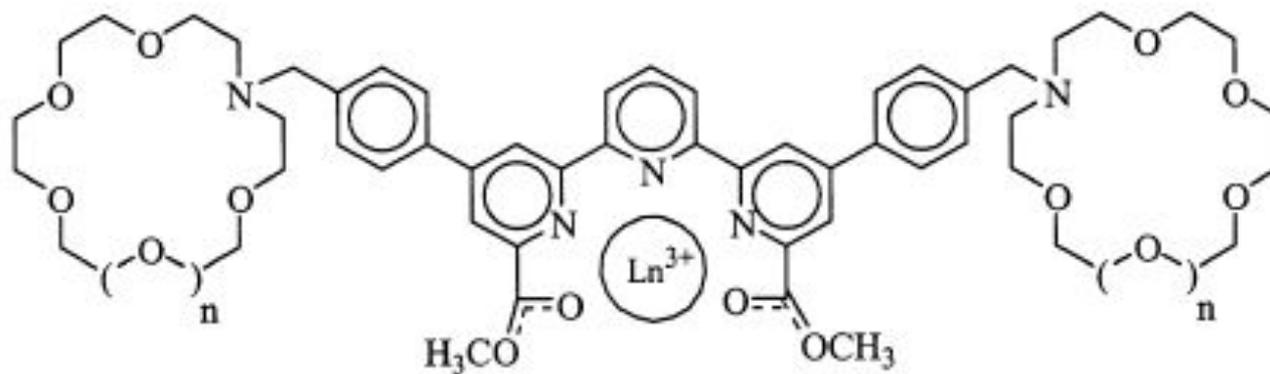


$\log K$ 3.9 1.0



660 nm - MetalLigandChargeTransfer

Zn: 700 nm, the emission intensity is enhanced 8-fold, and the luminescent lifetime increases from 1.6 to 84 ns.



42a $n = 0$

42b $n = 1$

600 nm - MetalLigandChargeTransfer

Na и K - увеличение интенсивности флуоресценции

ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С ДОЛГОЖИВУЩИМИ ВОЗБУЖДЕННЫМИ СОСТОЯНИЯМИ



**Комплекс:
эксимер
эксиплекс
долгоживущее
возбужденное
состояние**

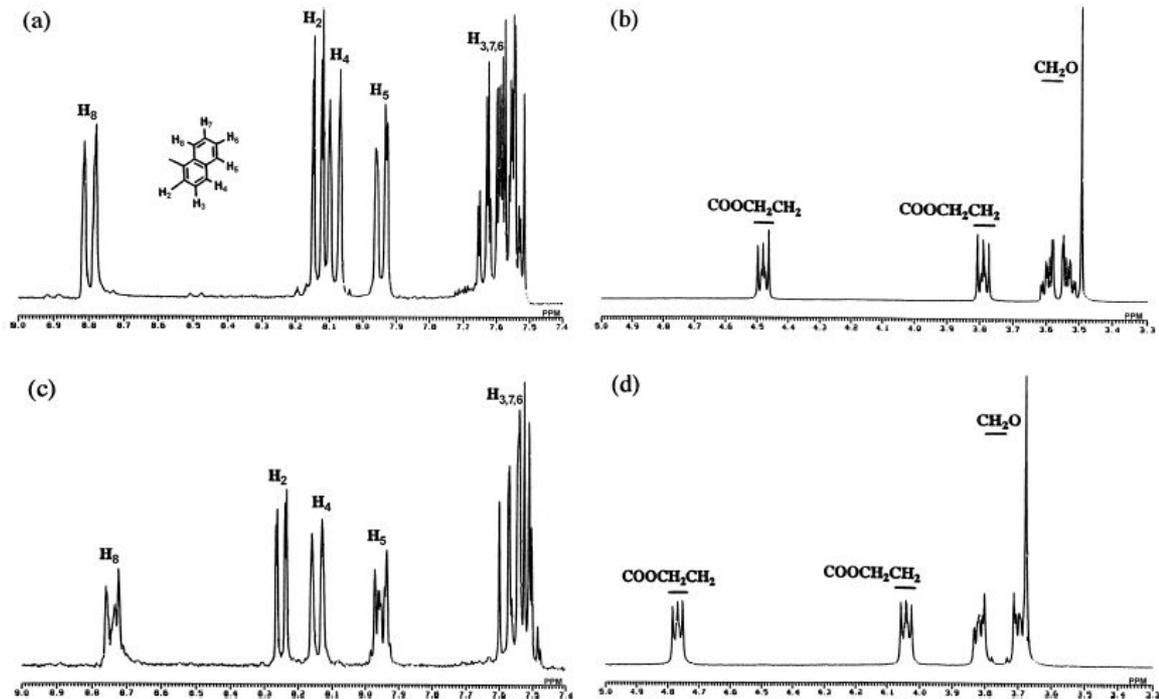
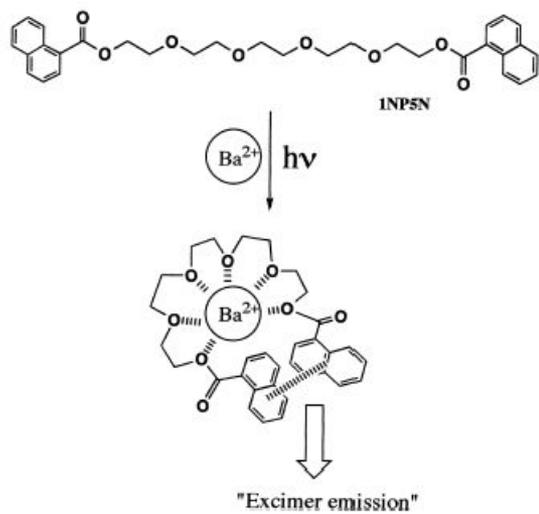


Fig. 6. ^1H NMR spectra of INPSN in the absence ((a) and (b)) and presence ((c) and (d)) of barium salt in acetonitrile- d_3 at room temperature.

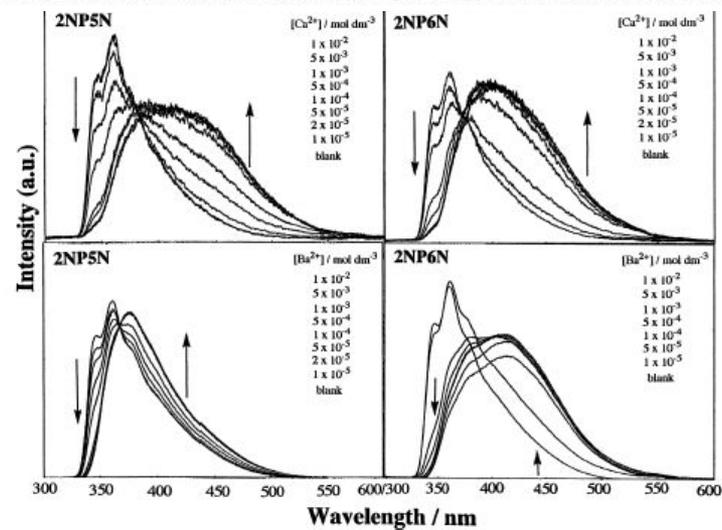
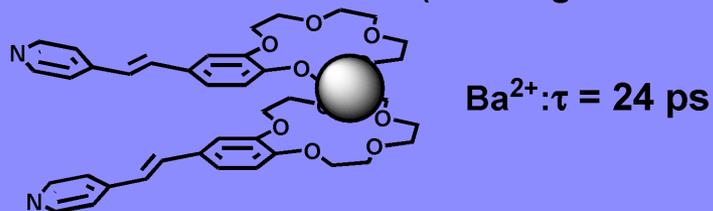
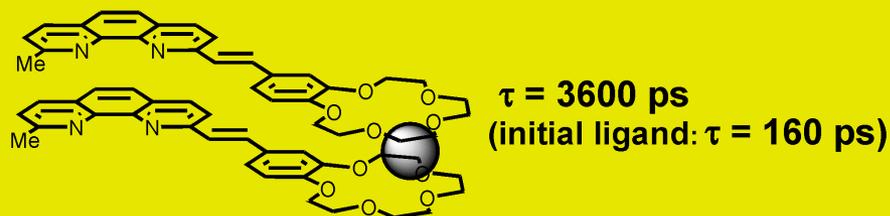
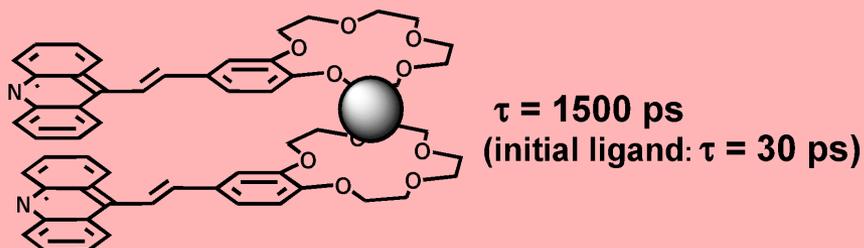
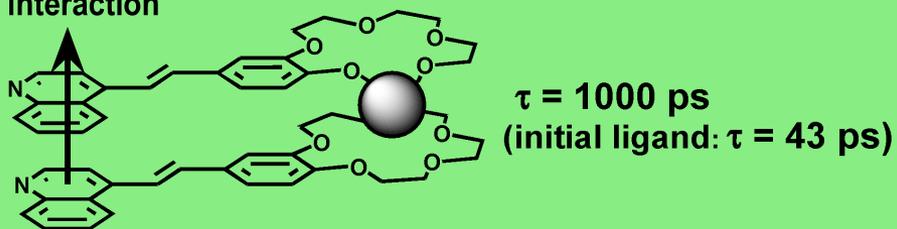


Fig. 5. Fluorescence spectra of 2NP n N ($n = 5, 6$) and their Ca^{2+} and Ba^{2+} complexes, as excited at 265 nm. $[\text{2NP}n\text{N}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile at 25°C.

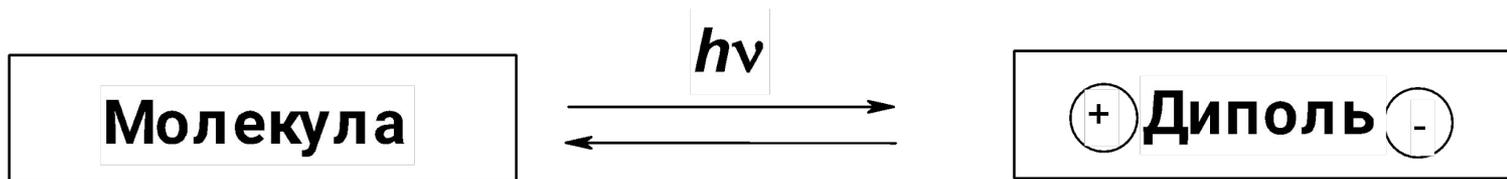
Время жизни возбужденного состояния комплексов Ba^{2+}



π - π -stacking
interaction

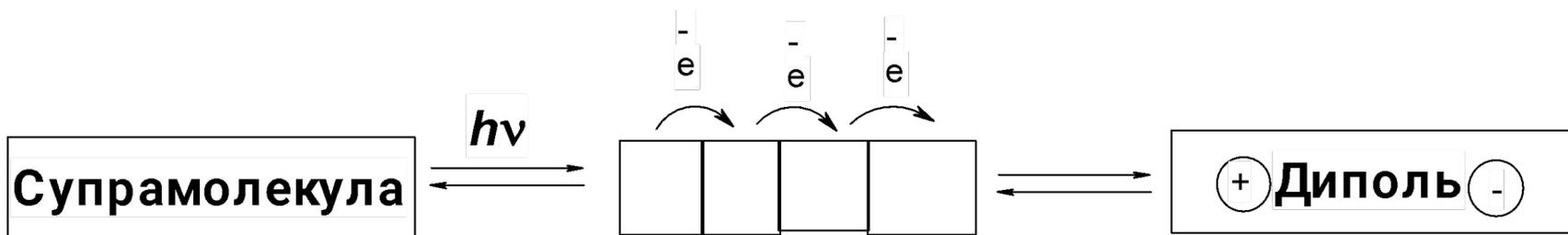


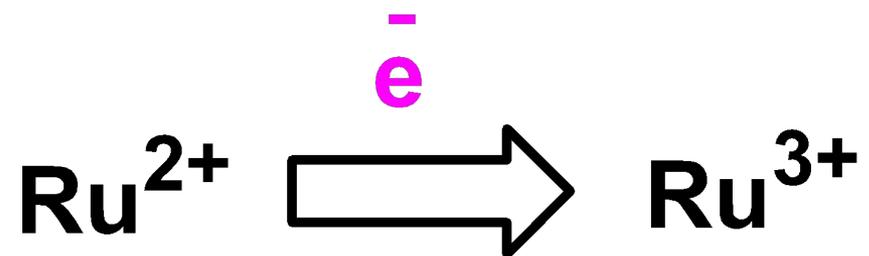
ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С НАПРАВЛЕННЫМ ПЕРЕНОСОМ ЭЛЕКТРОНА



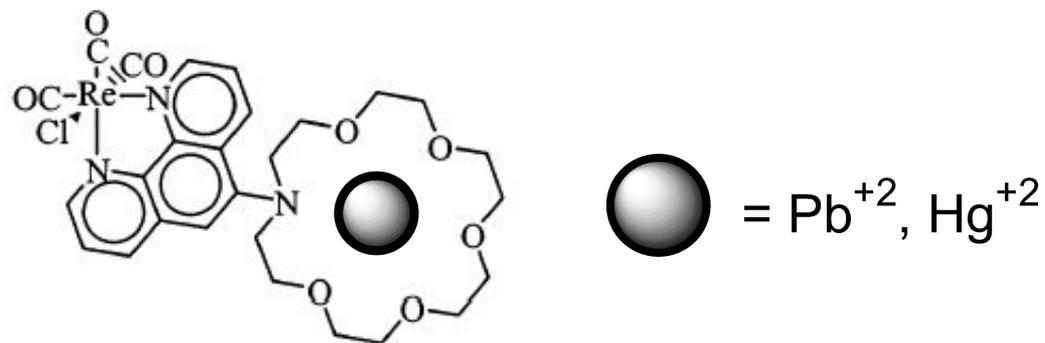
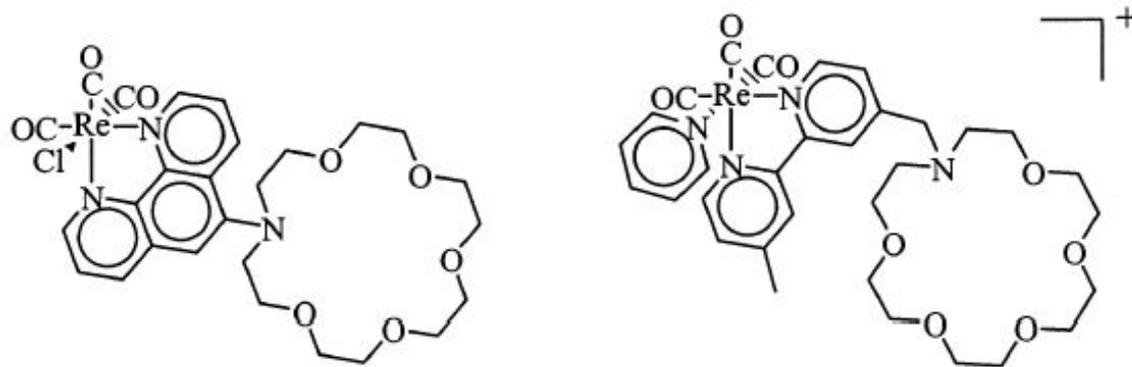
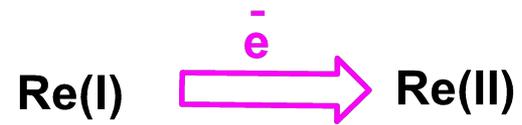
время жизни 10^{-10} с

Природный фотосинтетический цикл:
время жизни разделенных зарядов достигает $\sim 0,1$ с





Re(I), Os(II)



0.4 eV
 10^9 s^{-1}

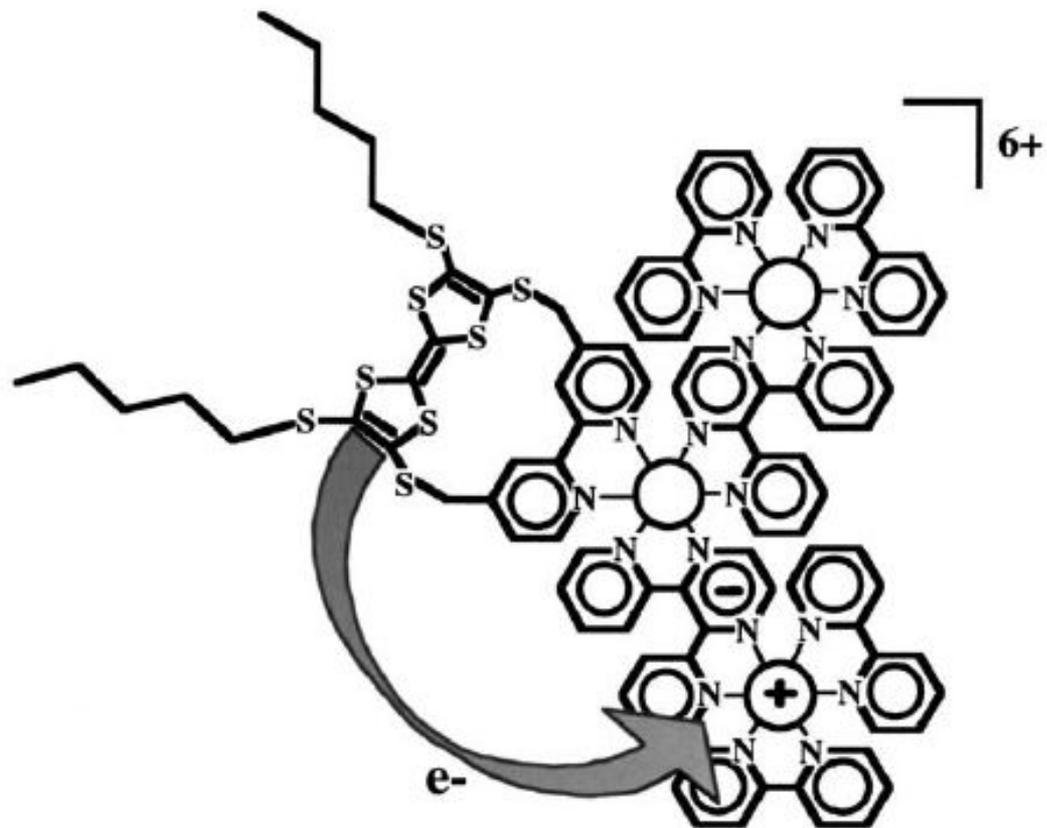
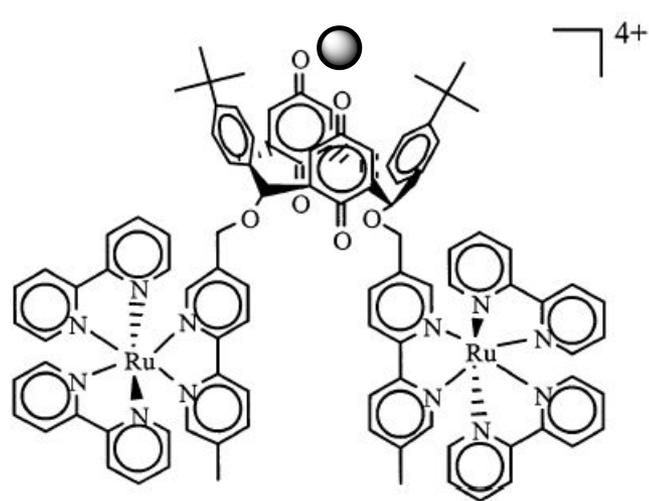
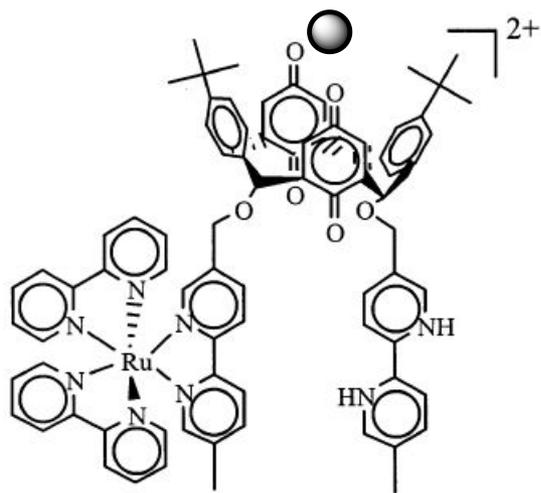
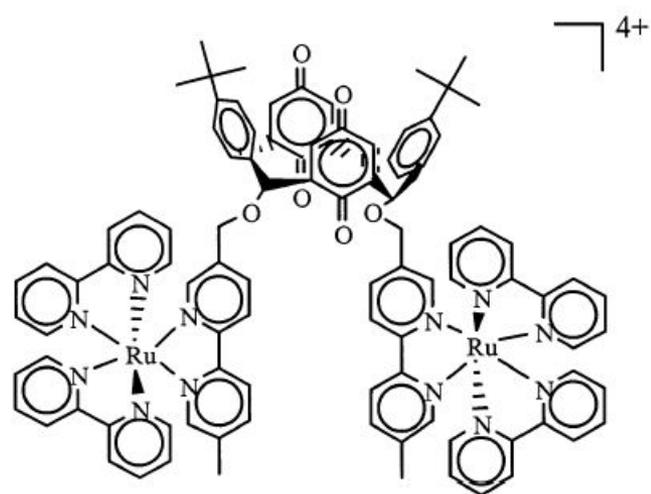
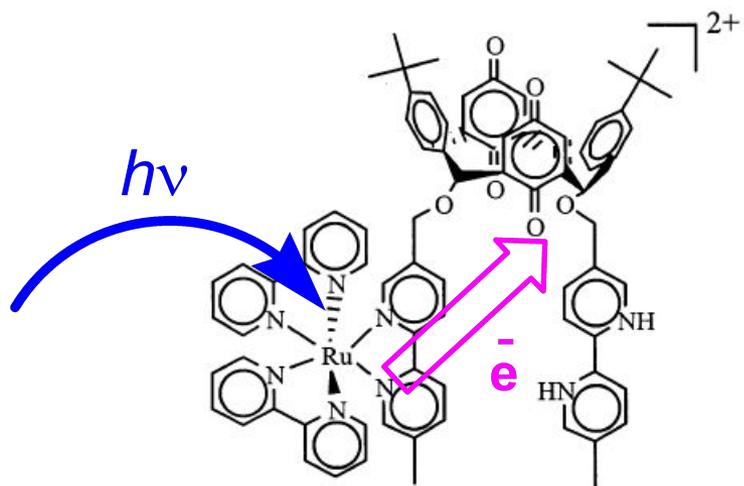


Fig. 11. Long-range photoinduced electron transfer, in **6**, from TTF to a non-adjacent (nominally Ru(III)) metal centre in a trinuclear antenna [19].



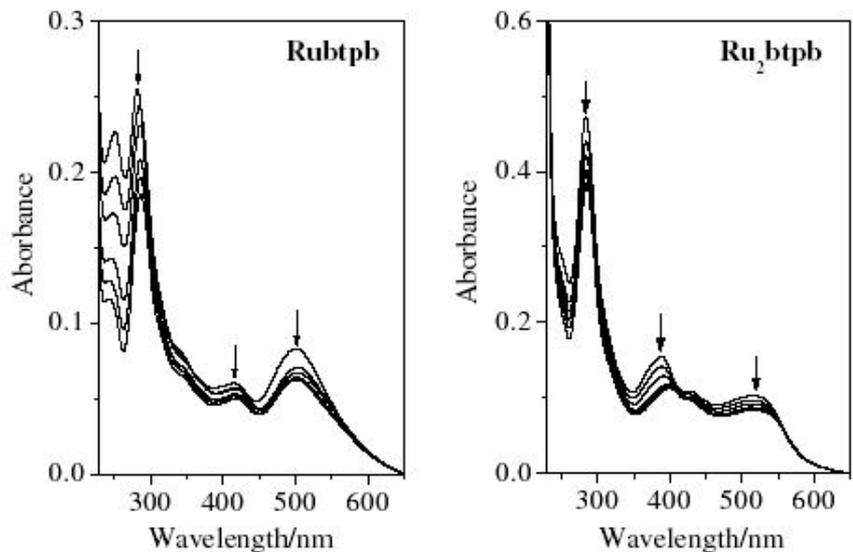
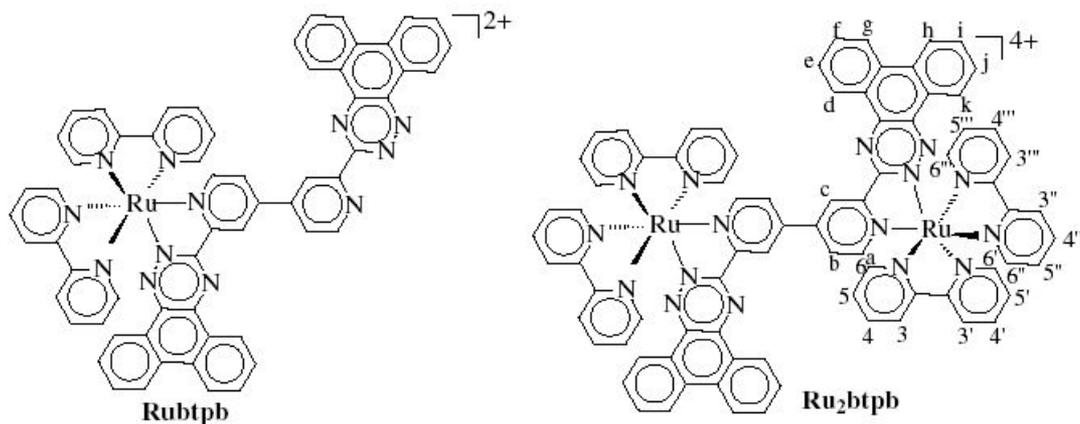


Fig. 2. Absorption spectra of the mono- and diruthenium(II) complexes in Tris-HCl buffer upon addition of CT-DNA. [Ru complex] = 4 μ M, [DNA] = (0–50) μ M. The arrow shows the absorbance change upon increasing DNA concentrations.

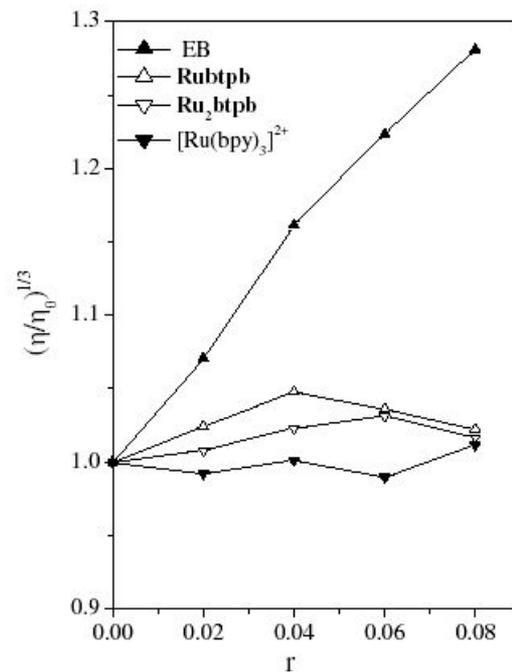


Fig. 3. Effect of increasing amounts of the mono- and diruthenium(II) complexes, EB and their parent complex [Ru(tpb)₃]²⁺ on the relative viscosities of CT-DNA at 28.0 (\pm 0.1) °C, [DNA] = 0.5 mM and $r = [\text{Ru complex}]/[\text{DNA}]$.

**отсутствие флуоресценции
при возбуждении
соединений светом 501 нм
и 511 нм**

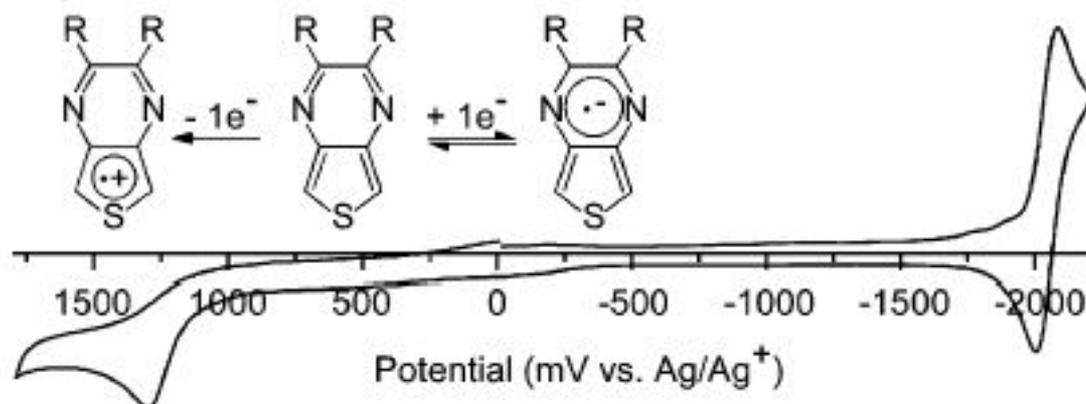


TABLE 2. Electrochemical Data for a Series of 2,3-Disubstituted Thieno[3,4-*b*]pyrazines^a

R	oxidation		reduction	
	E_p^a , V	$E_{1/2}$, V	$E_{1/2}$, V	ΔE , mV
H	1.55			
CH ₃	1.33	-2.04		85
C ₆ H ₁₃	1.35	-2.01		150
C ₈ H ₁₇	1.35	-1.99		130
C ₁₀ H ₂₁	1.33	-1.99		140
C ₁₂ H ₂₅	1.35	-1.96		130
Ph	1.27	-1.27		300

^a All potentials are vs Ag/Ag⁺. Voltammetric data were measured in millimolar argon-spurged CH₃CN solutions with 0.1 M TBAPF₆ as a supporting electrolyte.

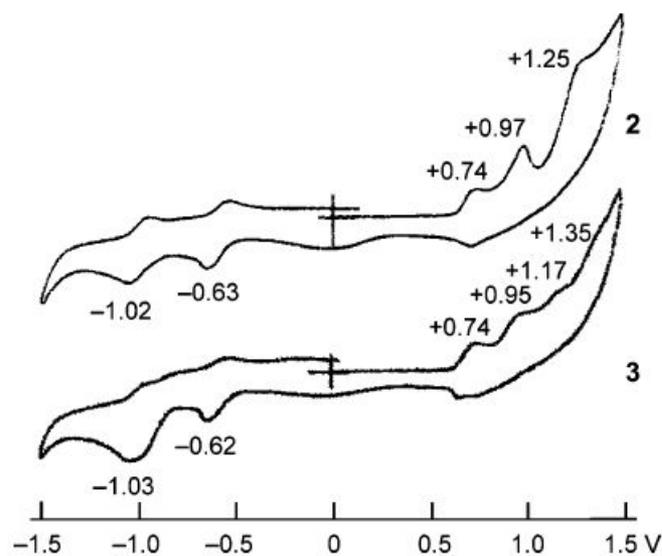
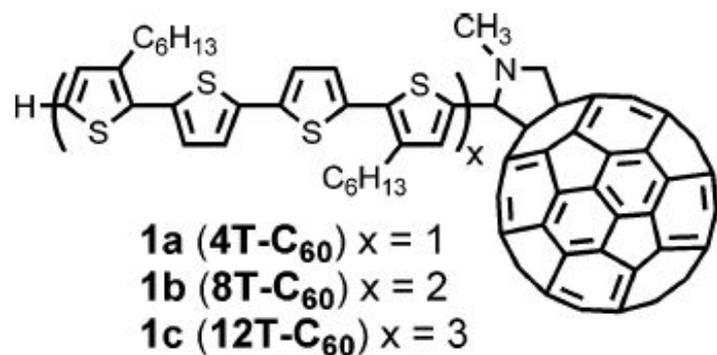


FIGURE 1. Cyclic voltammograms of the triads **2** and **3** in benzonitrile.

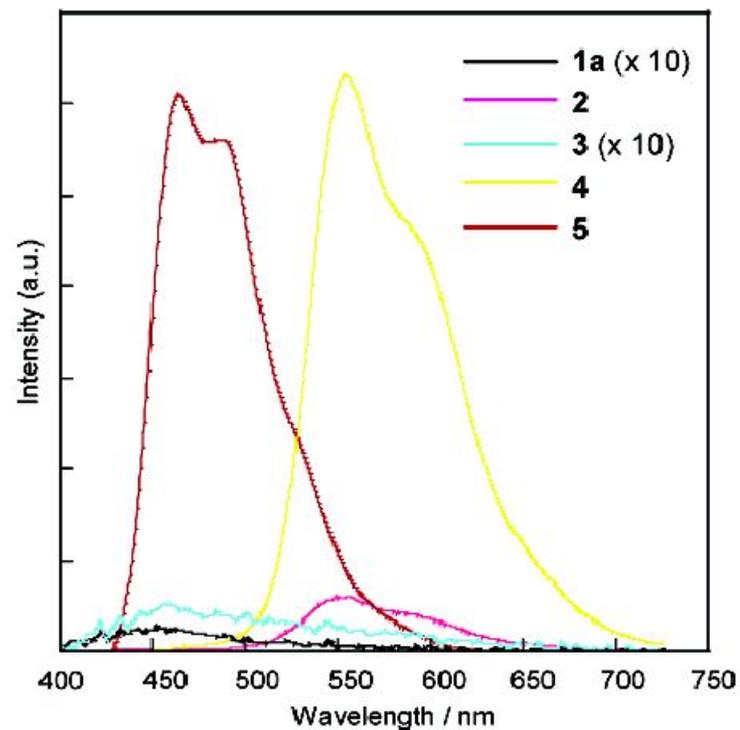
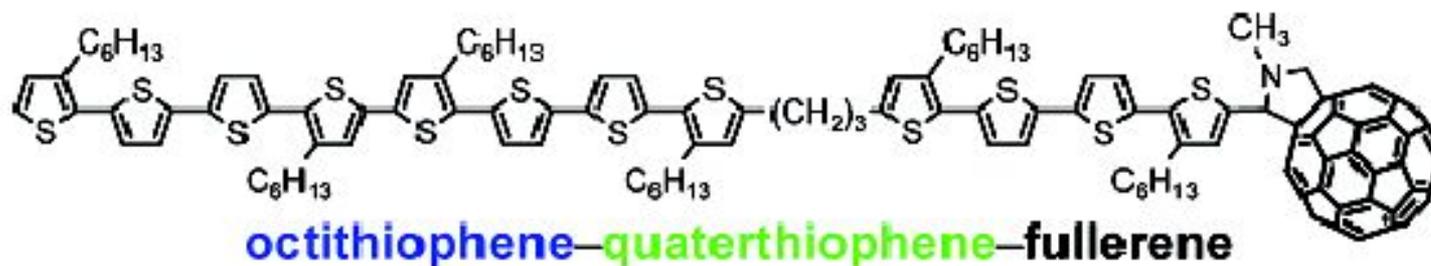


FIGURE 3. Emission spectra of 4T-C₆₀ (**1a**), 8T-4T-C₆₀ (**2**), 4T-8T-C₆₀ (**3**), 4T-8T (**4**), and 4T (**5**) with excitation at 379 nm in benzonitrile, where the absorbances of all samples were kept constant.



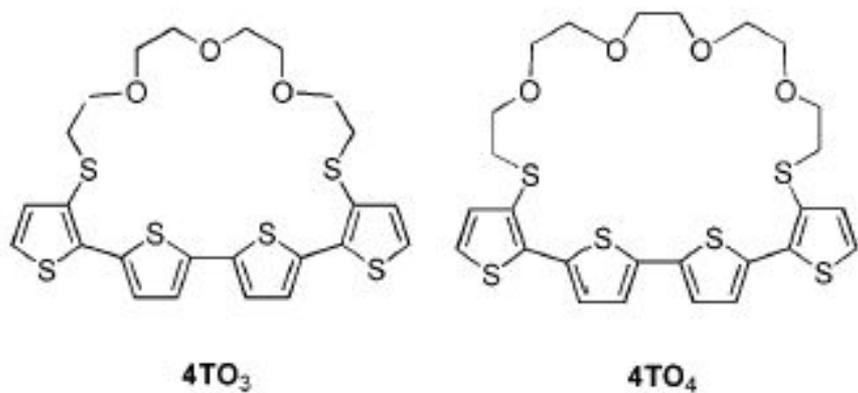
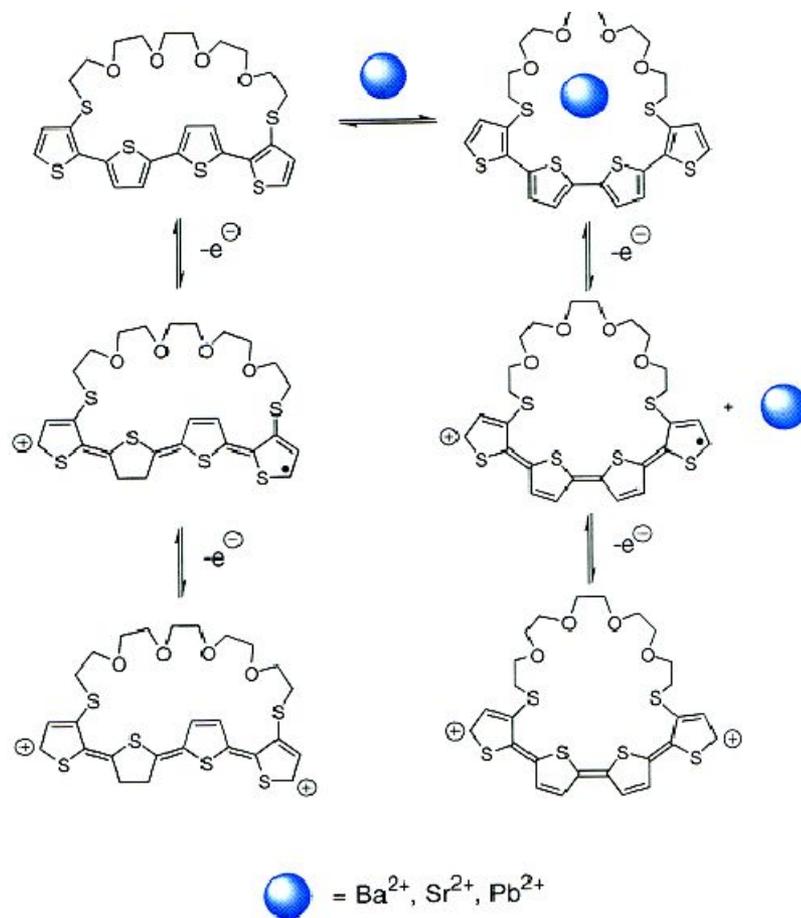
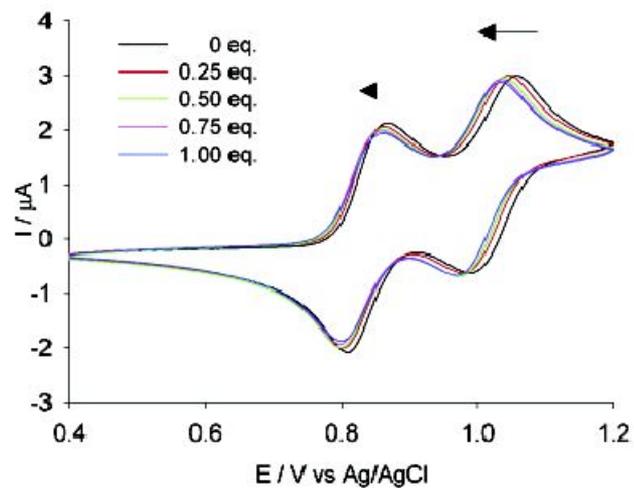


Table 6. Cyclic Voltammetric Data for Crown-Annulated Oligothiophenes^a

compd	addition ^b	E°_1 , V	ΔE°_1 , mV	E°_2 , V	ΔE°_2 , mV
1		0.98		1.13	
4TO₃		0.87		1.10	
4TO₄		0.87		1.10	
	+Ba ²⁺		-6		-30
	+Sr ²⁺		15		-25
	+Pb ²⁺		+14		-25



Фотоиндуцированный перенос электрона

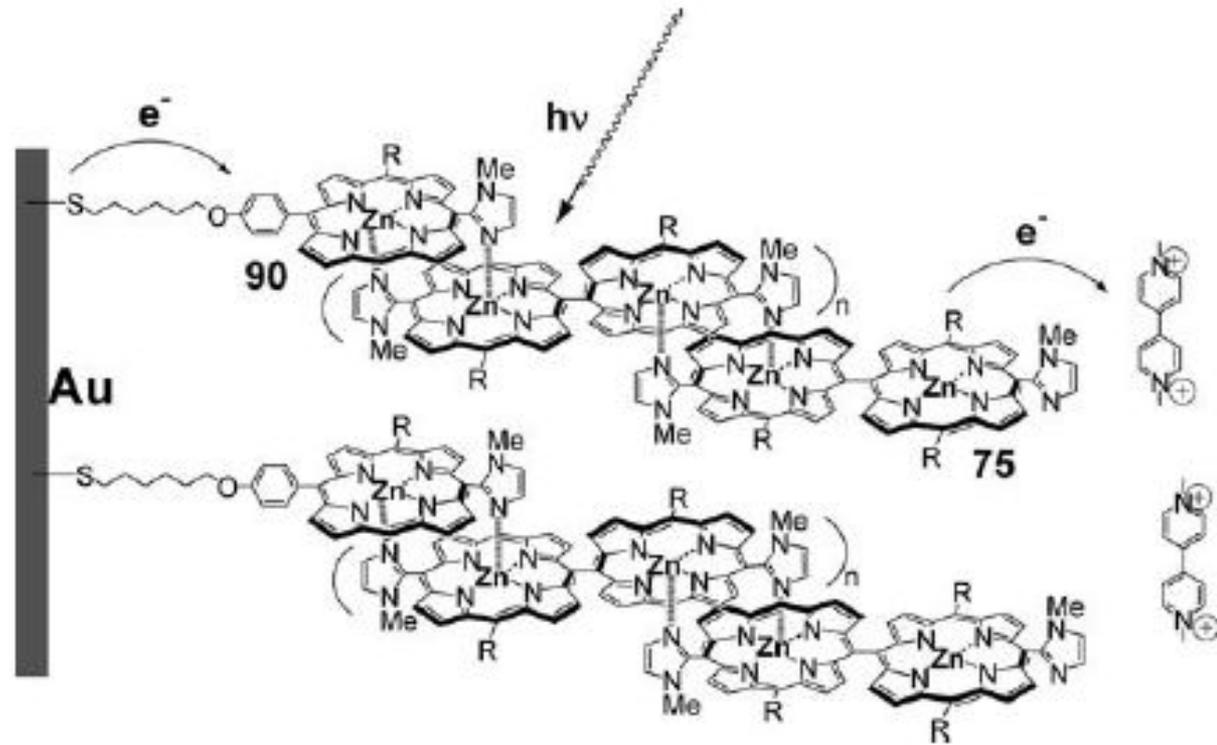
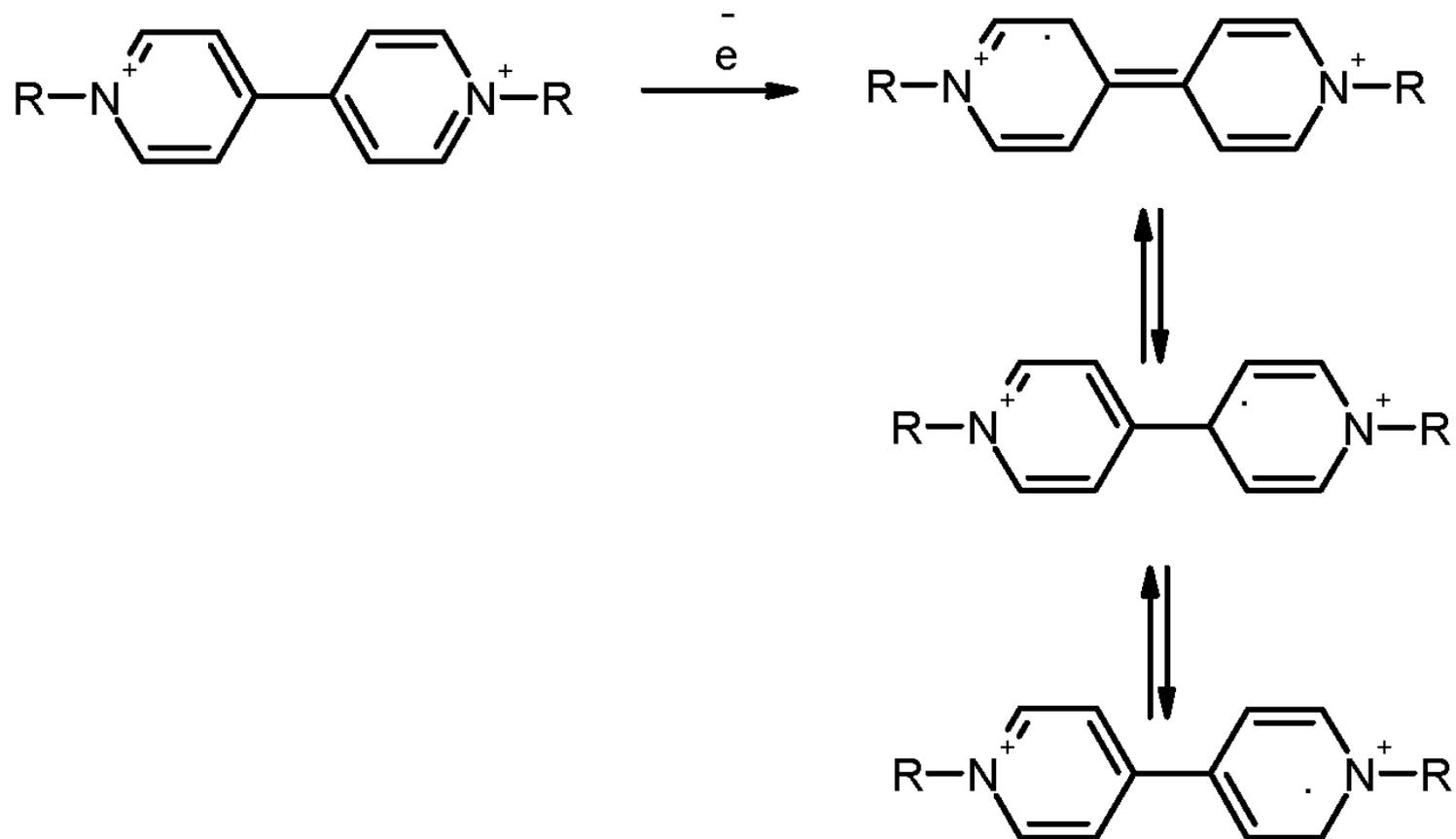


Figure 69. Complementary coordination assembly of antenna porphyrins on gold surface.¹²¹

Виологены



ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С НАПРАВЛЕННЫМ ПЕРЕНОСОМ ЭНЕРГИИ

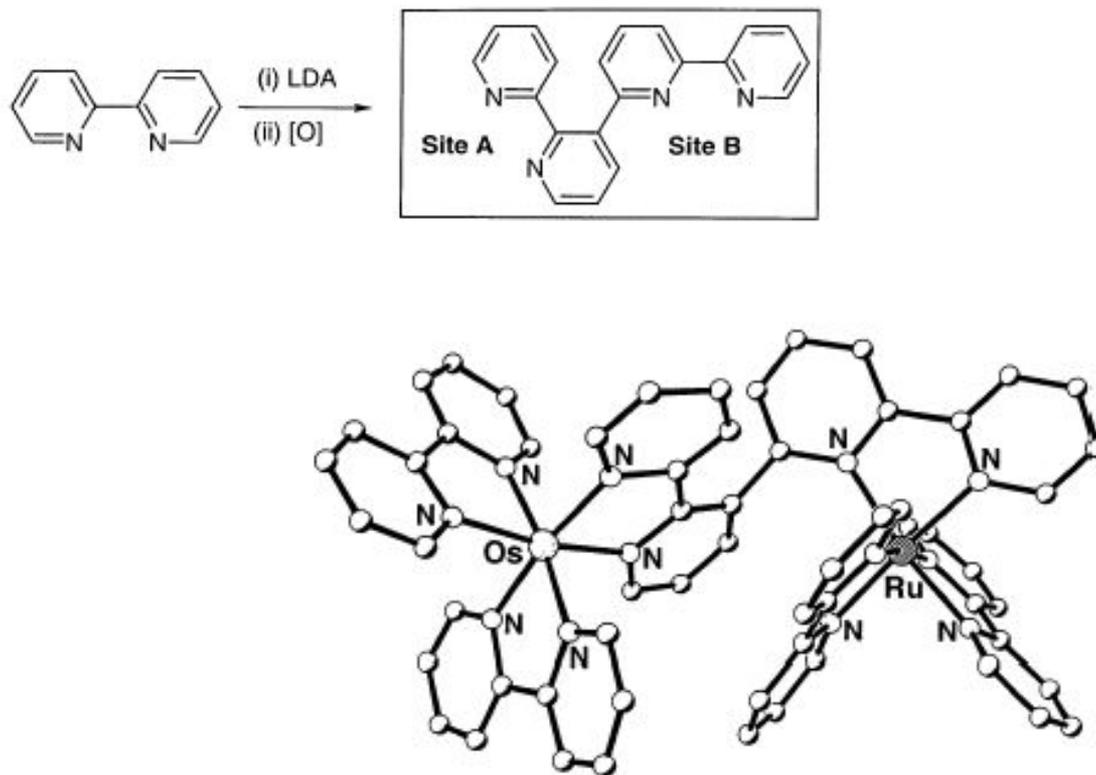


Fig. 1. Crystal structure of the complex cation of Os-AB-Ru.

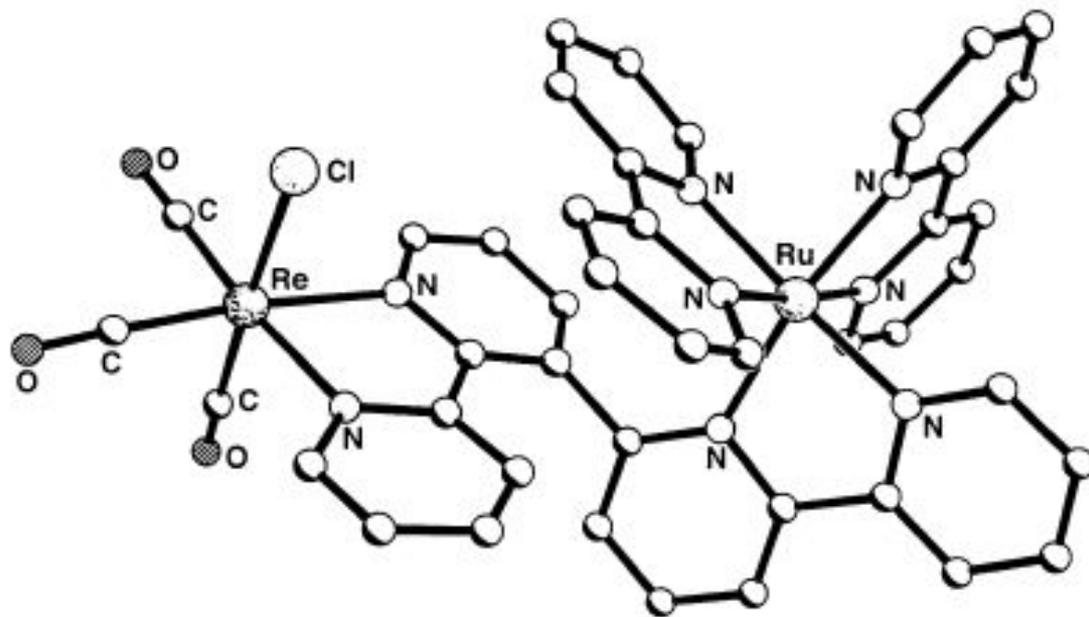


Fig. 2. Crystal structure of the complex cation of Re-AB-Ru.

Table 1

Summary of electrochemical and photophysical data for the complexes of 2,2':3',2'':6'',2'''-quaterpyridine (AB), and for the hydrogen-bonding complexes

Complex	Metal-centred redox potentials (V) ^a	Emission at room temperature			Emission at 77 K		Emission source
		λ_{max} (nm)	τ (ns)	Φ	λ_{max} (nm)	τ (μs)	
Ru-AB	+0.90	666 ^b	191	1.5×10^{-2}	588 ^c	5.9	Ru
Os-AB	+0.47	792 ^b	30	1.0×10^{-3}	722 ^c	1.3	Os
Re-AB	+0.98 ^e	626 ^d	11	9.2×10^{-4}	535 ^d	3.2	Re
Ru-AB-Os	+0.60, +1.05	756 ^b	41	3.2×10^{-3}	716 ^c	1.5	Os
Os-AB-Ru	+0.57, +1.09	808 ^b	26	1.3×10^{-3}	756 ^c	1.0	Os
Ru-AB-Re	+0.93, +1.17 ^e	644 ^d	410	2.8×10^{-2}	607 ^d	4.7	Ru
Re-AB-Ru	+1.04 ^{e,f}	623 ^d	23	1.4×10^{-3}	590 ^d	5.8	Re at RT; Ru at 77 K

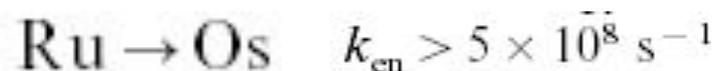
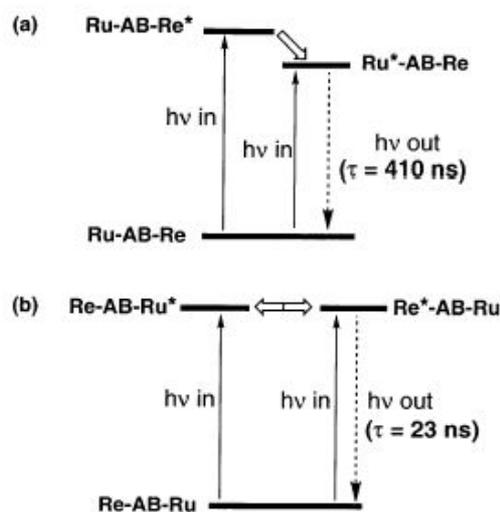
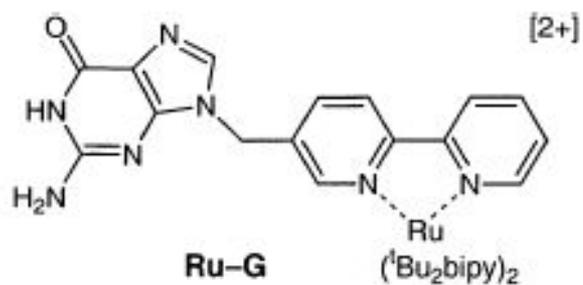
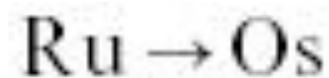


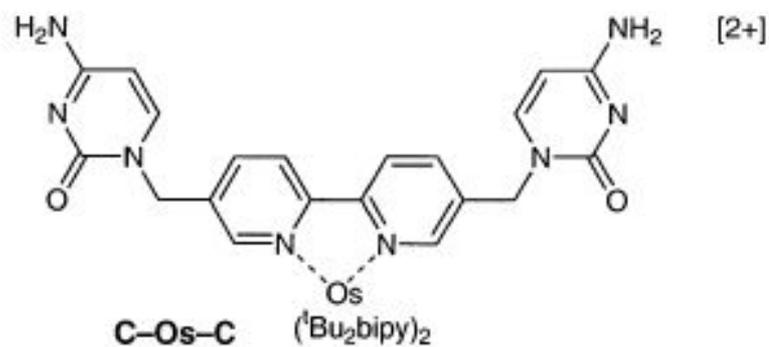
Fig. 3. Luminescence from (a) Ru-AB-Ru and (b) Re-AB-Ru. In case (a) the Ru chromophore is lower in energy, and is the site of emission following either direct excitation or Re \rightarrow Ru energy-transfer (denoted by the thick arrow). In case (b) the Re and Ru excited-states are almost isoenergetic and in thermal equilibrium (shown by the double-headed arrow); however emission is only seen from the Re chromophore due to its inherently much faster deactivation rate.

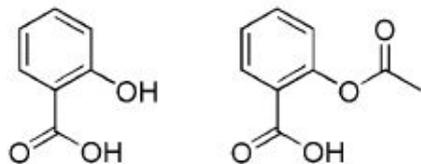
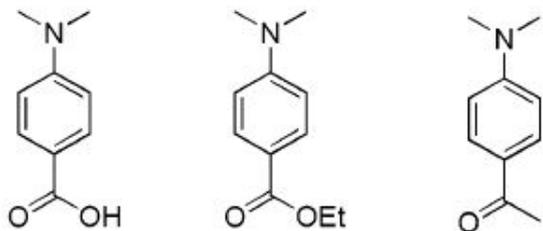
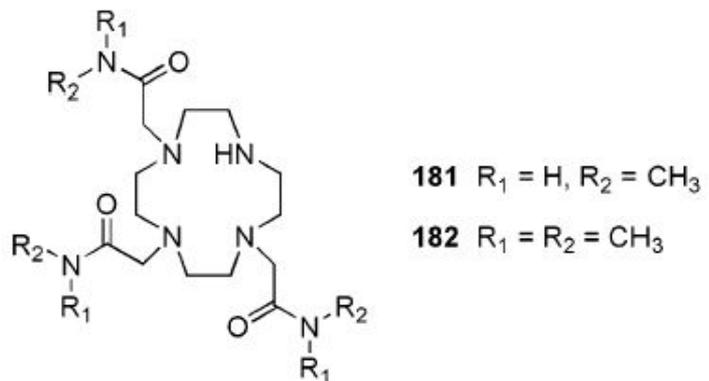


$$K_{\text{ass}} = 1.1 \times 10^4 \text{ M}^{-1}$$

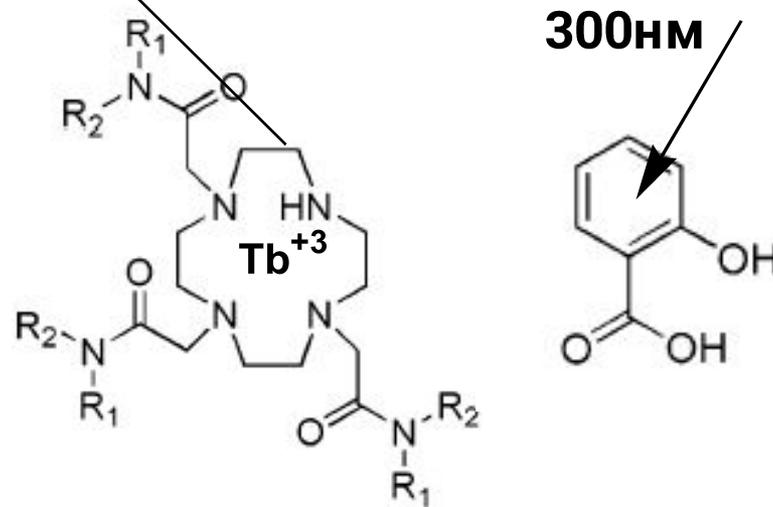


$$k_{\text{en}} = 8.0 \times 10^7 \text{ s}^{-1}$$



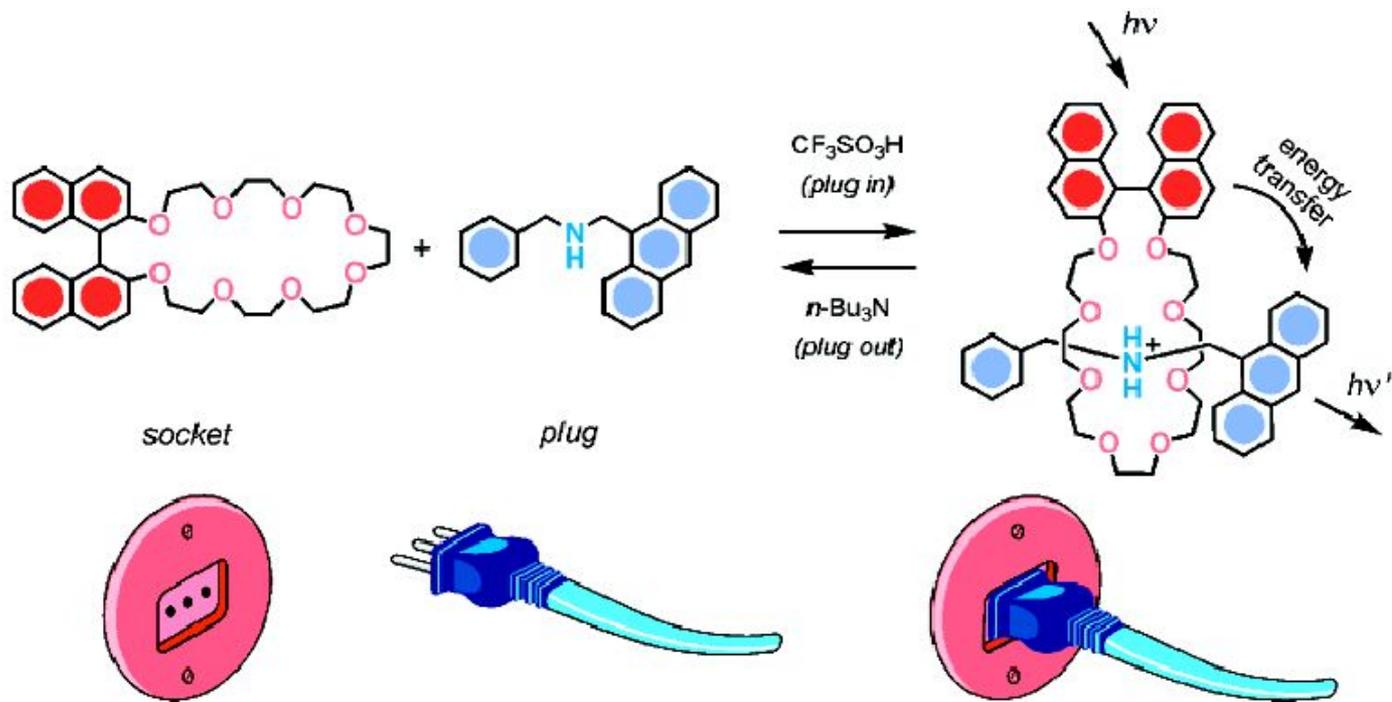


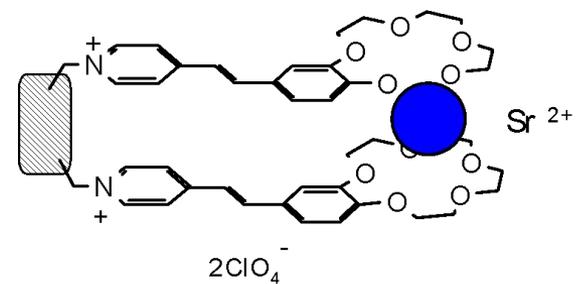
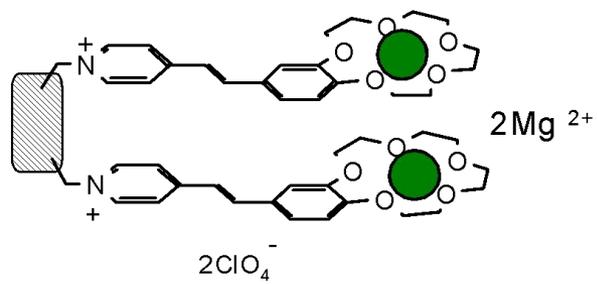
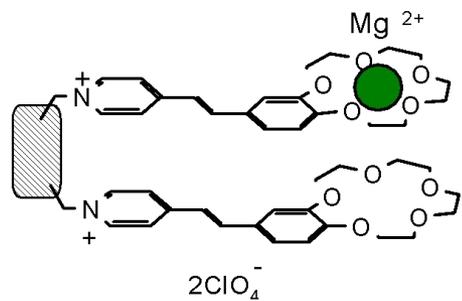
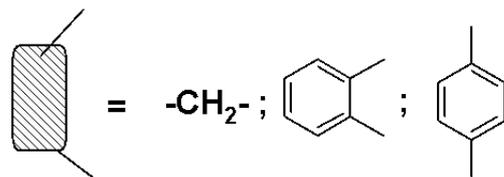
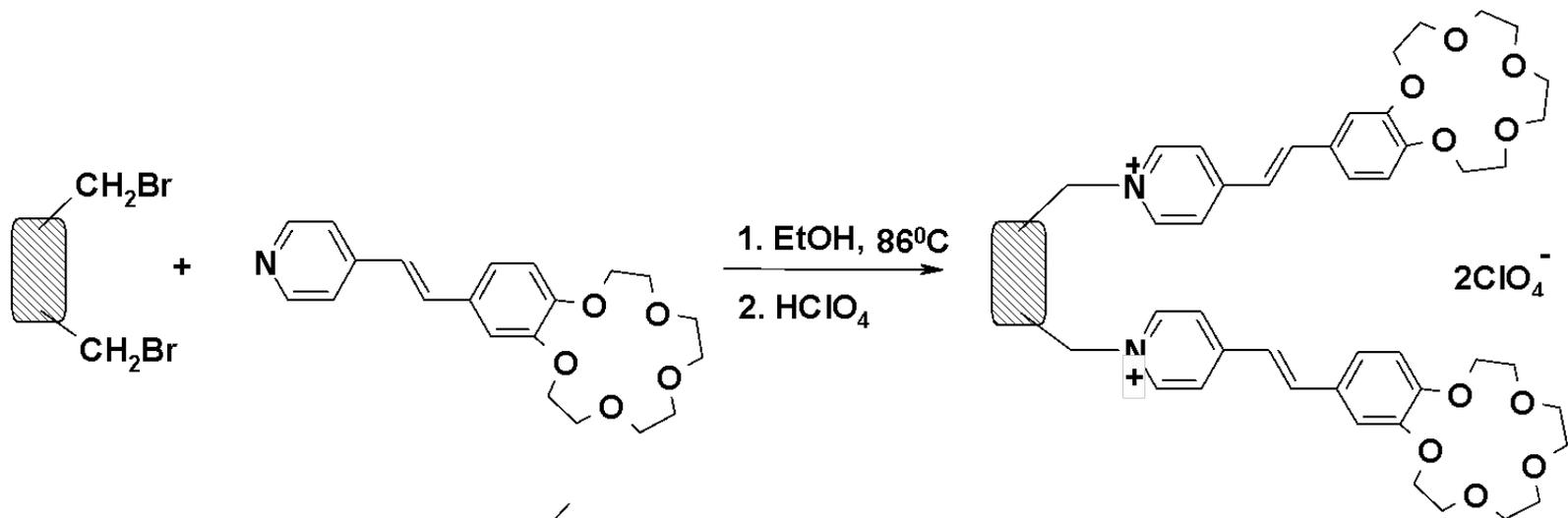
**Увеличение
 интенсивности
 флуоресценции Tb⁺³
 в 680 раз**

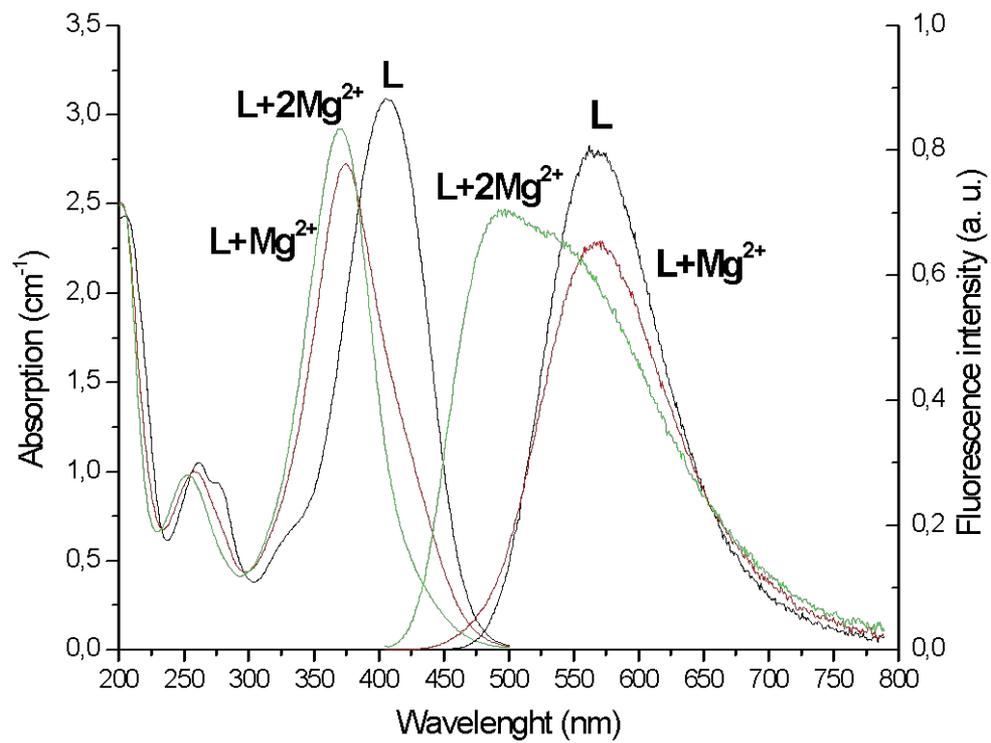
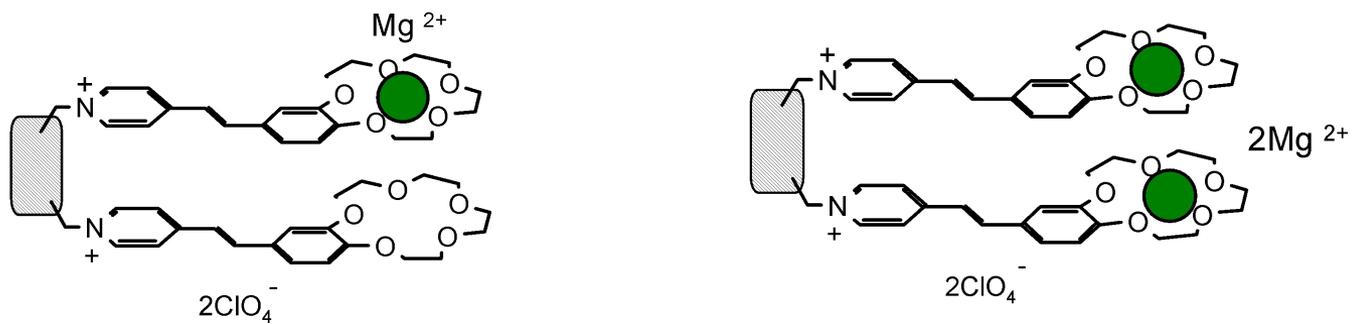


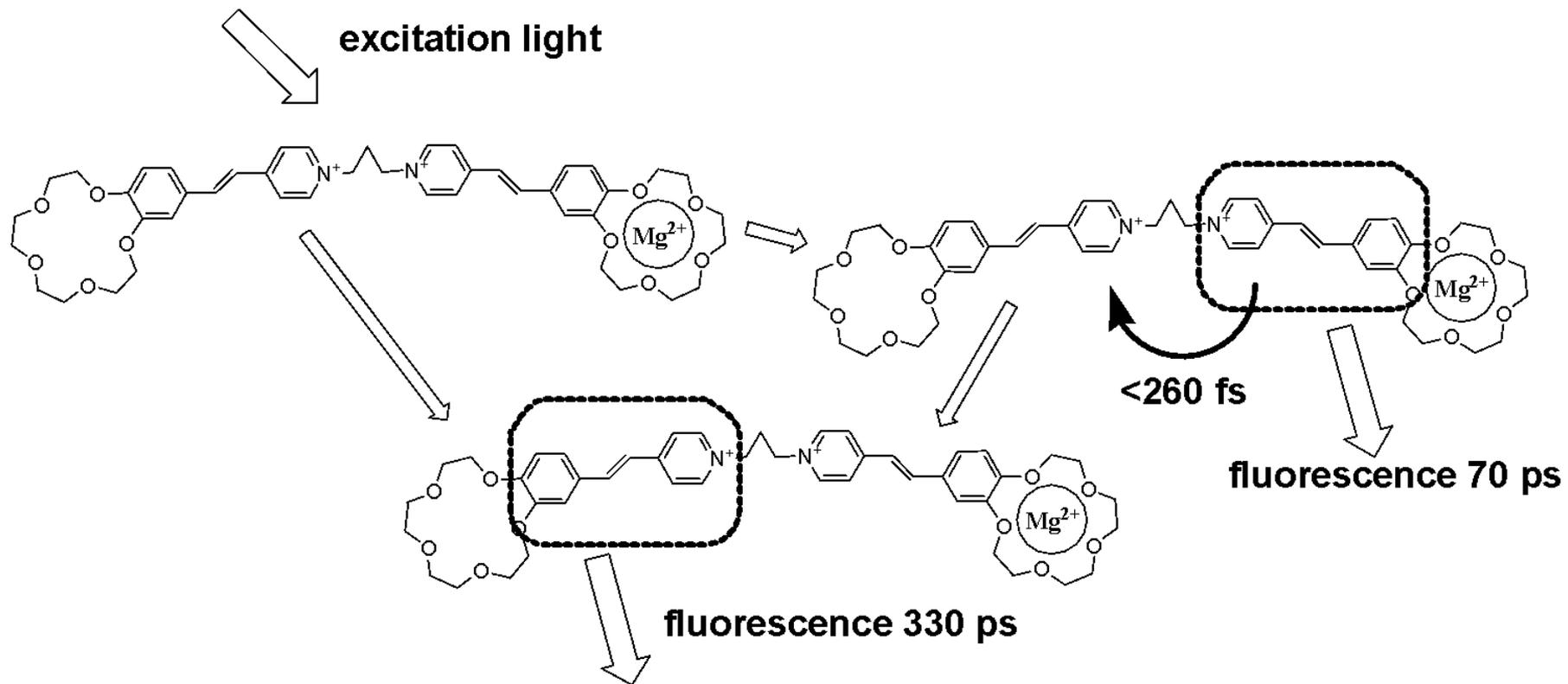
перенос энергии

ФОТОХИМИЧЕСКИЕ МОЛЕКУЛЯРНЫЕ УСТРОЙСТВА С НАПРАВЛЕННЫМ ПЕРЕНОСОМ ЭНЕРГИИ









Реакции, протекающие в полости ЦД

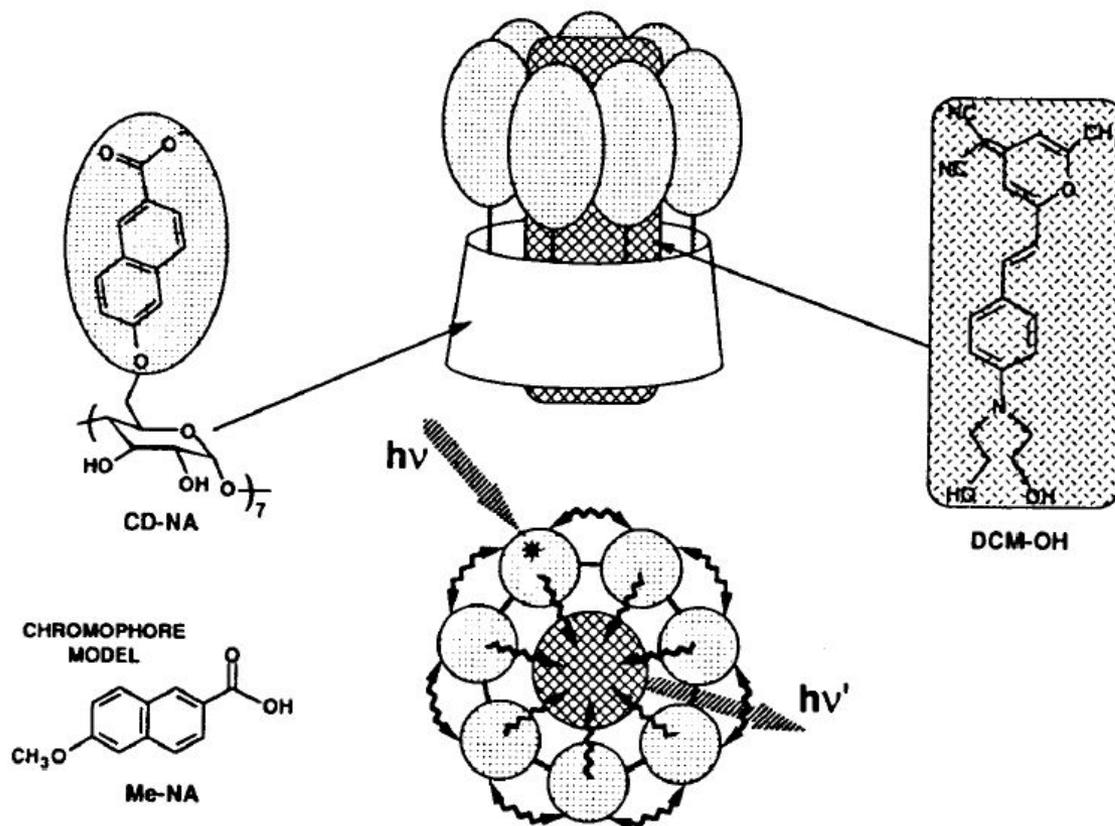


Figure 25. Complex between β -cyclodextrin-heptanaphthoate CDNA and the merocyanine laser dye DCM-OH.¹⁶⁶ (Reprinted with permission from ref 166. Copyright 1996 American Chemical Society.)

МОЛЕКУЛЯРНЫЕ МАШИНЫ

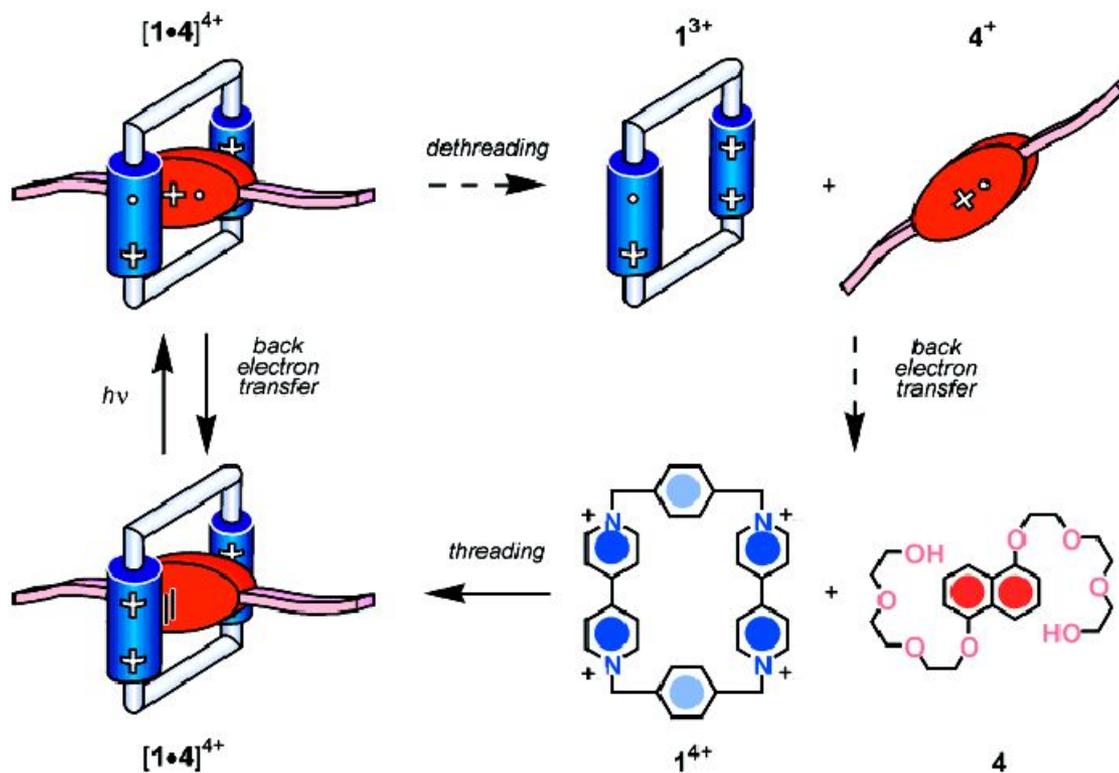


FIGURE 7. Light excitation of a pseudorotaxane based on CT interactions. The processes indicated by dashed arrows are unlikely to occur (see text).

МОЛЕКУЛЯРНЫЕ МАШИНЫ

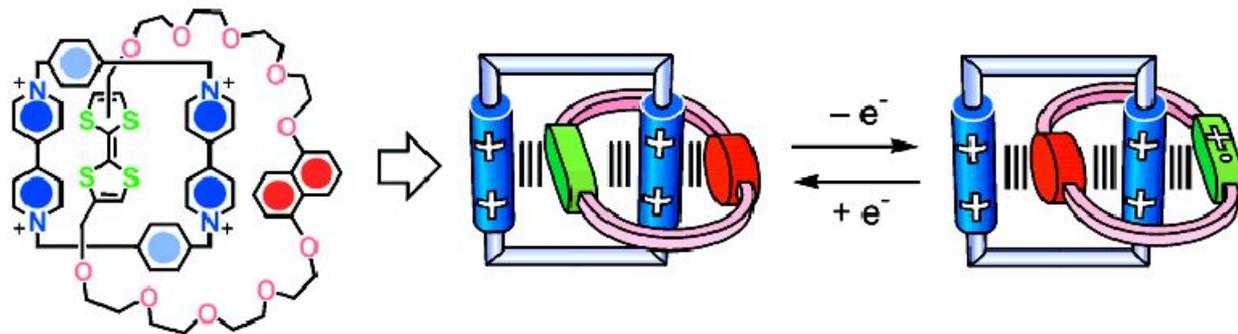


FIGURE 5. Electrochemically controlled movements upon one-electron oxidation/reduction of a TTF unit in a catenane containing a nonsymmetric ring (MeCN, room temperature).

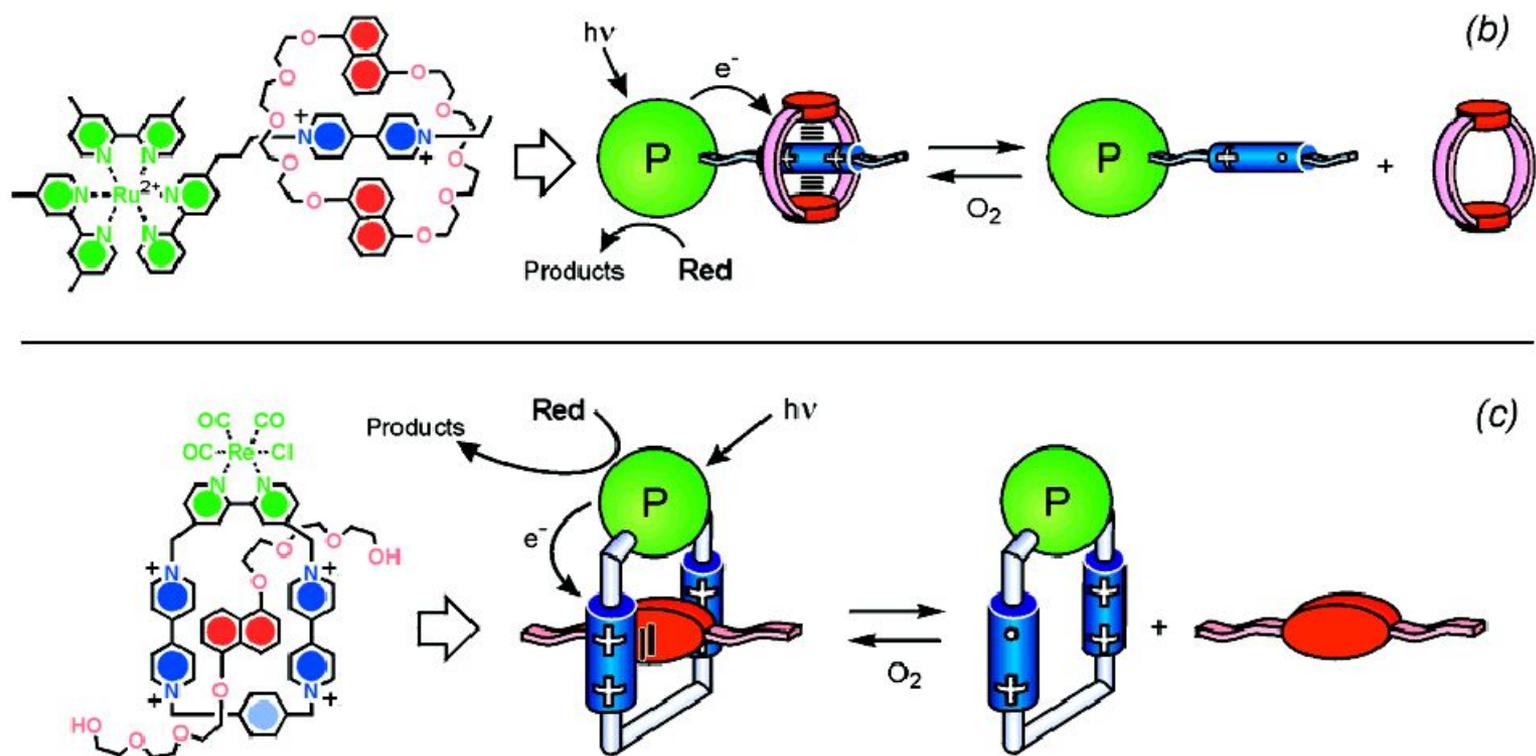
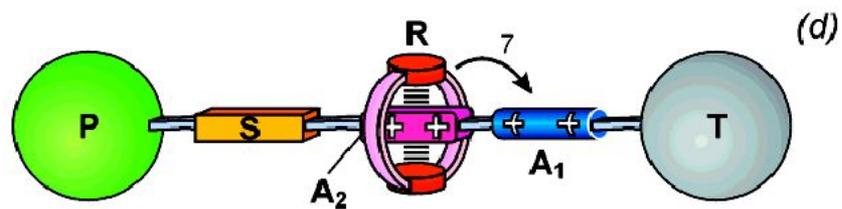
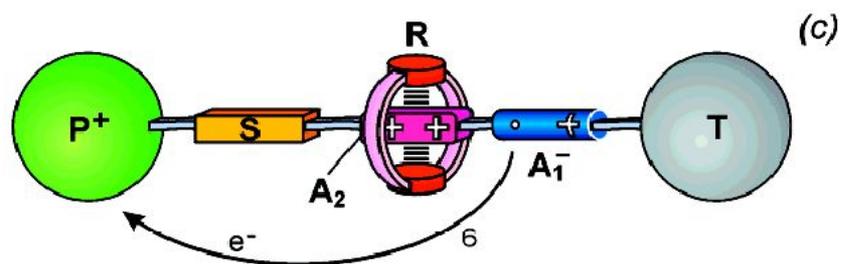
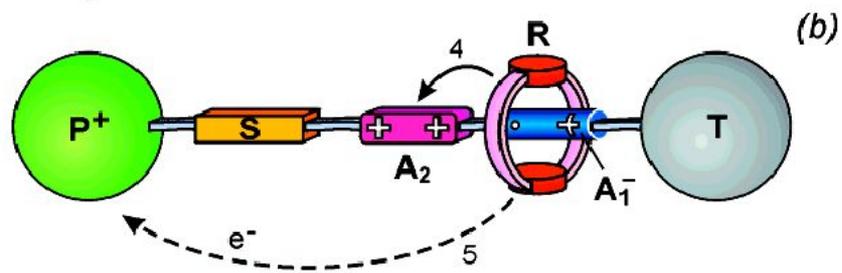
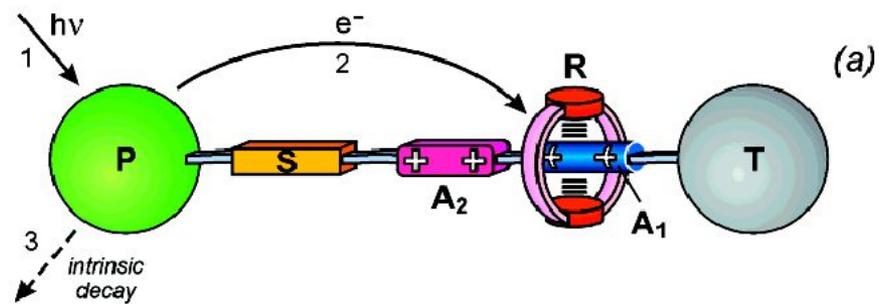
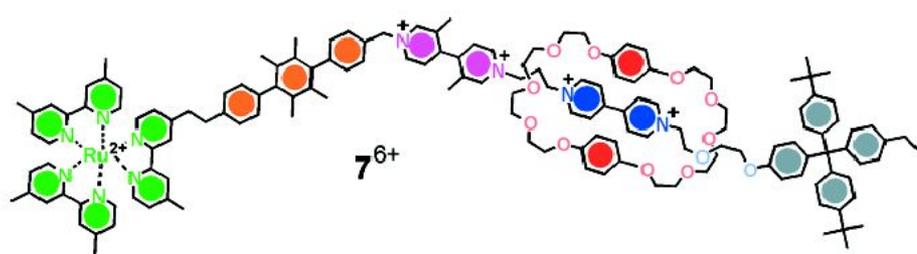


FIGURE 8. Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer **P** as (a) an external reactant (MeCN or H₂O, room temperature), (b) a stopper in the wire-type component (EtOH, room temperature), and (c) a component of the macrocyclic ring (H₂O, room temperature).



In the previously mentioned 1959 address to the American Physical Society, R. P. Feynman² concluded his reflection on the idea of constructing molecular-level machines as follows:

“What would be the utility of such machines? Who knows? I cannot see exactly what would happen, but I can hardly doubt that when we have some control of the rearrangement of things on a molecular scale we will get an enormously greater range of possible properties that substances can have, and of different things we can do.”