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Photoactive nanoscale devices and machines

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Why miniaturization?



ENIAC: the first electronic computer (1944)

Integrated microprocessor (today)



Weigth: ca. 2 kg *Power consumption:* ca. 60 W (CPU)

> *N. transistors:* 1.4 billions* *Elements size (min):* 25 nm*

* Intel i7 quad core processor (22-nm lithography), released Q3 2013. See http:\\ark.intel.com

Weigth: ca. 30 t *N. tubes:* 19000 *Power consumption:* 200 kW

Naturally occurring molecular machines



Cells have hundreds of different types of molecular motors, each specialized for a particular function. Many biological motor-like proteins have been discovered and characterized in recent years.

Artificial molecular devices



V. Balzani, A. Credi, M. Venturi, PNAS 2002, 99, 4814; Chem. Eur. J. 2002, 8, 5524

Complex synthetic structures







Artificial molecular devices: the role of light





Artificial molecular devices

• Devices for signal (information) processing

Wires, plug/socket devices, electrical extension cable systems, antennas, sensors, switches, logic gates,...

Devices for harvesting and converting light energy

Light harvesting antennas, wires, charge-separation devices, ...

Mechanical devices (molecular machines)

Tweezers, shuttles, muscles, valves, rotary motors, ...

Artificial molecular devices

Information processing devices

A.P. de Silva, S. Uchiyama, Nature Nanotech. 2007, 2, 399

K. Szacilowski, Chem. Rev. 2008, 108, 3481

V. Balzani, A. Credi, M. Venturi, Chem. Eur. J. 2008, 14, 26

A. P. de Silva, *Molecular Logic-based Computation*, RSC Publishing, Cambridge, **2012**.

Mechanical molecular machines

D.A. Leigh *et al.* Angew. Chem. Int. Ed. **2007**, 46, 72 Chem. Rev. **2015**, 115, 10081

S. Silvi, M. Venturi, A. Credi, *J. Mater. Chem.* **2009**, *19*, 2279; *Chem. Commun.* **2011**, *47*, 2483 (feature articles)

C. Bruns, J. F. Stoddart, *The Chemistry of the Mechanical Bond – From Molecules to Machines*, Wiley, New York, **2016**



Wiley-VCH, Weinheim, Germany, **2008**

Information processing devices based on transition metal complexes

An acid-base controlled luminescent switch



Ru







λ (nm)

With Ed Constable, University of Basel

Inorg. Chim. Acta 2007, 360, 1102



λ (nm)

$In_1 = H^+$	In ₁	In ₂	Out ₇₄₀	Out ₇₄₀	Out ₆₃₀
$In_2 = H^+$	0	0	0	0	1
Out = hv	0	1	0	1	0
	1	0	0	1	0
	1	1	1	1	1

AND OR XNOR

Photochemical operation of pH-controlled molecular switches



- compatibility of conditions
- no further chemical interactions between MS1 and MS2
- no interference of input/output signals
- correct timing of the switching processes
- $pK_a(\mathbf{N}H^+) < pK_a(\mathbf{D}_A) < pK_a(\mathbf{M}H^+)$

The spyropyran/merocyanine photochromic system





With Françisco Raymo, University of Miami

Coupled operation of the two switches



Photocontrol of molecular logic gate operation







740 nm

630 nm



In ₁	In ₂	Out
0	0	1
0	1	0
1	0	0
1	1	1

Photochemical switching of luminescence and ¹O₂ generation



Chem. Commun. 2009, 1484

Nanoscale devices based on semiconductor nanocrystal quantum dots