

# Metallic Nanoparticles – General Considerations

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Periodensystem der Elemente																		
Periode	Hauptgruppen		Hauptgruppen															
	1 IA	2 IIA	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	Nebengruppen (Übergangselemente)									
1 K-Schale	1,008 H																4,002 He	
2 L-Schale	6,94 Li	9,01 Be															20,18 Ne	
3 M-Schale	22,99 Na	24,31 Mg															39,95 Ar	
4 N-Schale	39,10 K	40,08 Ca	44,96 Sc	47,88 Ti	50,94 V	52,00 Cr	54,93 Mn	55,85 Fe	58,93 Co	58,69 Ni	63,55 Cu	65,38 Zn	69,72 Ga	72,61 Ge	74,92 As	78,96 Se	79,90 Br	83,80 Kr
5 O-Schale	85,47 Rb	87,62 Sr	88,91 Y	91,22 Zr	92,91 Nb	95,94 Mo	(98) Tc	101,07 Ru	102,9 Rh	106,42 Pd	107,8 Ag	112,41 Cd	114,82 In	118,71 Sn	121,76 Sb	127,60 Te	126,90 I	131,29 Xe
6 P-Schale	132,91 Cs	137,33 Ba	La-Lu 57-71	178,49 Hf	180,95 Ta	183,85 W	186,21 Re	190,23 Os	192,22 Ir	195,08 Pt	196,9 Au	200,59 Hg	204,38 Tl	207,20 Pb	208,98 Bi	(209) Po	(210) At	(222) Rn
7 Q-Schale	(223) Fr	(226,03) Ra	Ac-Lr 89-103	(261) 104	(262) 105	(263) 106	(262) 107	(265) 108	66 109	(209) 110	(212) 111	(?) 112						
Elemente der Lanthanreihe			138,91 La 57	140,12 Ce 58	140,91 Pr 59	144,24 Nd 60	(145) Pm 61	150,36 Sm 62	151,97 Eu 63	157,25 Gd 64	158,92 Tb 65	162,50 Dy 66	164,93 Ho 67	167,26 Er 68	168,93 Tm 69	173,04 Yb 70	174,97 Lu 71	
Elemente der Actiniumreihe			227,03 Ac 89	232,04 Th 90	231,04 Pa 91	238,03 U 92	237,05 Np 93	(244) Pu 94	243 Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(262) Lr 103	

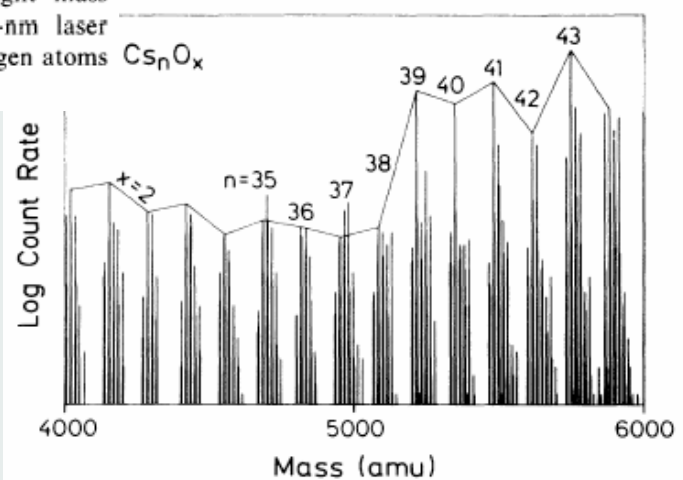
Metalle   
  Nichtmetalle   
  Nebengruppenelemente   
  Elemente mit teils metallischem, teils nichtmetallischem Charakter

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## Alkali Metal Clusters Metal Clusters in Chemical Compounds

T. Bergmann, H. Limberger, and T. P. Martin *American Physical Society* 1988  
VOLUME 60, NUMBER 17 1767

FIG. 2. Portion of a high-resolution time-of-flight mass spectrum of Cs-O clusters photoionized with 480-nm laser light. The mass peaks of clusters containing two oxygen atoms have been connected.



Unusually high ionization energies have been observed for Cs-O clusters having certain sizes and compositions, namely for Cs<sub>2n+z</sub>O<sub>n</sub> with z=8, 18, 34, 58, and 92. The anomalies are well defined for clusters containing from one to seven oxygen atoms. The indicated values of z are identical to the numbers of electrons in closed shells of angular momentum.

# From Clusters in Solids to Polymer Clusters

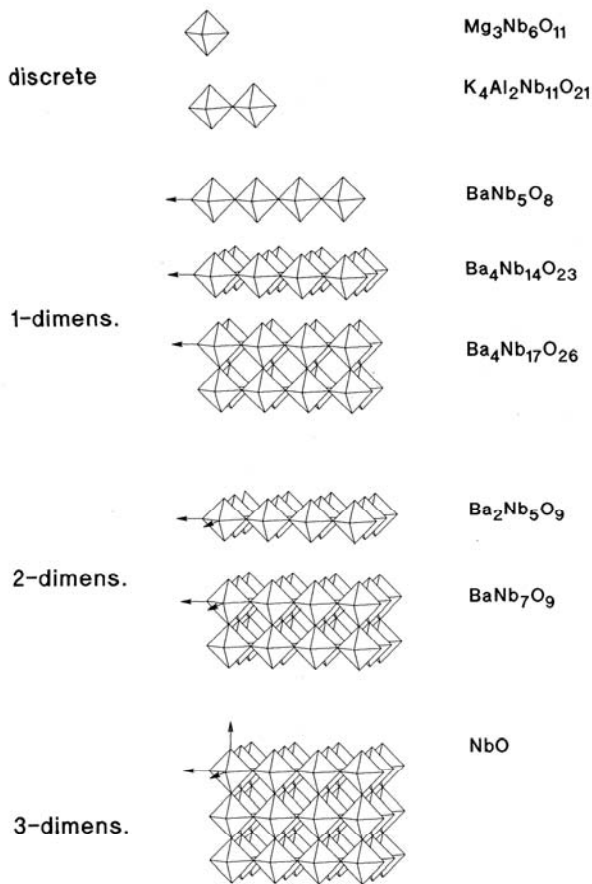
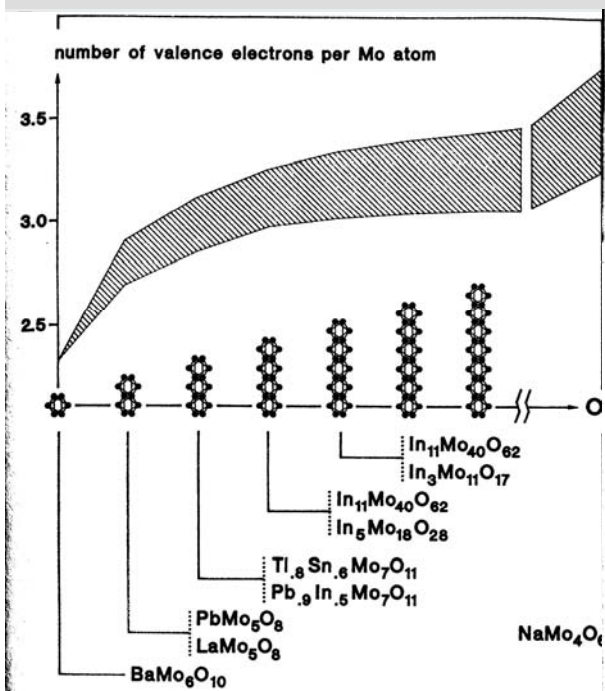


Figure 5-19. Condensed  $[\text{Nb}_6\text{O}_{12}]$  clusters in reduced oxoniobates (schematic octahedra drawn).

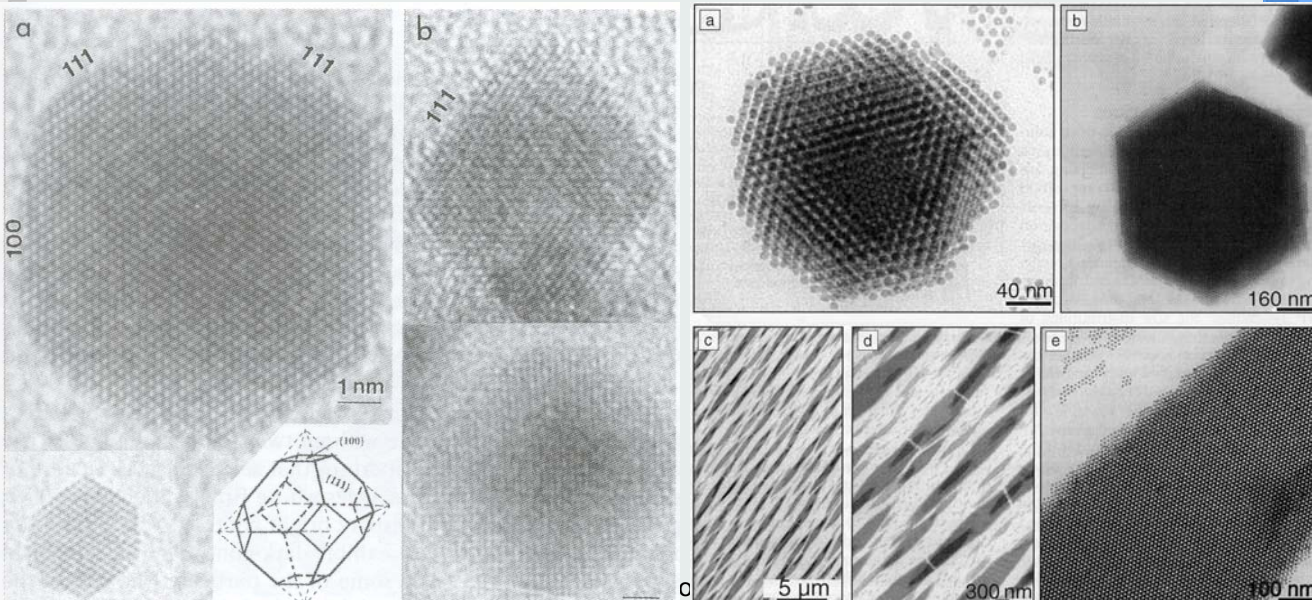
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## Au-Clusters, G. Schmid et al.

Gezielte Synthese von  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$

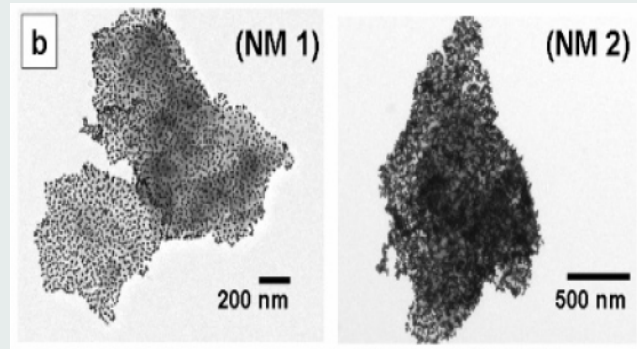
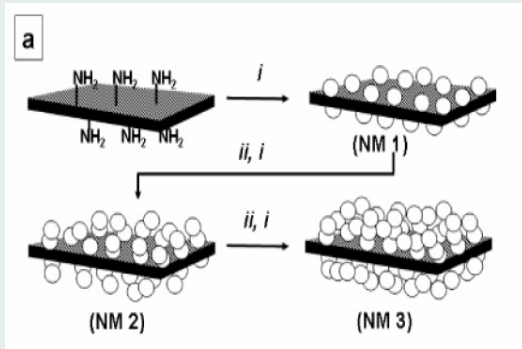
$[\text{Ph}_3\text{PAuCl}] + \text{B}_2\text{H}_6$  in Toluol



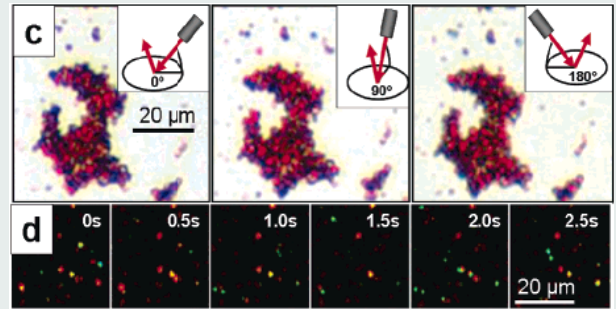
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# Planar Gold Nanoparticle Clusters as Microscale Mirrors



(a) Synthesis of mirror plates. For detailed structure of amine terminated nanoplates, see ref 7. (i) Citrate-coated gold nanoparticles in water:ethanol (1:1 v/v), followed by centrifugation; (ii) 1,8-octanedithiol in ethanol.  
 (b) Transmission electron micrographs of types 1-3 NMs

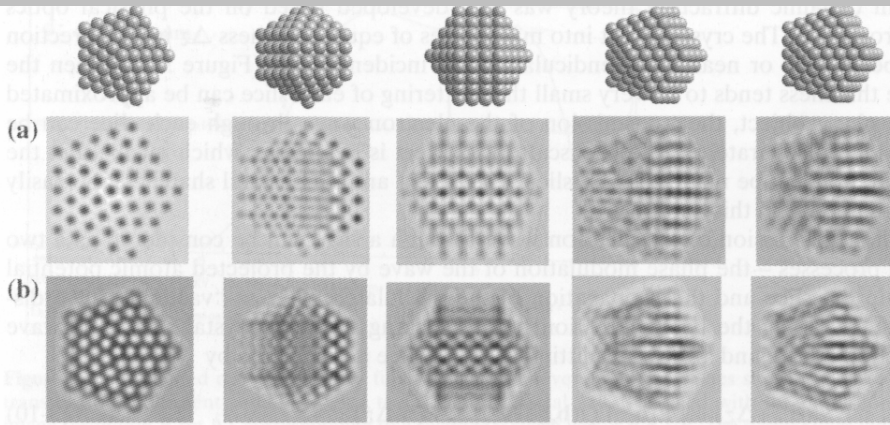


J. AM. CHEM. SOC. 2006, 128, 3868-3869

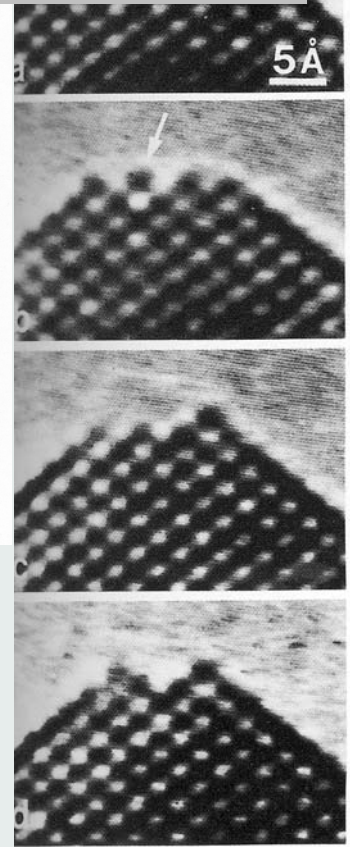
## Metallic and Elemental Nanorods

1 H																	2 He
3 Li	4 Be	<b>Metals</b>										5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

# Au-Clusters



**Figure 3-5.** Theoretically simulated images for a decahedral Au particle at various orientations and at focuses of (A)  $\Delta f = 42$  nm and (B)  $\Delta f = 70$  nm. The Fourier transform of the image is also displayed (Courtesy of Drs. Ascencio and M. José-Yacamán).



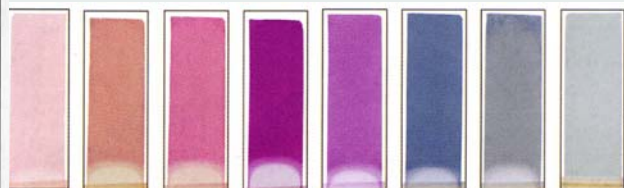
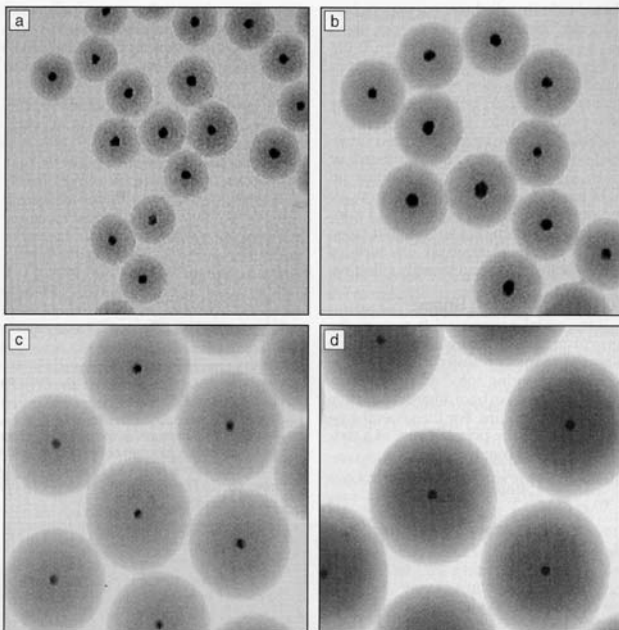
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# Gold-NPs at different Distances

*Figure 5. The transmitted colors of a series of gold particle films with decreasing particle spacing. The gold core particles are 15 nm in diameter; the shell thicknesses are, from left to right, 17.5 nm, 12.5 nm, 4.6 nm, 2.9 nm, 1.5 nm, 1.0 nm, 0.5 nm and 0 nm. Films are each 1 cm × 3 cm. The spectra shift smoothly between the two curves shown in Figure 3 as the spacing is varied.<sup>9</sup>*



Decreasing gold particle spacing →

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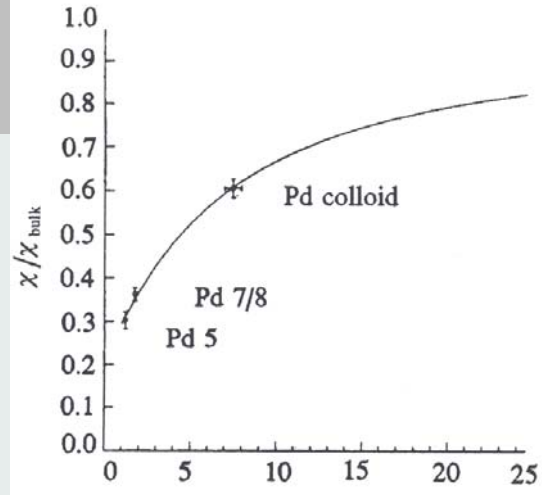
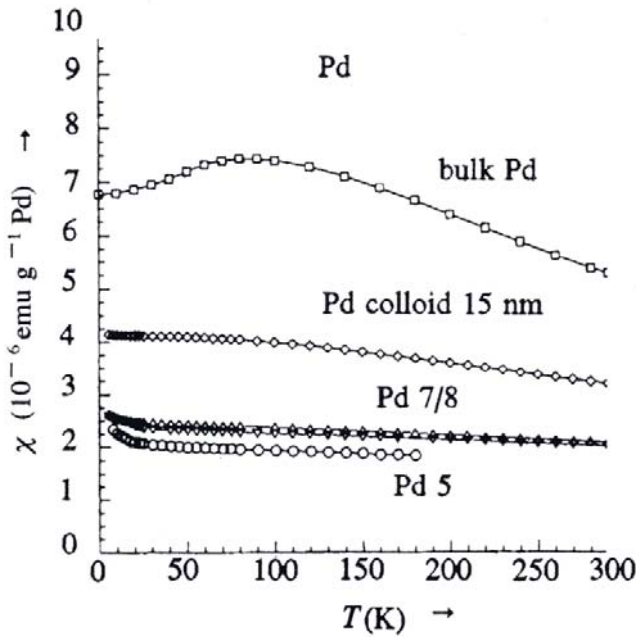
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# Pd-Clusters

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**Figure 3-37.** The susceptibility values of Pd5, Pd7/8 and 15 nm Pd colloids extrapolated to  $T = 0$  and the best fit curve of the model describing the size dependence.

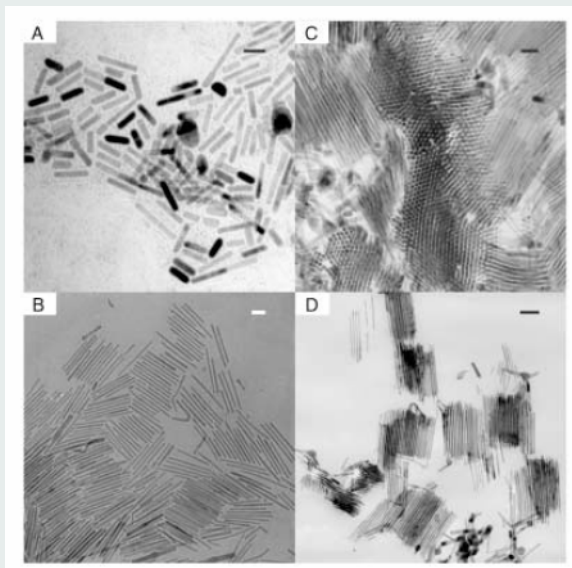
**Figure 3-36.** The temperature dependence of the susceptibility of various Pd particles compared to bulk palladium. The values are corrected for their diamagnetic contributions and normalized to the estimated weight of the Pd cores.

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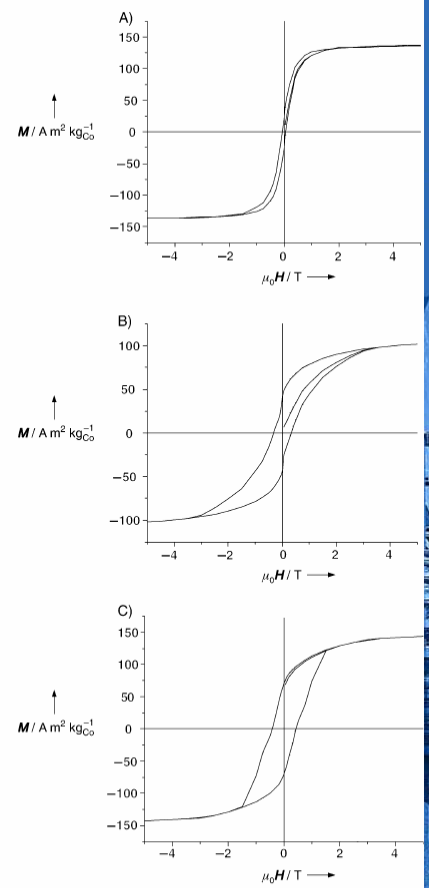
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# Cobalt –NRs - Selforganization

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**Figure 1.** TEM micrographs of nanorods synthesized using hexadecylamine and A) octanoic acid (2), B) lauric acid (1), and C, D) stearic acid (3). The sample used in (C) was prepared by ultramicrotomy. Scale bar: 30 nm.



**Figure 3.** Magnetization curves recorded at 2 K of cobalt nanorods obtained in the presence of: A) HDA and octanoic acid (1:1) (2); B) HDA and lauric acid (1:1) (1); and C) HDA and stearic acid (1:1) (3).

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# Cobalt –QDot Arrays

JM

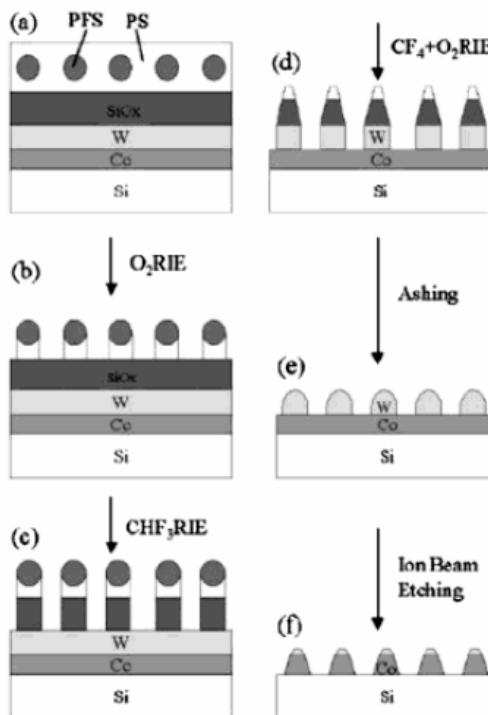
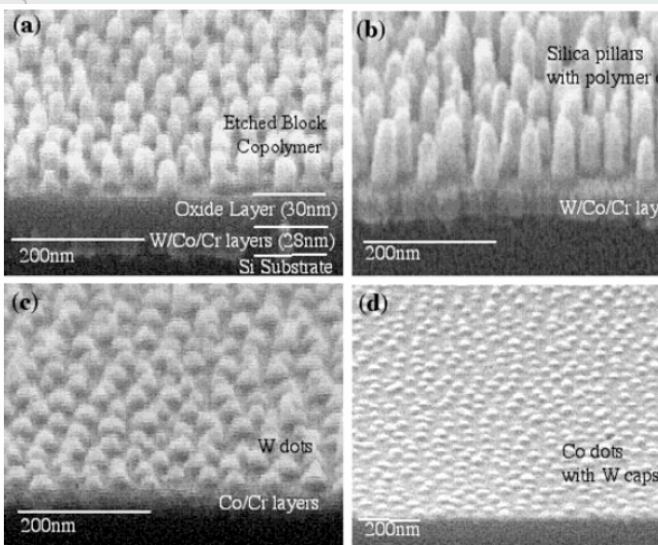


Fig. 2. Fabrication process of the cobalt dot array via block copolymer lithography. a) A block copolymer thin film on a multilayer of silica, tungsten, and cobalt. b) The block copolymer lithographic mask is formed through  $O_2$ -RIE process. The PFS domains are partly oxidized. c) The silica film is patterned using  $CHF_3$ -RIE. d) The tungsten hard mask is patterned using  $CF_4 + O_2$ -RIE. e) Removal of silica and residual polymer by high pressure  $CHF_3$ -RIE. f) The cobalt dot array is formed using ion beam etching.

**30Gdots per  $cm^2$**

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# Semiconductors

*J. Am. Chem. Soc.* 1990, 112, 1327–1332

1327

## Nucleation and Growth of CdSe on ZnS Quantum Crystallite Seeds, and Vice Versa, in Inverse Micelle Media

A. R. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. J. Carroll, and L. E. Brus\*

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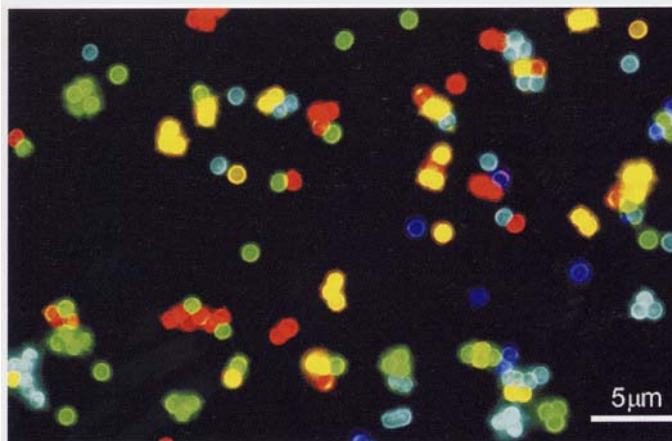
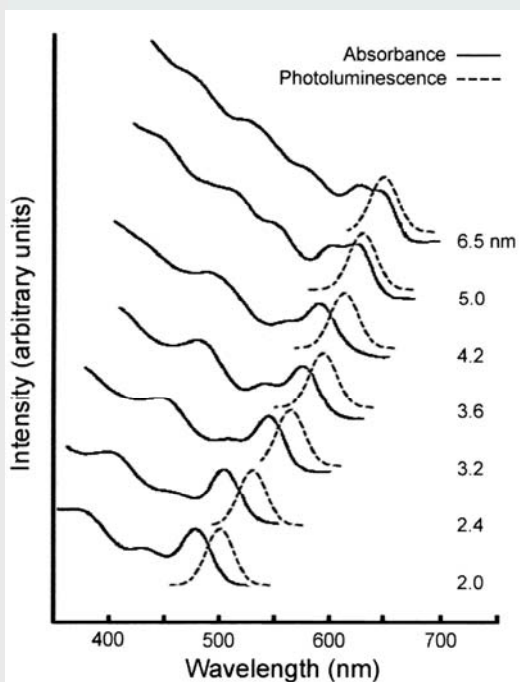


Fig. 12.5. Fluorescence micrograph of a mixture of CdSe/ZnS QD-tagged beads emitting single-color signals at 484, 508, 547, 575, and 611 nm. Reproduced with permission from [55].

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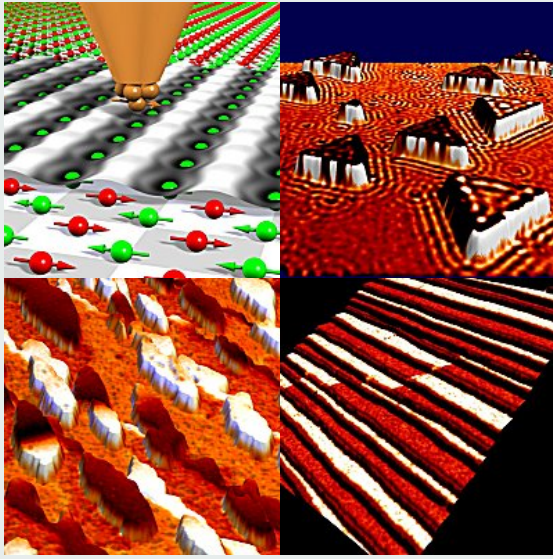
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# Magnetic Q-Dots

spin structures at the atomic level

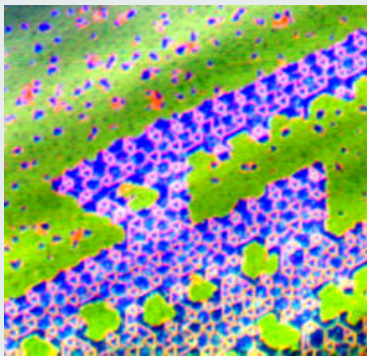


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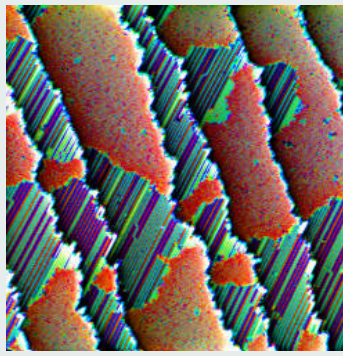
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# Structures at the Atomic Level



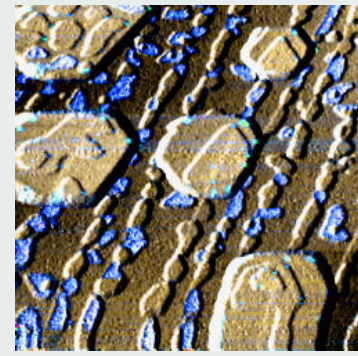
## Reconstruction on terbium

The origin of this reconstruction are adsorbates ( possibly CO ) from an insufficient degassing process



## Tb on a W(110)

single crystal with thickness less than one single atomic layer. At this low coverage the Tb atoms arrange in parallel lines, so-called "superstructures", visible as stripes.



## Gadolinium on W

Where the surface appears **blue**, hydrogen has been adsorbed on it changing the surface electronic structure drastically.

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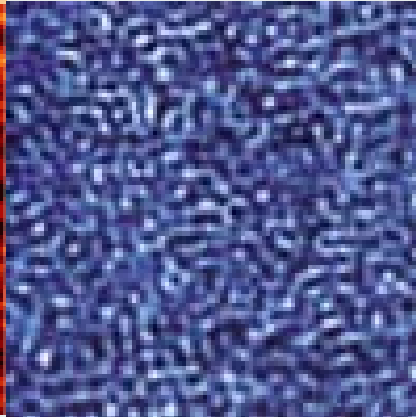
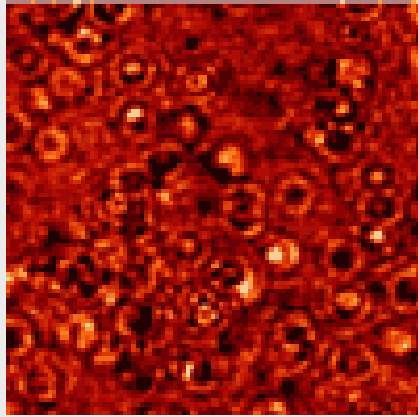
# Electron States Mapped

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In 3D electron systems we find simple **Bloch states** which are scattered at ionized dopants.

In **2D** much more complicated and much stronger standing wave pattern than in the 3D electron system.

**1D systems** containing one or two subbands have been found below charged step edges. Their local density of states shows nearly 100 % corrugation pointing to weakly localized states. Alignment with the disorder potential is directly observed.



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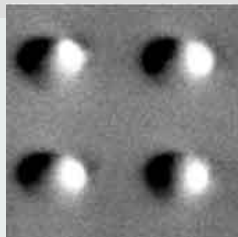
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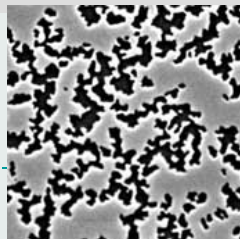


# Surface Probe Gallery

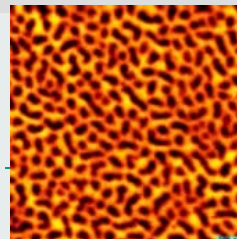
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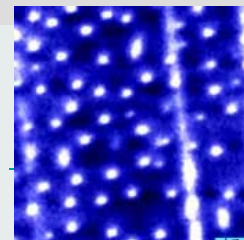
Switching behavior of single domain particles



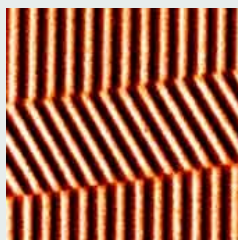
Magnetic Domains on CoPt-multilayers



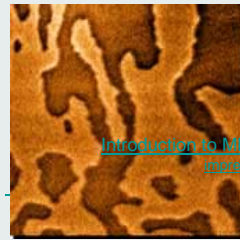
Domain growth on manganite perovskites



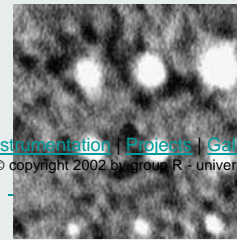
Vortices on High Tc Superconductors



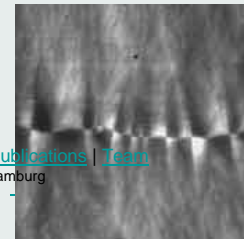
Investigation of magnetic bit structures



Reorientation transition of ultrathin cobalt films on Au(111)



Domain writing with MFM on ultrathin cobalt films



Domain walls and ripple structure of thin cobalt films

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# Semiconductors

## CdSe Nanocrystal Rods/Poly(3-hexylthiophene) Composite Photovoltaic Devices\*\*

By Wendy U. Huynh, Xiaogang Peng, and A. Paul Alivisatos\*

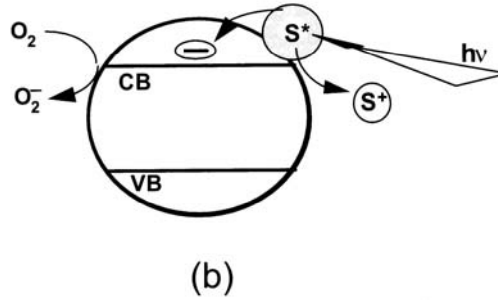
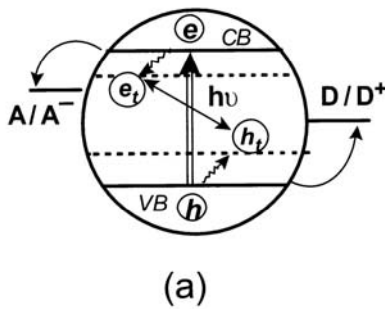
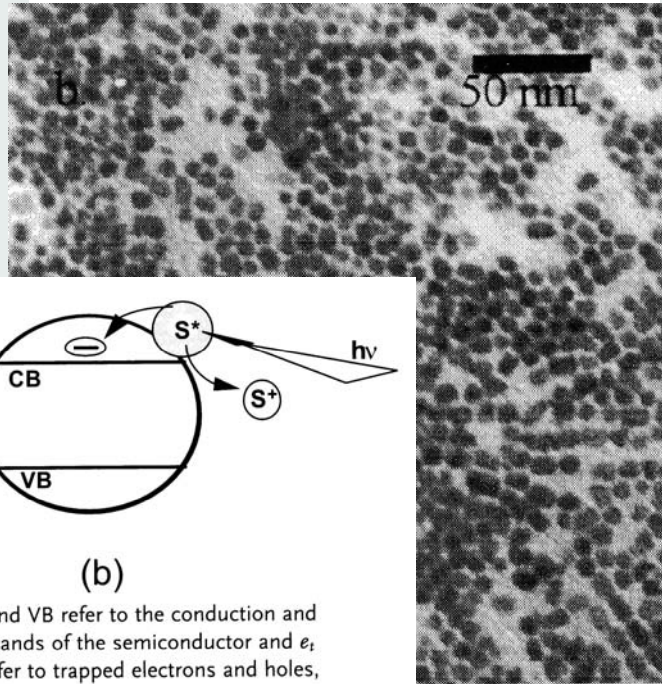


Fig. 19.1. Photoinduced charge transfer processes in semiconductor nanoclusters. (a) Under bandgap excitation and (b) sensitized charge injection by exciting adsorbed sensitizer

(S). CB and VB refer to the conduction and valence bands of the semiconductor and  $e_t$  and  $h_t$  refer to trapped electrons and holes, respectively.

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# Semiconductors

*J. Am. Chem. Soc.* 1990, 112, 1327-1332

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## Nucleation and Growth of CdSe on ZnS Quantum Crystallite Seeds, and Vice Versa, in Inverse Micelle Media

A. R. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. J. Carroll, and L. E. Brus\*

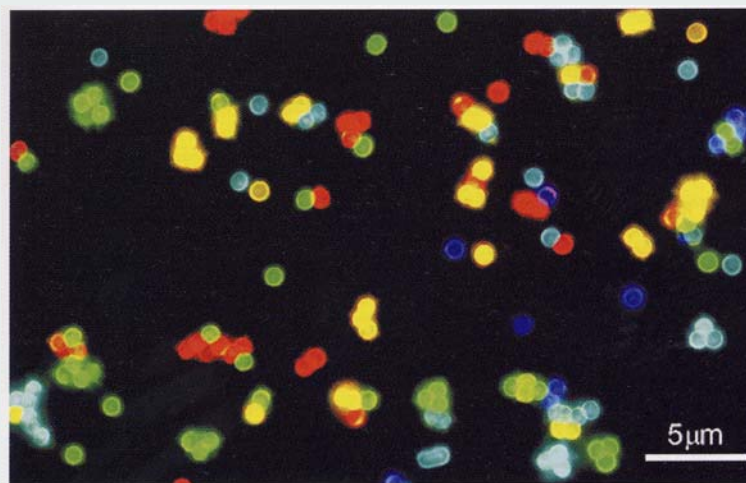
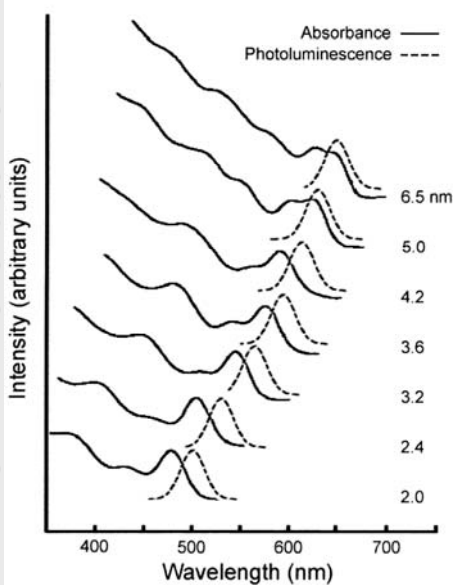


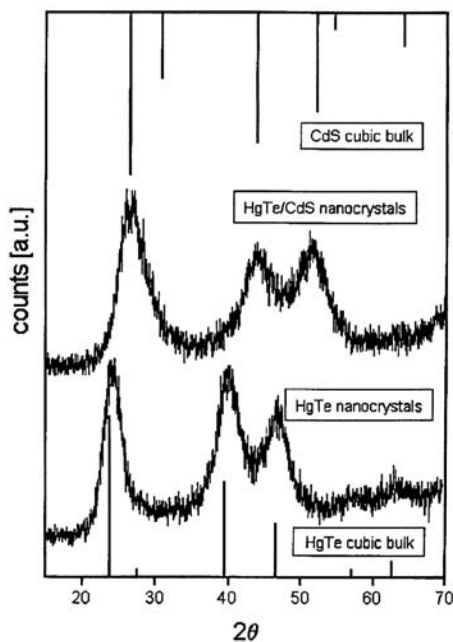
Fig. 12.5. Fluorescence micrograph of a mixture of CdSe/ZnS QD-tagged beads emitting single-color signals at 484, 508, 547, 575, and 611 nm. Reproduced with permission from [55].

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By Mike T. Harrison, Steve V. Kershaw, Andrey L. Rogach, Andreas Kornowski, Alex Eychmüller, and Horst Weller\*



The starting nanocrystalline HgTe samples were prepared as follows: H<sub>2</sub>Te gas, buffered in a slow nitrogen flow, was passed through a vigorously stirred N<sub>2</sub>-saturated solution of 0.471 g Hg(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (Alfa, 99.9 %) and 0.250 mL 1-thioglycerol (Fluka, ≥ 99 %) in 60 mL de-ionized water. The reaction was carried out in basic conditions by adjusting the pH to 10.0 using 1 M NaOH, and the H<sub>2</sub>Te gas was generated in situ by the reaction of 20 mL 0.1 M H<sub>2</sub>SO<sub>4</sub> with 49 mg Al<sub>2</sub>Te<sub>3</sub>. Thus, the molar ratio of Hg<sup>2+</sup>/RS<sup>-</sup>/Te<sup>2-</sup> was 1:2.88:0.32.

In order to attempt the growth of a layer of CdS on the bare organically capped HgTe nanocrystals, a 10 mL portion of the as-prepared HgTe solution was diluted down to 100 mL and 0.161 g Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa, 99.9 %) was added along with an extra 0.042 mL 1-thioglycerol. The pH was again adjusted to around 10, producing a slightly turbid solution. A 0.38 mmol portion of H<sub>2</sub>S, either passed directly from a cylinder or generated in situ by the reaction of dilute H<sub>2</sub>SO<sub>4</sub> with 30 mg Na<sub>2</sub>S, was then injected into the vigorously stirred solution. The turbidity disappeared, resulting in a clear, golden-brown solution. Both the bare and capped solutions were then separately placed in flasks fitted with a reflux condenser and thermometer, and heated under an N<sub>2</sub> atmosphere with vigorous stirring to boiling point using a heating mantle. Aliquots were removed at various time intervals to monitor the effect of the heating process.

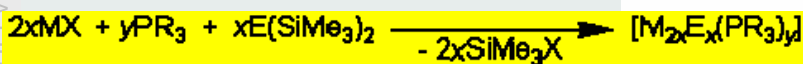
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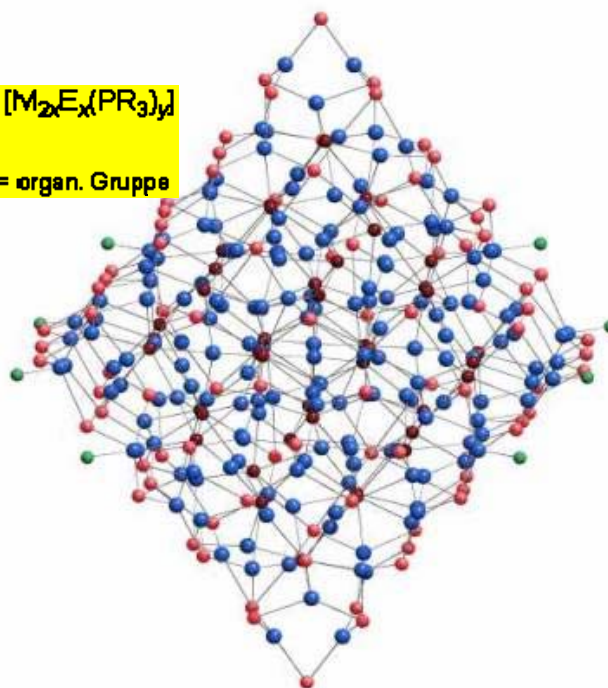
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## Chalcogenide Clusters in Chemical Compounds

D. Fenske et al.



M = Metall    X = Halogen    E = S, Se, Te    R = organ. Gruppe



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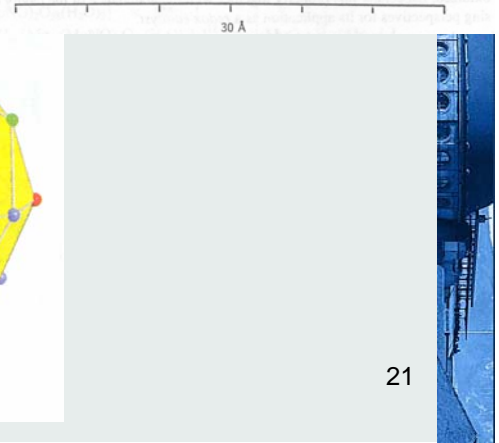
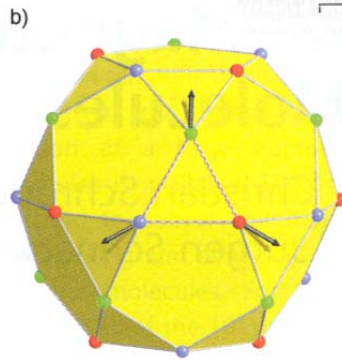
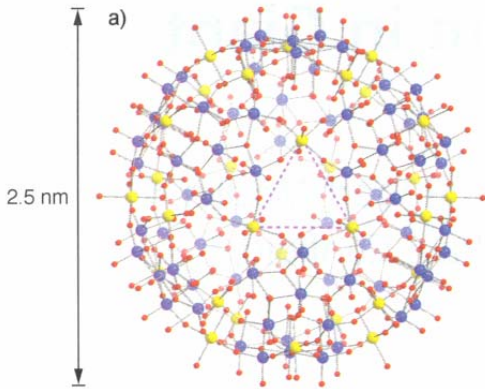
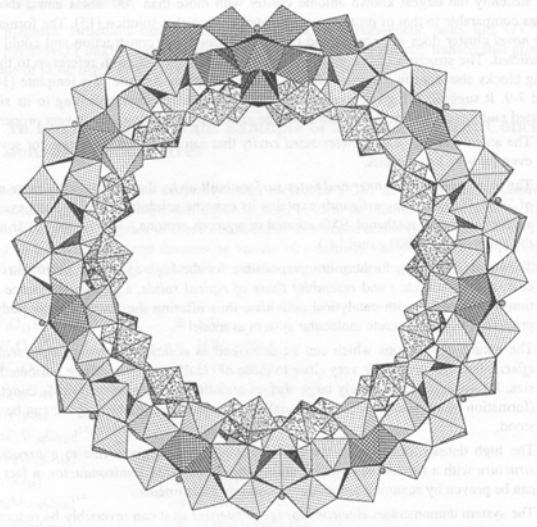
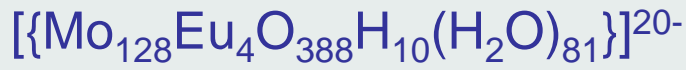
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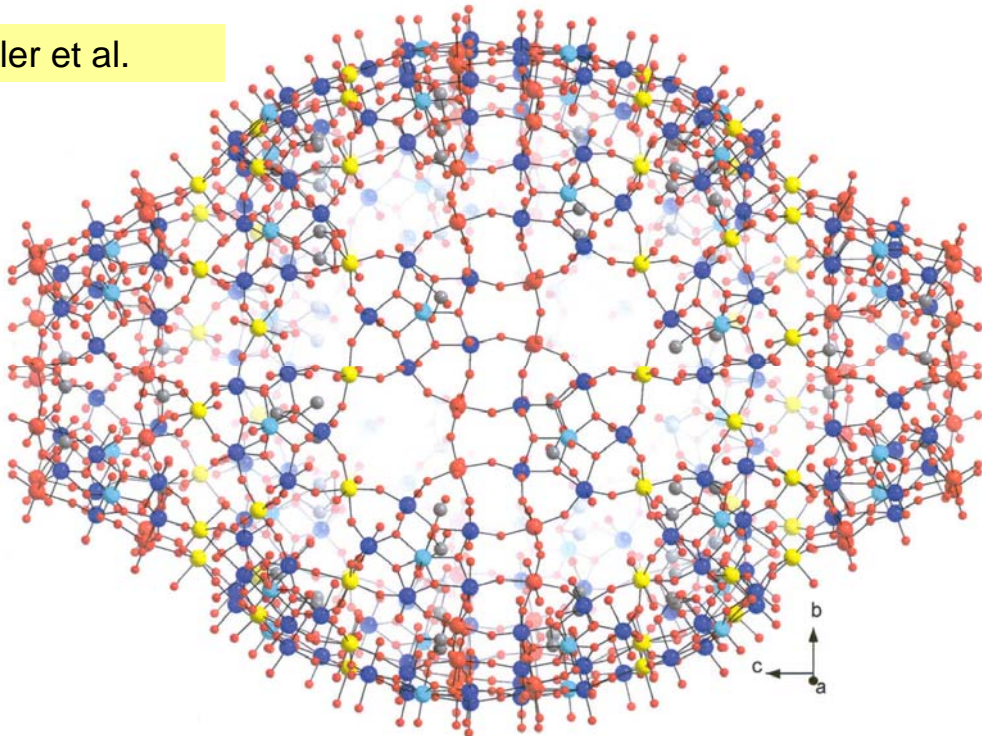
# Huge Molecu

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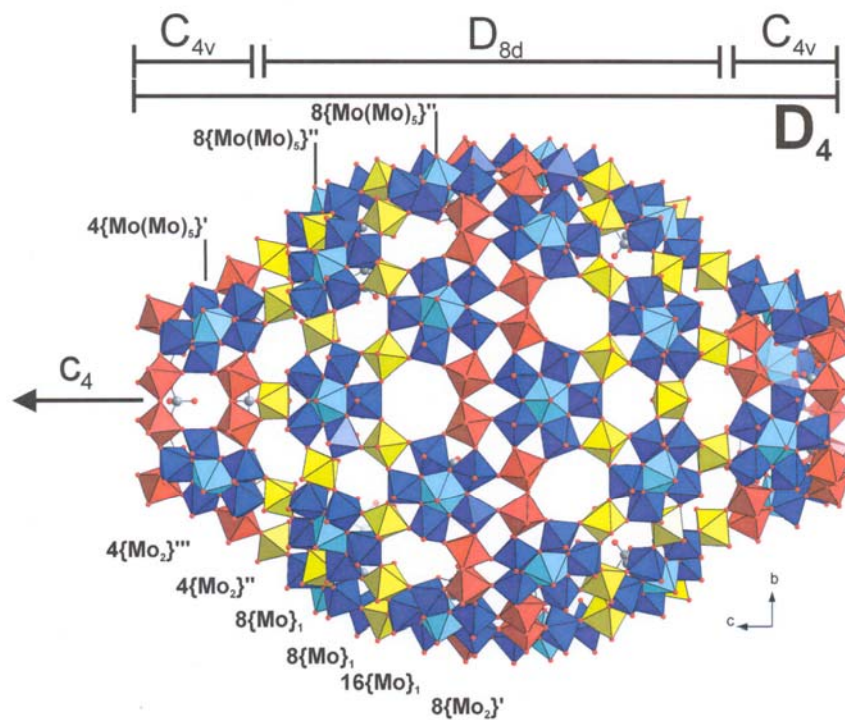
# Huge Molecules

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# Huge Molecules

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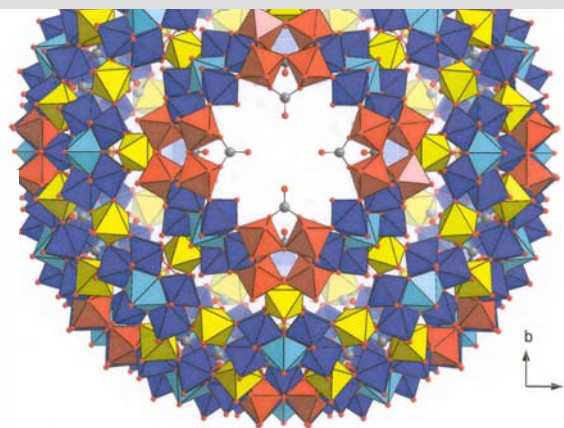
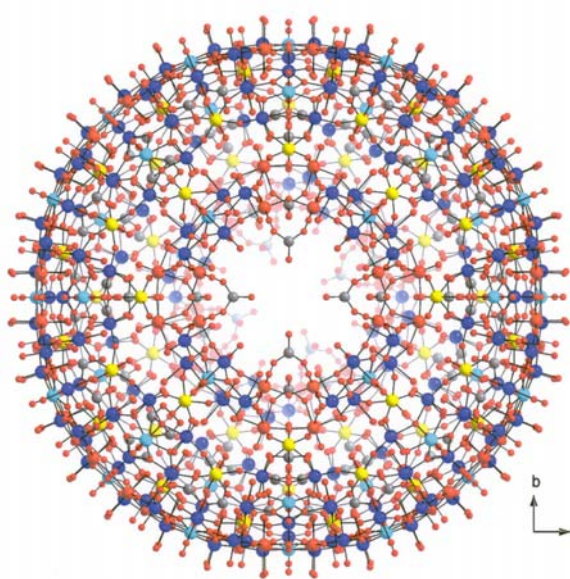
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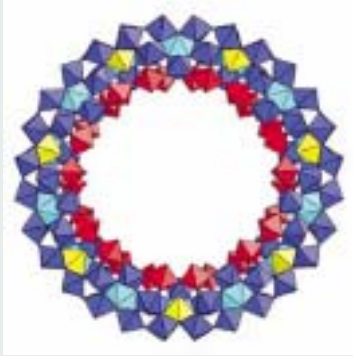
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# Assembly of Huge Molecules

A. Müller, E. Diemann,  
Nature



03.11.2006

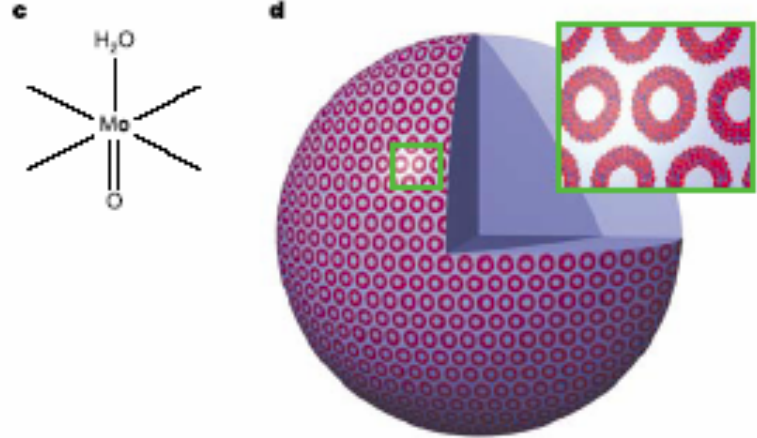


Figure 1 Structure of the 3.6mm size {Mo154}-type nanowheel with a hydrophilic surface and nanosized central cavity. a, Space-filling representation (blue and light blue, Mo atoms; red, O atoms). b, Polyhedral representation, demonstrating the abundance of pentagonal (Mo)Mo5 units (in blue) probably influencing the water structure (Mo2 units in red, Mo1 units in yellow). c, The typical smallest fragment with a metal atom and its coordination sphere, that is, with one of the 70 H<sub>2</sub>O ligands causing the extreme hydrophilic nature that is responsible for the interaction with solvents such as water. d, Schematic plot of the vesicle structure formed from nanowheels (45 nm radius) in aqueous solution, with inset showing enlarged nanowheels.