Casting Light on Fundamentals with Cutting Edge Research

Fundamentals

Molecular Orbitals

Not Only Paramagnetism of Molecular Oxygen

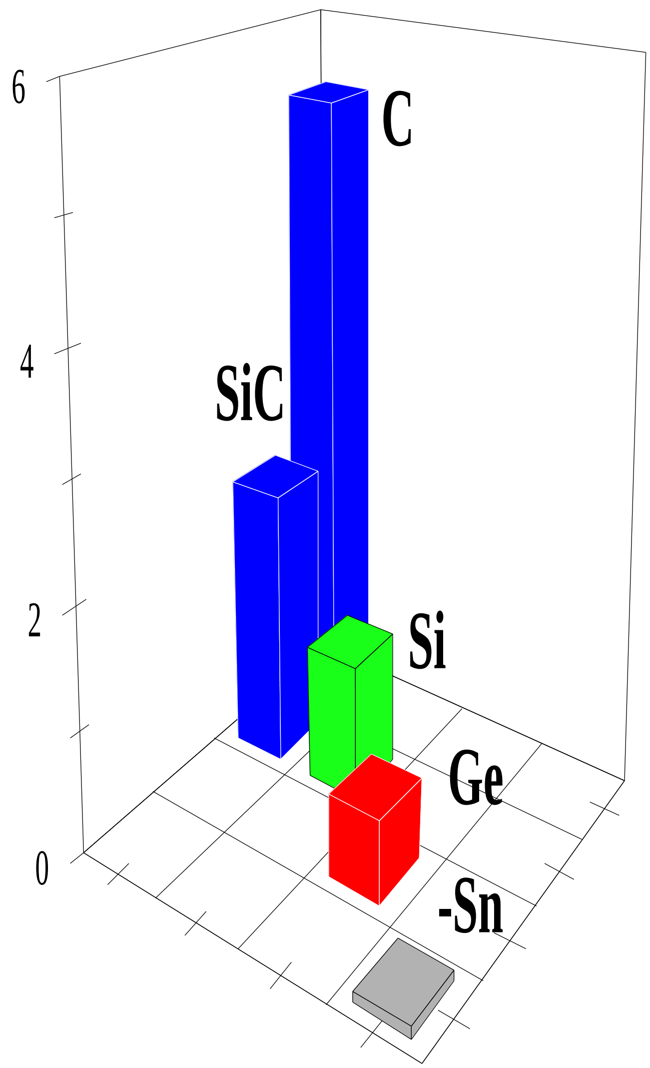
Particle-in-a-Box

Beyond Dye Molecules

Hydrogen Atom Expanded

Spherical Waves on Small Clusters

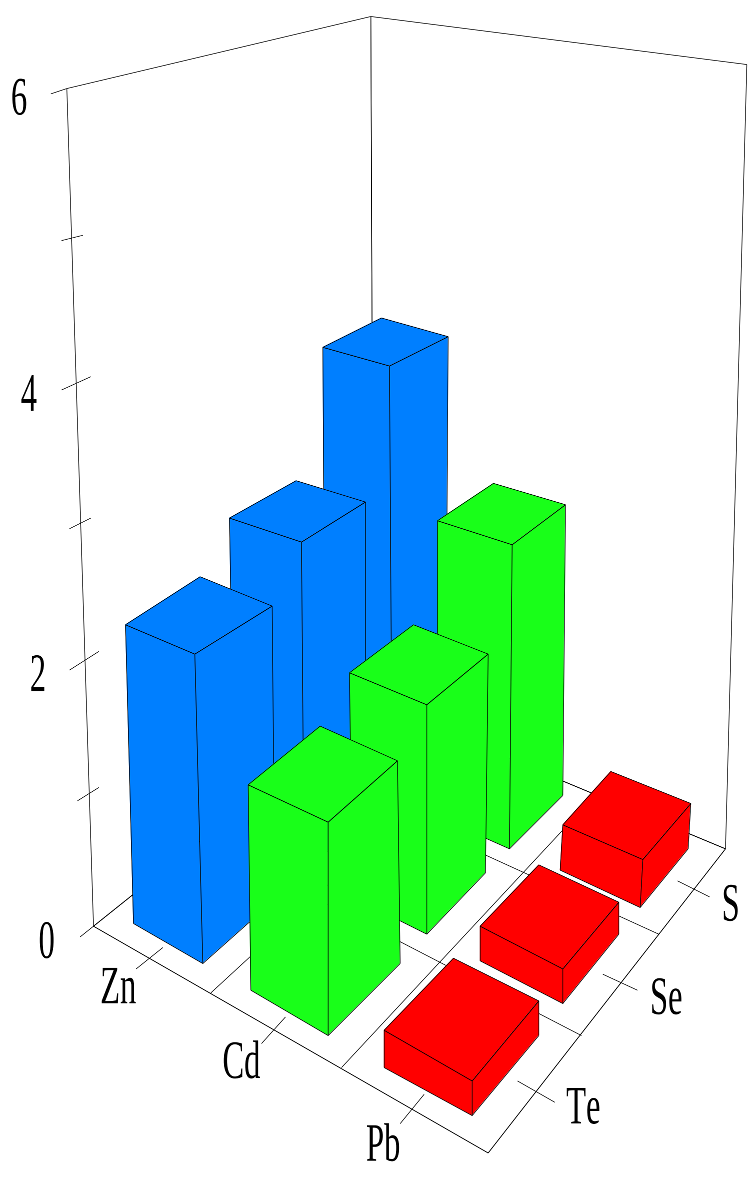
Introduction: Band Gap in Group IV ¾ The Semiconductor Group ¾ depends on size of atoms in semiconductor.



Band Gap in Group IV Semiconductors.

Moving Out from Group IV, Band Gap Increases with Increasing Electronegativity Difference.

We shall focus on the II-VI semiconductors, primarily CdS.



Band Gap in Binary II-VI Semiconductors.

Small Clusters:

Why Miniaturize?

Speed

Cost

Ultimately

Too Small to be a Solid

Too Big to be a Molecule

Quantum Dots

Why Miniaturize?
Speed
Cost

If Aircraft had advanced at the same rate as electronic components, i.e. fallen in cost and increased speed ,

Boston → LA
would now cost $20
and take 10 min!!!

Optical Properties:

CdS Bulk Material - a Lemon-Yellow, opaque solid.

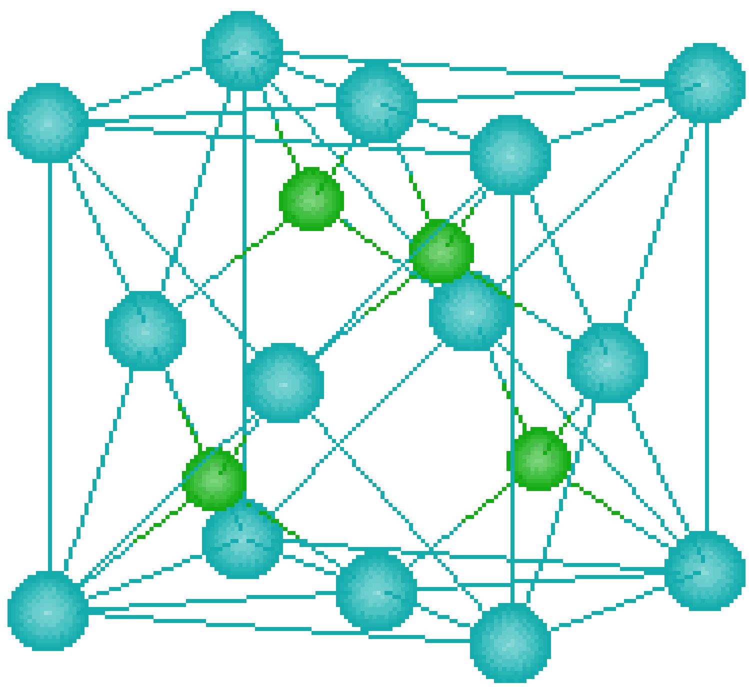
Quantum Cluster:
Transparent, Colorless Solution

Fluorescent in Blue-Green

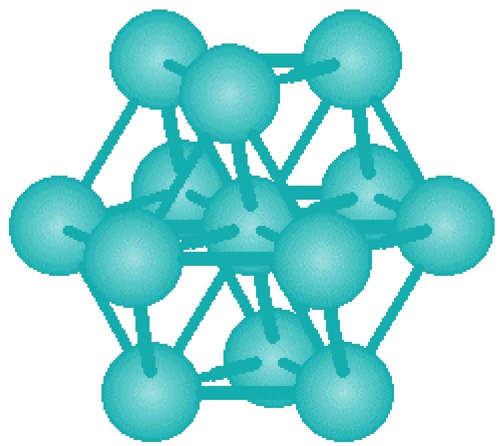
PbS - Bulk is a Sooty, Black Solid.
Quantum Cluster:
Transparent, Red Solution
Fluorescent in the Green.

CdS is a Zinc Blend Structure

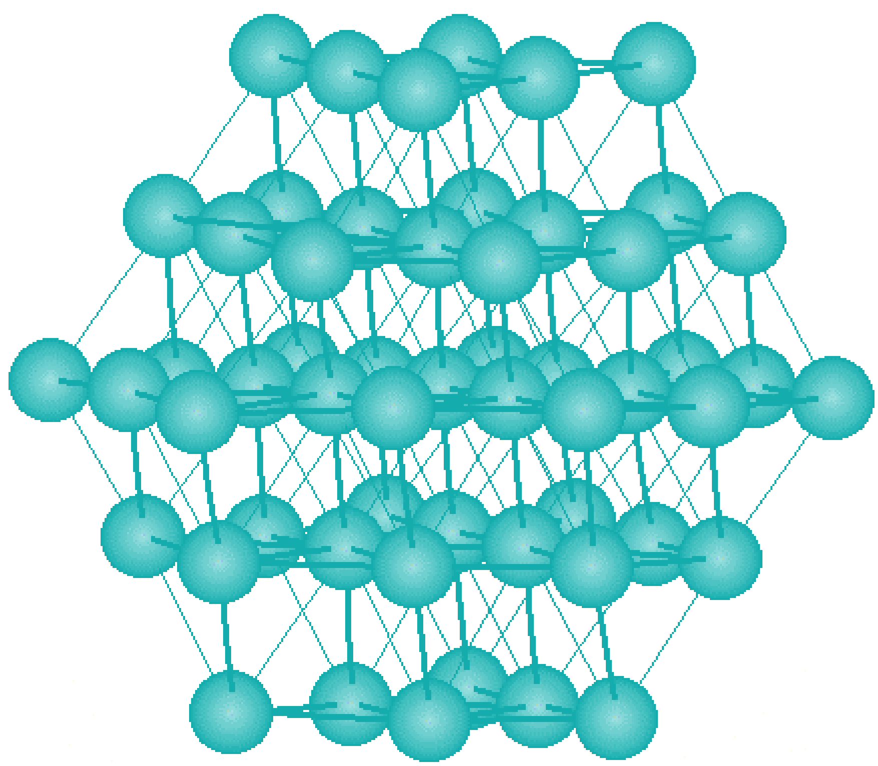
FCC lattice of S^{2-} with every other tetrahedral hole occupied by the smaller Cd^{2+} ions.



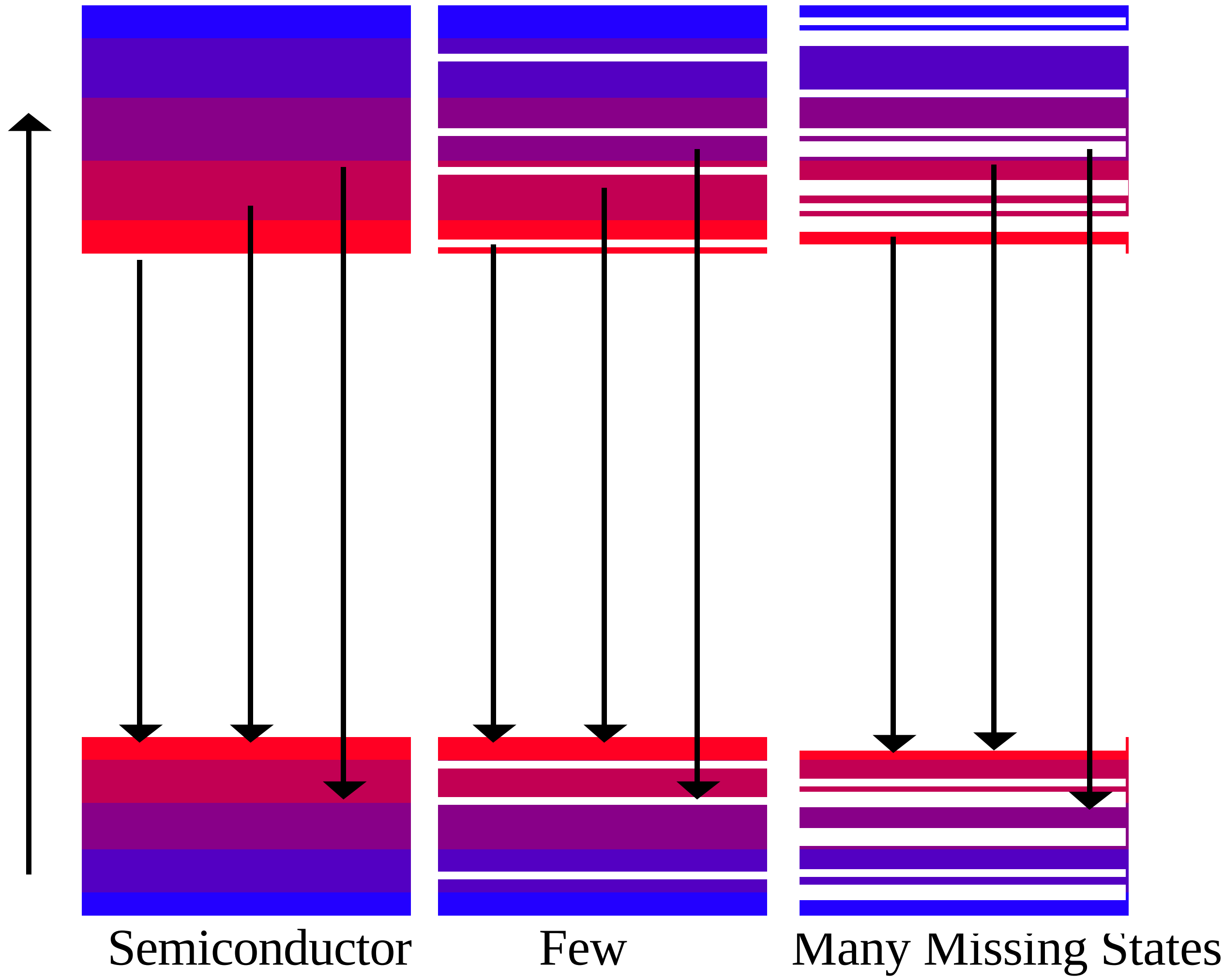
Cluster: 13 S^{2-}



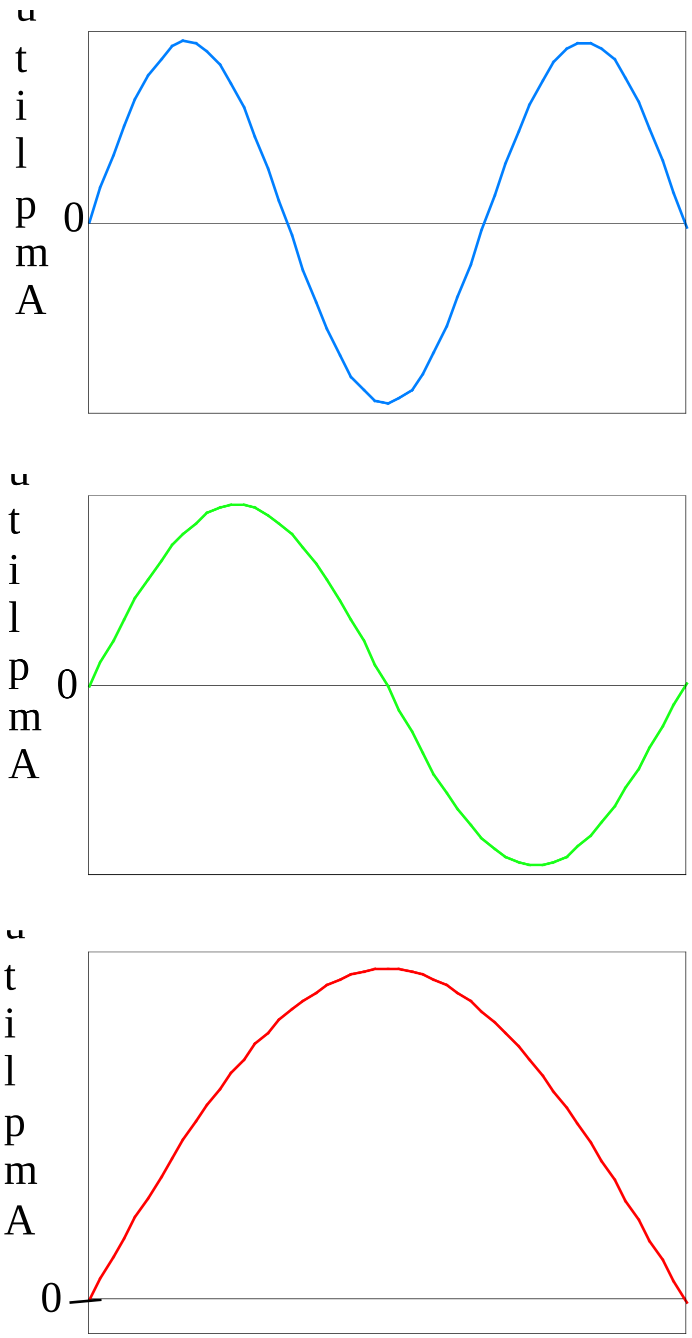
Cluster 55 S^{2-}



In these small clusters, quantum effects begin to be important: they are too big to be molecules, too small to be solids. Typical cluster has about 1,000 atoms, about 1/3-1/2 are on the surface. There are corner atoms and flat atoms. The chemistry of these are interesting too. Our focus today is the optical properties. In particular, the band gap is larger than the corresponding solid. How can we understand this? Simple model: missing states.


Semiconductor
Few
Many Missing States

Next more sophisticated, introductory or physical chemistry model, a particle-in-a-box model:



$$\Delta E = \frac{(2n+1)h^2}{8m_e L^2}$$

m_e mass of electron

L = Box Length

Finally:

Model as an “atom”

coulombic potential with heavier hole localized in cluster center

CdS hole mass ~ 4× electron mass. bulk exciton diameter 60Å

Ref: Bawendi, Ann. Rev. Phys. Chem. *41*, 477 (1990)

parabolic potential:

$$E_{n,\ell}=\acute{a}\omega_0(2n+|\ell|+1)$$

In presence of magnetic field, $\pm\ell$ split, electrons shuffle

Ref: Ashoori, *Nature*, *379*, 413 (1996)

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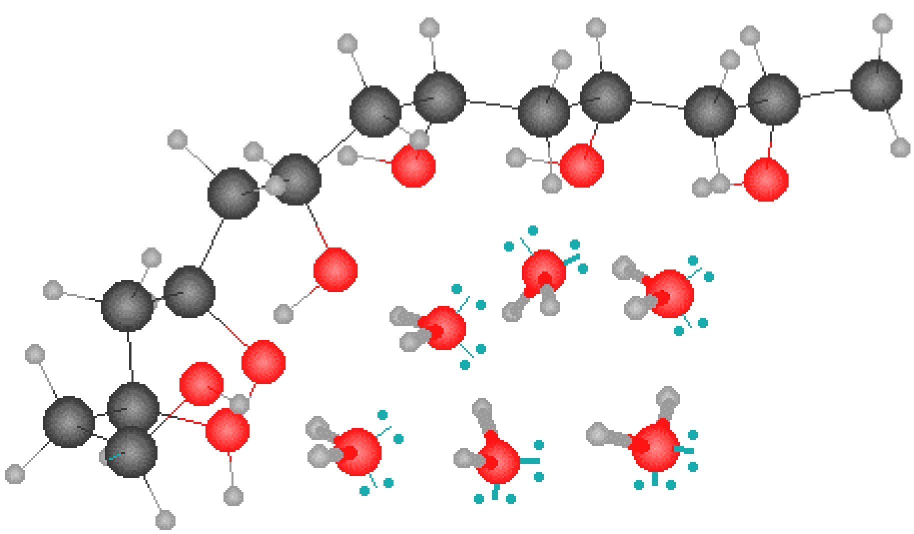
Question: How do you synthesize these small clusters?

Three Methods:

1. Polymer Method: 4% polyvinyl alcohol solution, polyvinyl alcohol is 124,000-186,000 molecular weight. Heat water to ~80°C, stir vigorously, add PVA *slowly*. Continue to maintain 80°C with stirring for a couple of hours. Solution should be nearly clear. Use for PbS clusters. Makes large clusters.



Polyvinyl alcohol surrounding water.

2. Surfactant Method: surfactant solution (25.6 g AOT per liter heptane, AOT is dioctyl sulfosuccinate, sodium salt). Inverse Micelle in toluene. Ref: R. R. Chandler, S. R. Bigham, and J. Coffer, *J. Chem. Ed.*, **70**, A7 (1993).

Used for CdS, makes smaller clusters.

Instructions for these two on attachment.

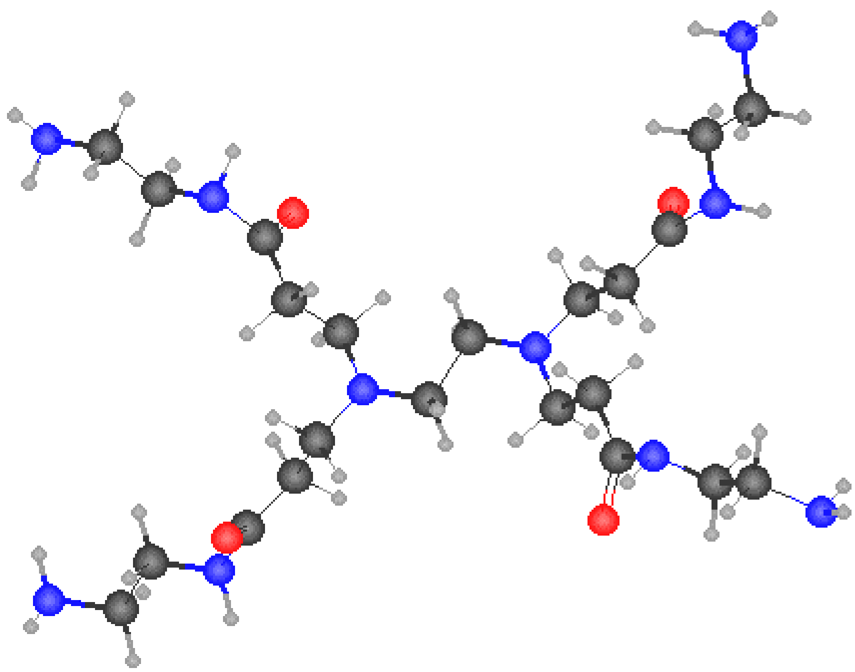
3. Dendrimer Method:

Makes smallest clusters, ~2-4 nm miameter.

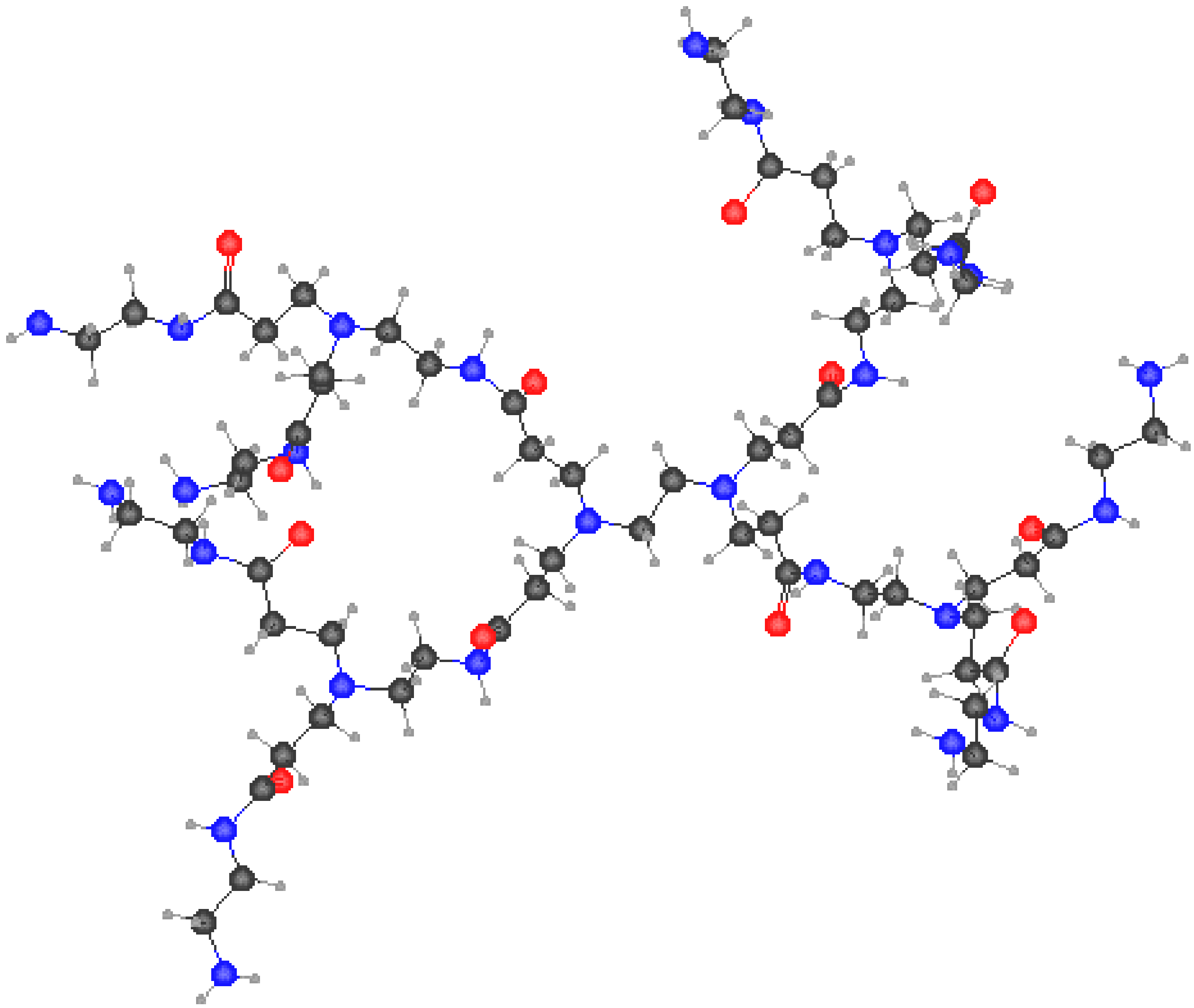
Ref: Sooklal, Kelly; Hanus, Leo; Ploehn, Harry J.; Murphy, Catherine J., "A Blue-Emitting CdS/Dendrimer Nanocomposite" *Adv. Mater.* **1998**, *10*, 1083-1087.

Dendrimer Source: Aldrich

Generation 0 PAMAM Dendrimer:



Generation 1 PAMAM Dendrimer



Larger ones have increasingly more amines.