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Shape Control of Zinc Oxide Crystals with Succinate Derivatives

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Shape Control of Zinc Oxide Crystals with Succinate Derivatives

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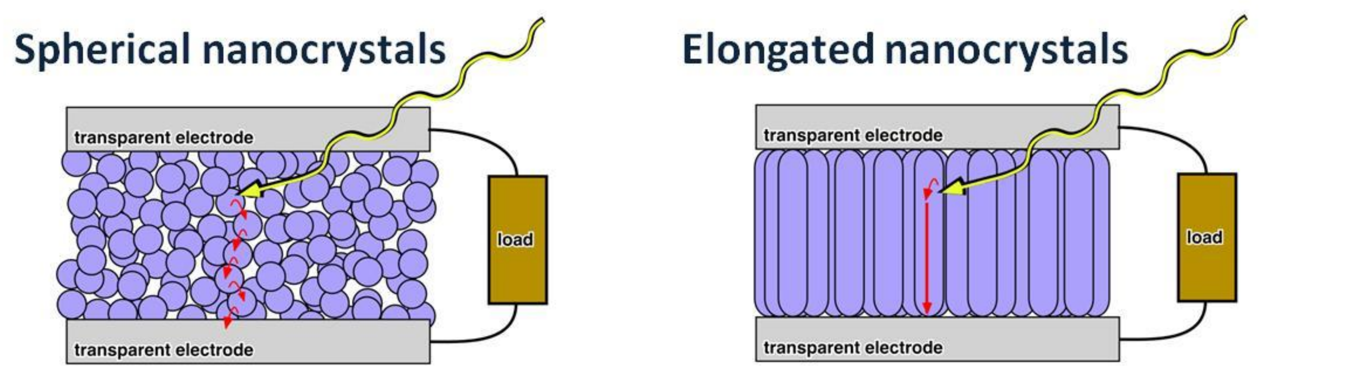
Motivation



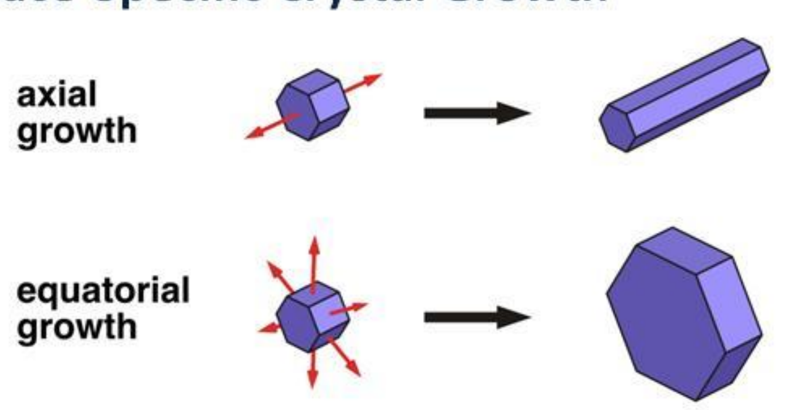
Grain-like crystals found in current solar cells.
Electron "hopping" decreases efficiency.

Rod-like crystals in potential solar cells.
Reduced electron "hopping" increases efficiency.

Control of crystal shape can enable new semiconducting materials for photovoltaic applications, such as more effective solar cells.

Background

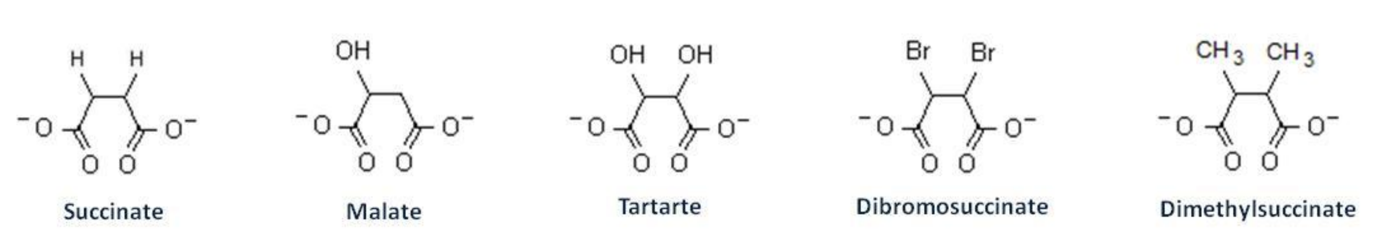
Face-Specific Crystal Growth



Face-specific growth allows for ligand-based shape-control.

Can organic ligands bind to these faces and change their growth rates?

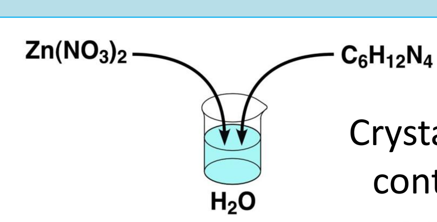
Ligands: Succinate & Its Derivatives



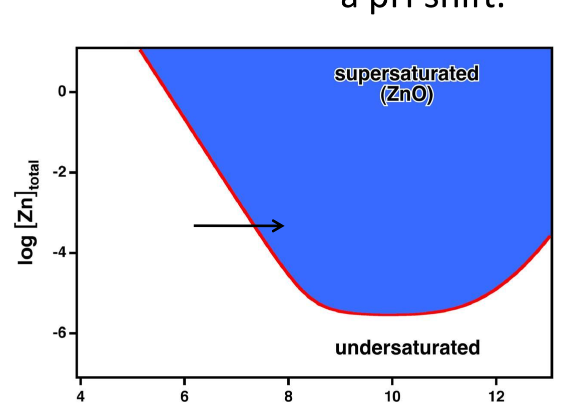
Methods

Predictions:
If steric hindrance is responsible for ligand effectiveness, then shape-control activity will be the same for all di-substituted succinates.

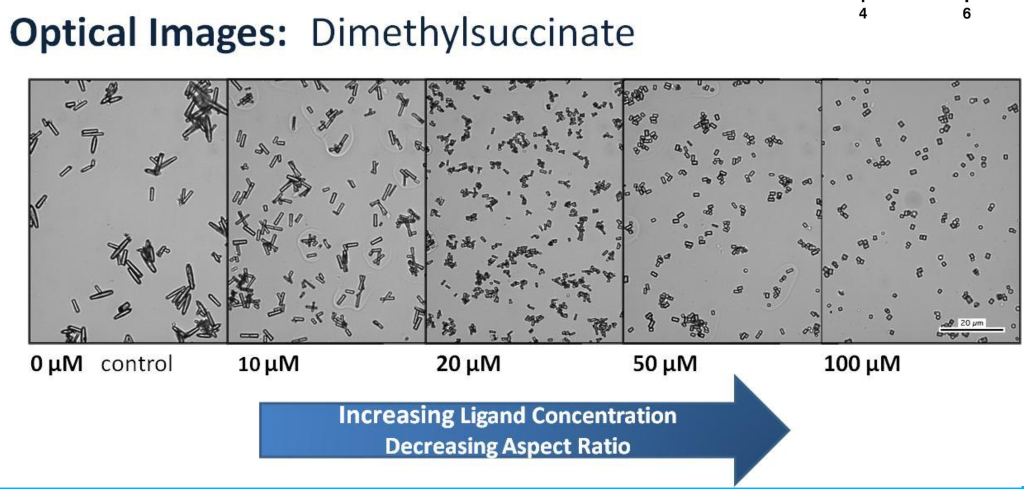
If electronic effects are responsible for ligand effectiveness, then shape-control activity will vary based on the substituent.



Crystallization is controlled by a pH shift.

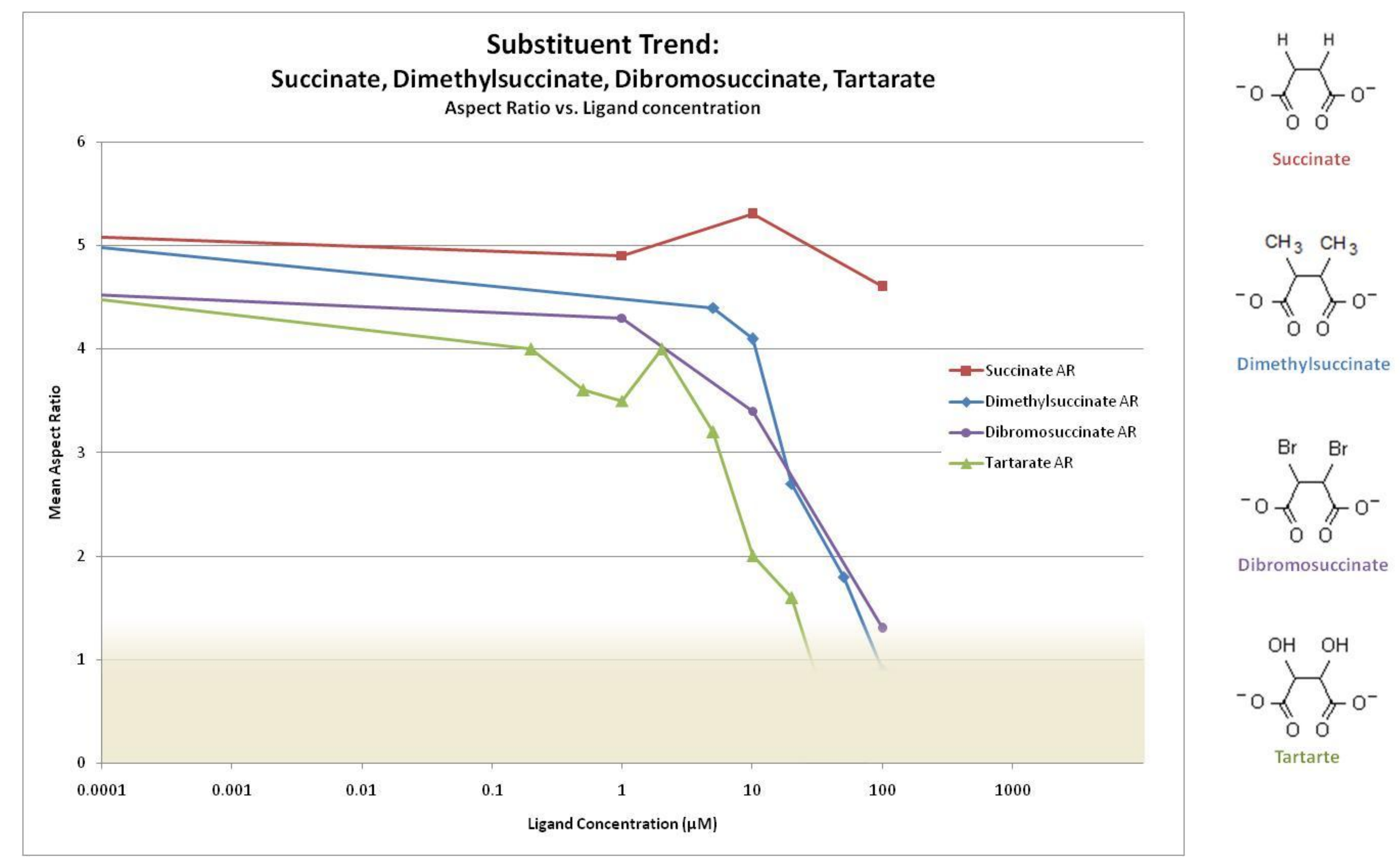


Optical Images: Dimethylsuccinate



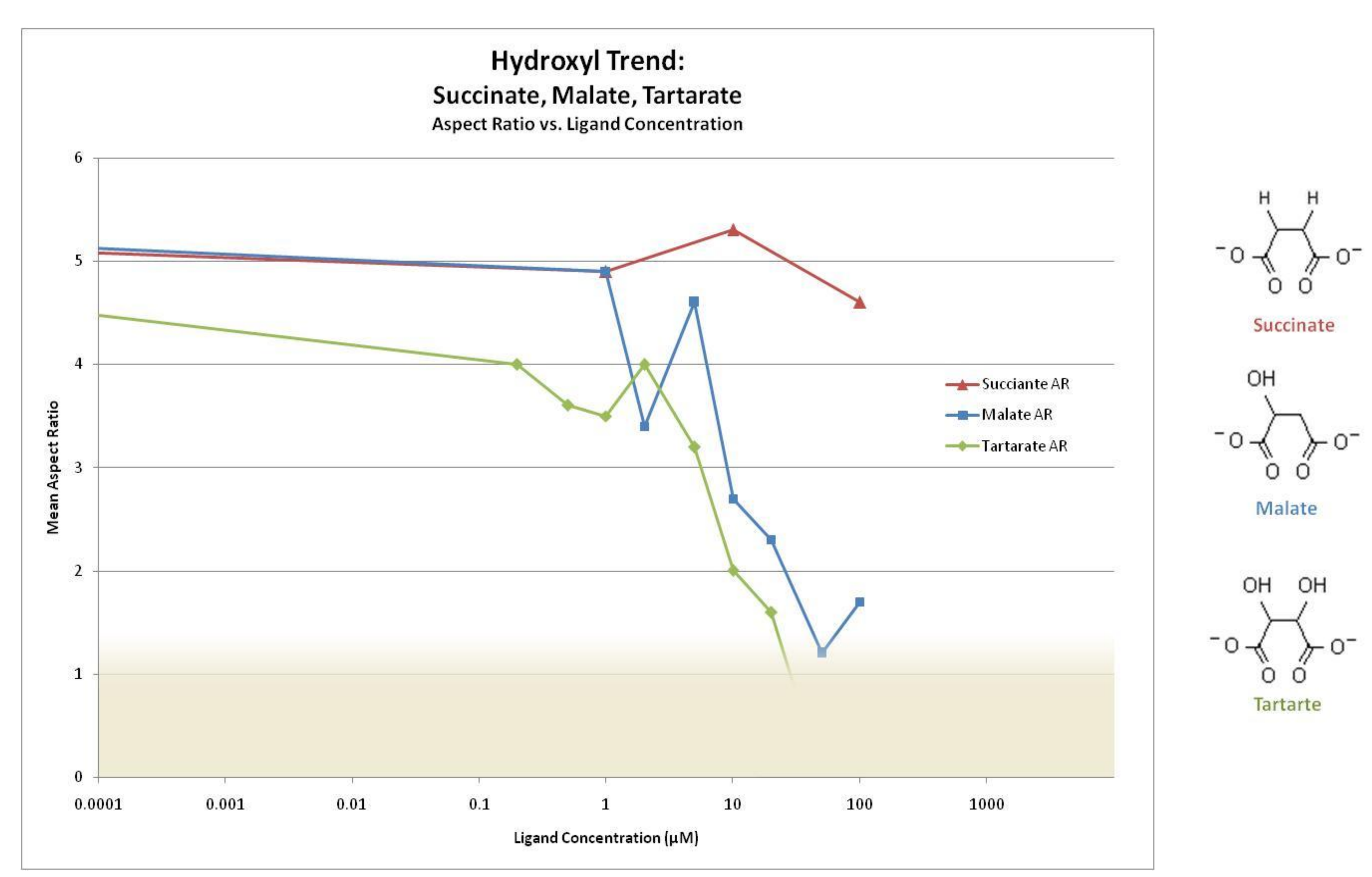
Results

Question: Which substituents enable shape control?



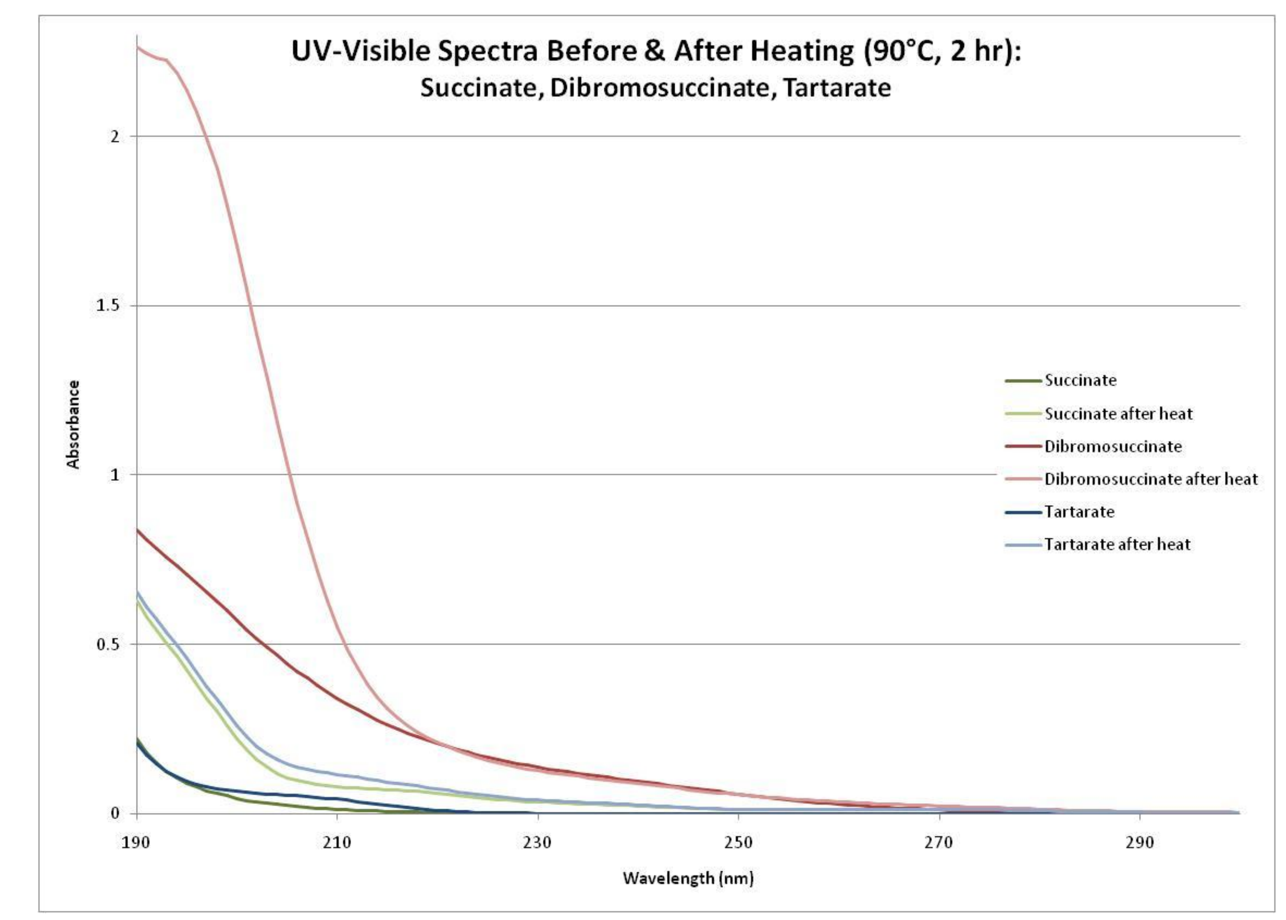
Answer: They all do!
All the di-substitutied succinates have similar shape-control activities, implying that it is not the specific substituent, but the general steric hindrance of the substituent which is required for ligand effectiveness.

Question: How many substituents are required?



Answer: One is enough, but two are better.
Malate (one backbone substitution) is more effective than succinate, but less effective than tartarate (two substitutions).

Question: Do ligands hydrolyze during heating?



Answer: Yes, all ligand spectra were altered.
But the products do not appear to be responsible for shape control since tartarate and succinate have similar spectra, yet exhibit different shape control activities.

Conclusions

Different di-substitutes on the succinate bridge did not affect the threshold concentration, implying that subtle electronic effects do not determine shape-control activity.

Increasing the number of substituents on the succinate backbone can increase ligand effectiveness.

Ligand uv-vis spectra were altered by reaction-condition heating, but these products do not appear to be active in shape-control, as illustrated by tartarate and succinate.

Further Study

Examine additional trends in ligand structure.
Identify products of ligand hydrolysis.
Time-dependent study of crystal growth.
Rate and amount of zinc depletion during reaction.
Determine manner of ligand binding:
  on crystal surface, or incorporated into crystal structure

Acknowledgments

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