

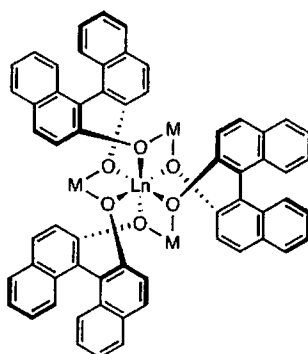
Self-Assembly from a Molecular Viewpoint

Little by little one goes far

Both consciously and unconsciously the concept of self-assembly have been used to achieve something in chemistry. The applications of self-assembly have been widespreading in various field. I think self-assembly can be separated to three parts; 1. the factor of self-assembly, 2. the change in molecular level, 3. total result. In this seminar especially I will talk about 2. the change.

Factor	Change	Result
<ul style="list-style-type: none"> • Metal template • Hydrogen bonding • π-π stacking • CH-π interaction 	<ul style="list-style-type: none"> • Transform • Aggregation: new function multi function (multiplication) addition 	<ul style="list-style-type: none"> • Ligand library • Catalyst • Sensor • Gelation • Material <p>etc.</p>

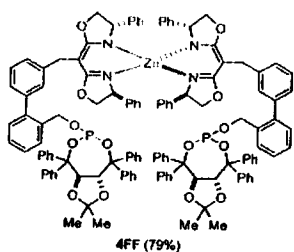
Ex.



- Metal Template
- Aggregation: multi functions (multiplication)
- Asymmetric Catalyst

Asymmetric Catalysis Using Self-Assembled Chiral Bidentate *P,P*-Ligand

James M. Takacs*, D. Sahadeva Reddy, Shin A. Moteki, Di Wu, and Hector Palencia
JACS. 2004, 126, 4494.



- Metal template
- Aggregation: multi function
(addition)
- Ligand library

Asymmetric allylic amination catalyst

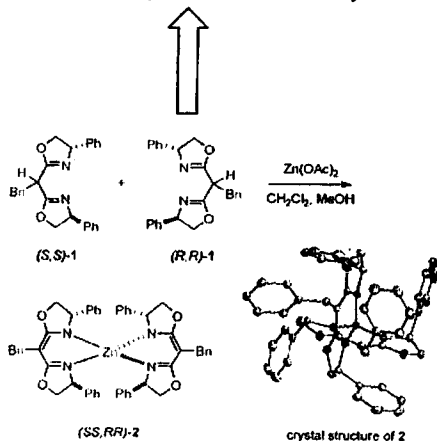
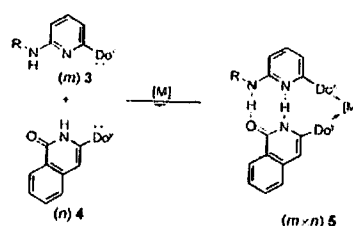


Figure 2. Preparation and crystal structure of (box)Zn complex 2.

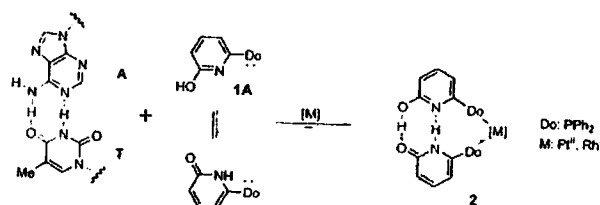
Self-Assembly of Bidentate Ligands for Combinatorial Homogeneous Catalysis Based on an A-T Base-Pair Model

Bernhart Breit and Wolfgang Seiche
Angew. Chem. Int. Ed. 2005, 44, 1640.



- Hydrogen bonding
- Aggregation: multi function
- Ligand library

Hydroformylation catalyst



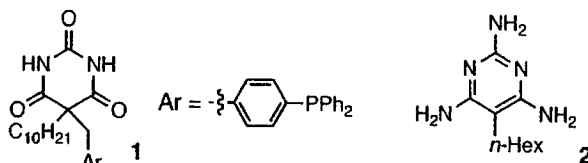
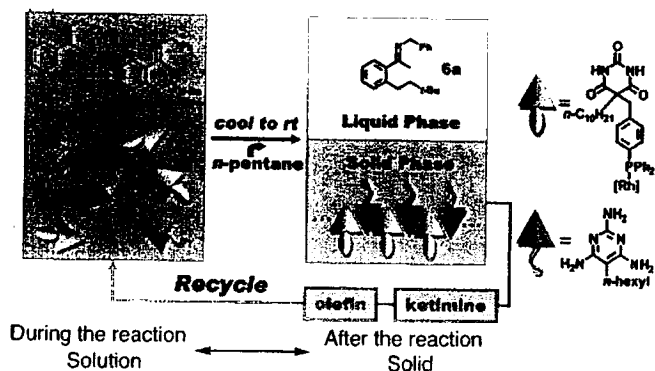
Recyclable Self-Assembly-Supported Catalytic System for Orthoalkylation

Jong Huem Yoon, Young Jun Park, Jun Hee Lee, Jaeho Yoo, and Chul-Ho Jun*
Org. Lett. 2005, 7, 2889

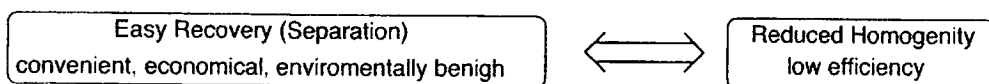
- Hydrogen-Bonding
- Aggregation: New Function (Solbility)
- Polymer Supported Catalyst

Abstract

A New recyclable supported catalyst system for orthoalkylation was devised using a self-assembly consisting of the barbiturate 1 and 2,4,6-triaminopyrimidine 2 H-bonding motifs.



The Features of Heterogeneous Catalyst



Various attempts have been made to overcome the low efficiency.

ex.

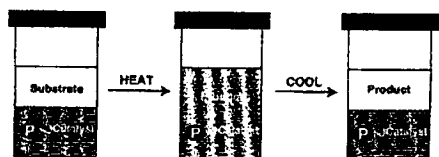
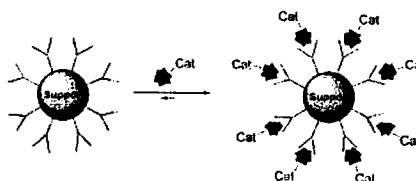


Figure 1. Schematic representation of thermomorphic catalysis. Selective solubility of the polymer support under biphasic conditions ensures quantitative catalyst recovery.

Scheme 1. The Concept of Supramolecular Anchoring of Catalysts to a Soluble Support



Hybrid materials

Non covalent tagging etc.

Hyperbranched polymers

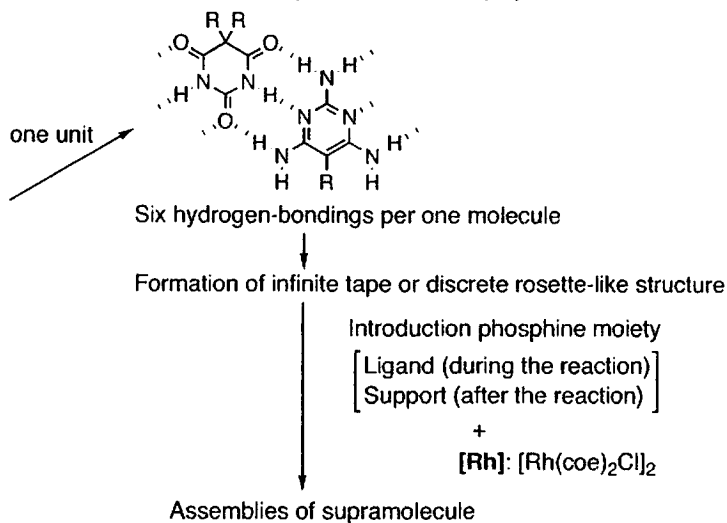
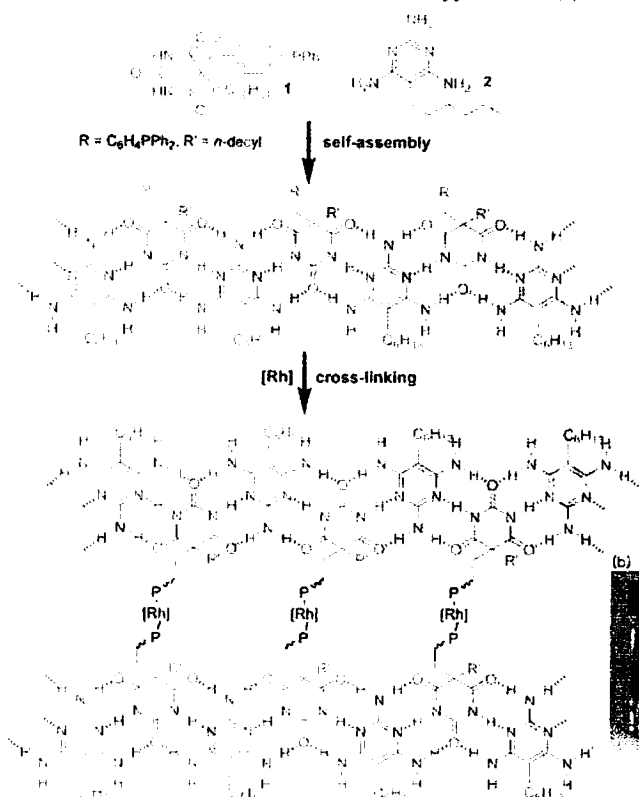
(*JACS* 2001, 122, 9058., *JACS* 2001, 123, 11105., etc.)

Dendrimers

(*JACS*, 2001, 123, 8453., *Angew. Chem. Int. Ed.* 2001, 40, 1829. (review))

In this literature new approach to high efficiency heterogeneous catalyst is presented using the self-assembly system.

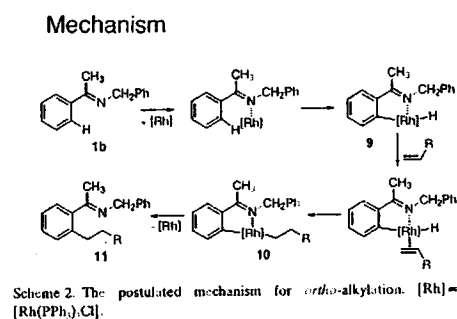
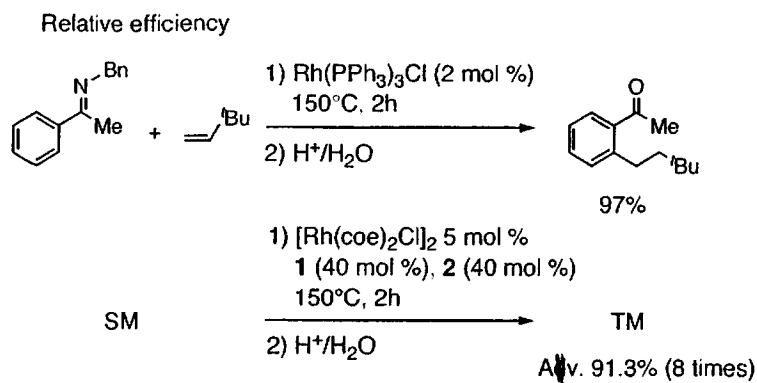
Scheme 1. Barbiturate-Substituted Phosphine Ligand (1) and Its Possible Interaction with Triaminopyrimidine (2)



(b): Homogeneous phase consisting of 1, 2, [Rh], SMs after heating

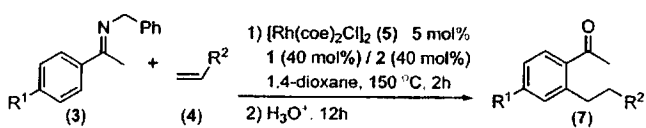
(c): Precipitation from (b) on addition of *n*-pentane after cooling to room temperature

(d): Nonprecipitation in the absence of 2 under the same conditions as that of (c)



• Recycle

Table 1. Recycle of the Catalyst for Orthoalkylation of **3** with **4^a**



entry	R ¹ (3)	R ² (4)	ketone (7)	isolated yield of product (%)							
				1	2	3	4	5	6	7	8
1	H (3a)	<i>t</i> -Bu (4a)	7a	87	91	94	97	95	92	89	86
2	MeO (3b)	4a	7b	85	90	89	85	88	87	84	87
3	CF ₃ (3c)	4a	7c	92	95	94	97	93	93	89	91
4	3a	<i>n</i> -Bu (4b)	7d	68	73	77	76	76	74	79	75

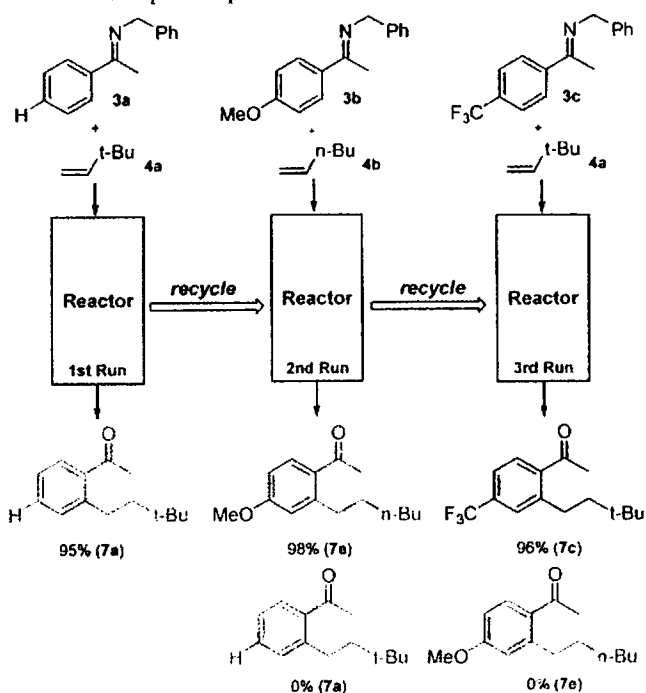
^a A quantity of 0.216 mmol **3** and 3 equiv of **4** were used; *coe* = cyclooctene.

• Leaching

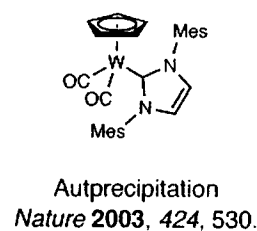
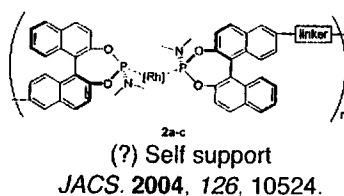
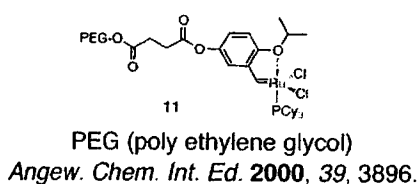
0.024, 0.009, 0.012% leaching of Rh over three cycles

• Separation (catalyst and TM + SM)

Scheme 4. Orthoalkylation with Different Substrates Showing the Complete Separation of the Product in Each Run



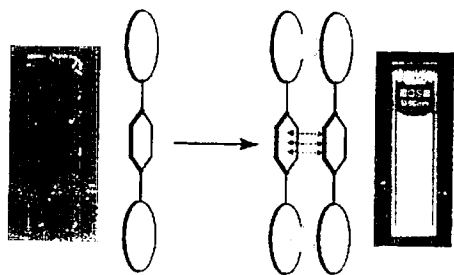
Other Homogeneous-Heterogeneous Catalyst



A Prototype for the Chemosensing of Ba²⁺ Based on Self-Assembling Fluorescence Enhancement

Maurizio Licchelli*, Alessio Orbelli Biroli, and Antonio Poggi
Org. Lett. ASAP

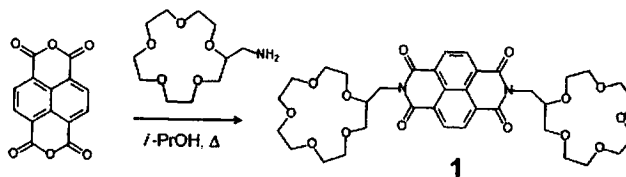
- Electrostatic Interaction (Between Ba²⁺ and 15-crown-5 derivatives)
- Aggregation (formation of 2+2 complex): New Function, Fluorescence
- Chemosensor



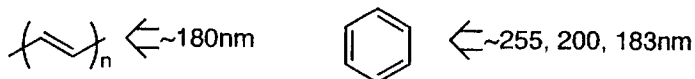
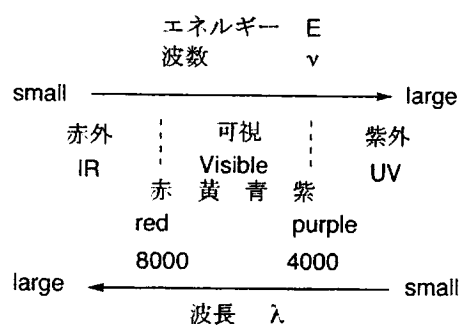
Abstract

Barium ion can be revealed at the micromolar concentration level by the blue-green fluorescence which arises upon the self-assembling process involving the metal ion and a novel bis-15-crown-5-naphthalenediimide derivative.

Scheme 1. Synthesis of **1**

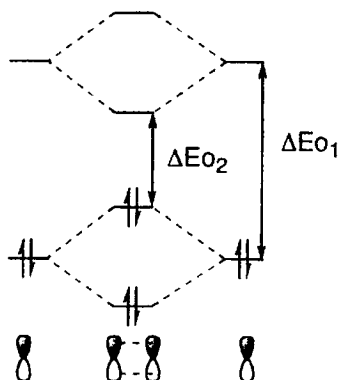


•What is the Origin of Fluorescence ?



It is well known that (conjugated) olefines and arenes have absorption spectrum in UV region. (TLC check, HPLC, etc.)

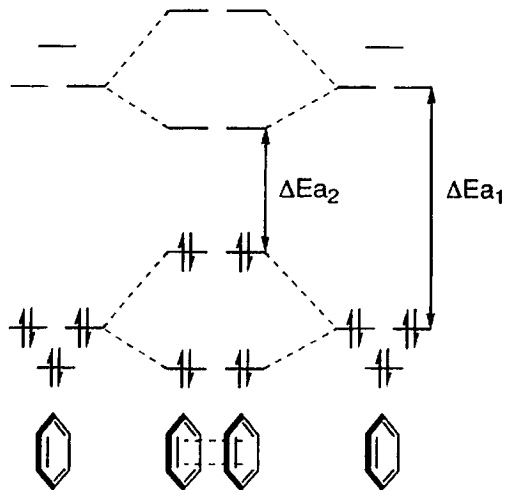
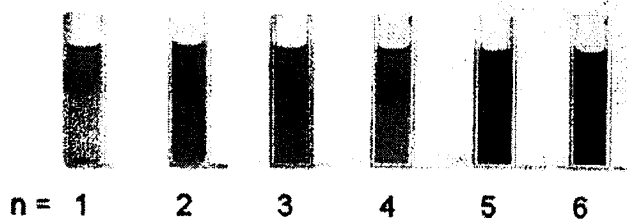
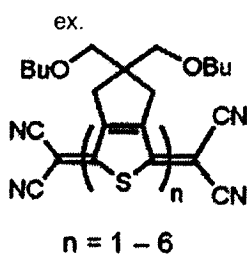
When the absorption spectrum is moved to longer λ side (red shift) the compound should have fluorescence in visible region.



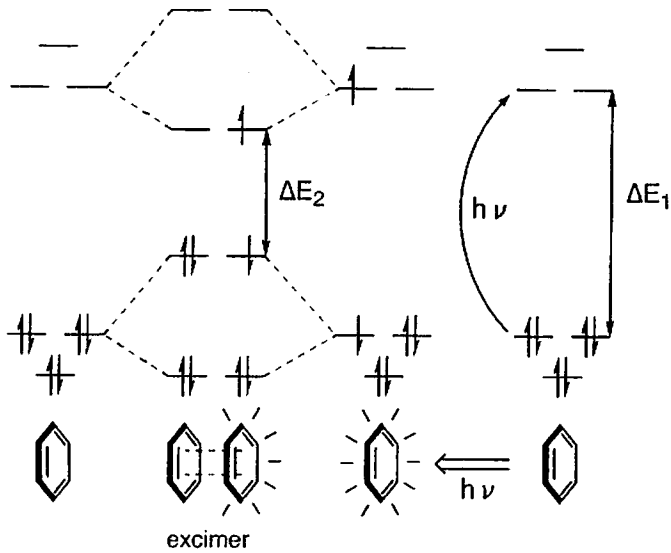
One of the simplest way to shift the absorption spectrum is extending the conjugated system.

$$\Delta E_{01} > \Delta E_{02} \equiv \lambda_{01} < \lambda_{02} \equiv \text{Red shift}$$

($E = h/\lambda$, $h = \text{plank constant value}$)



In the case of arenes similarly when each orbitals overlap new molecular orbitals are reconstructed and red shift should occur.



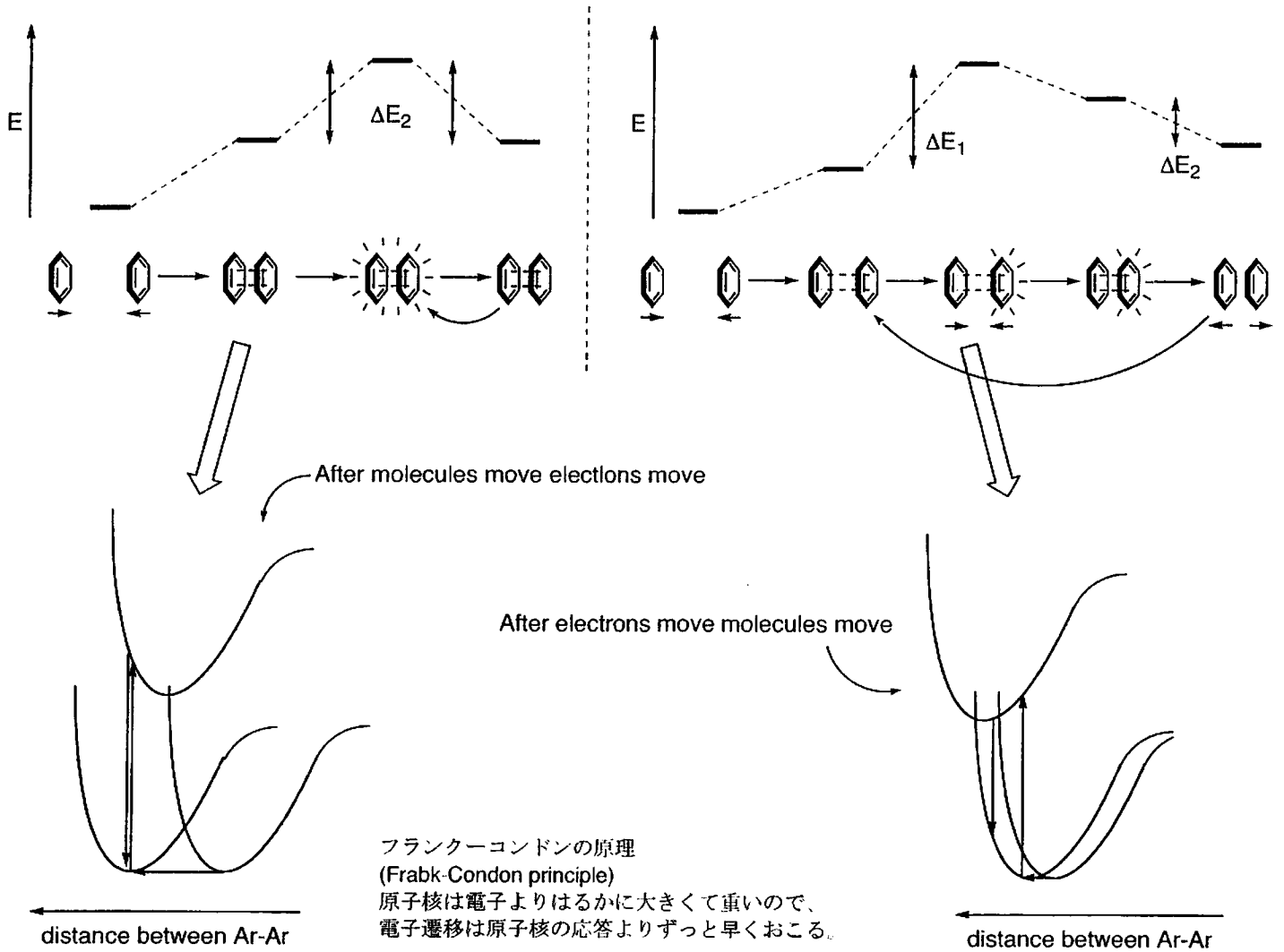
One molecule is excited.

It makes excimer with another ground-state molecule.

After emission of fluorescence the one parts from the other.

エキシマー(excimer)

ファンデルワールス力などの弱い分子間力で結びついた分子二量体が、片方の分子が電子励起されると安定化され非常に強く結合する場合があります。同種の分子の二量体ではエキシマー、異種の場合はエキシプレックスと呼ばれる。発光は本来の単体の電子遷移よりも非常に超波長側に現れる。



•The Reason Why Ba²⁺ Is Selectively Needed

Acturally whith Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺ or Sr²⁺ almost no fluorescence is observed.



Whith these metal ions the formation of excimers scarcely occur.



What is needed for the formation of excimers ?

- The formation of sandwich-like [2 +2] complex
- (•Adequate distance between naphthalenediimide moieties)

suggesting the fomation of 1:1 complexes

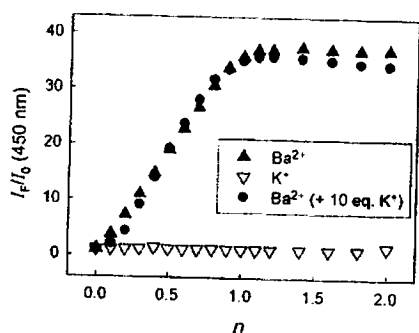


Figure 3. Spectrofluorimetric titration plots of **1** (10^{-6} M in MeCN, $\lambda_{exc} = 335$ nm) with Ba²⁺, K⁺, and Ba²⁺ in the presence of excess K⁺ (10 equiv).

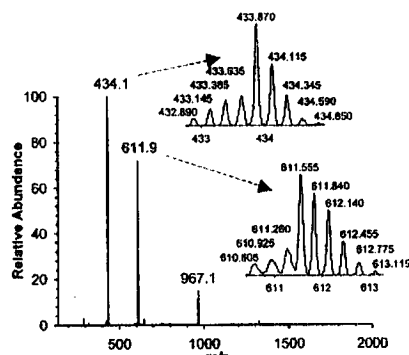
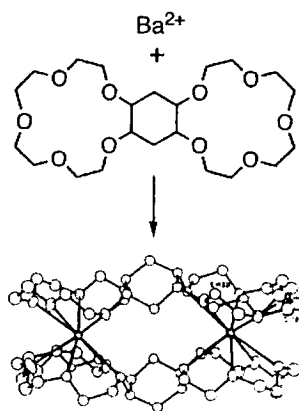


Figure 4. ESI-MS spectrum of an equimolar mixture of **1** and Ba(ClO₄)₂ in acetonitrile (10^{-4} M). The high-resolution spectra corresponding to the peaks at 434.1 and 611.9, reported in the insets, show typical peak separations (about 0.25 and 0.33, respectively) which are expected for the tri- and tetrapositive ions, {[Ba₂(1)₂](ClO₄)³⁻ and [Ba₂(1)₂]⁴⁺, respectively.

suggesting the fomation of [2 + 2] complexes



suggesting the interaction between naphthalenediimides and the distance is changed (shorten)

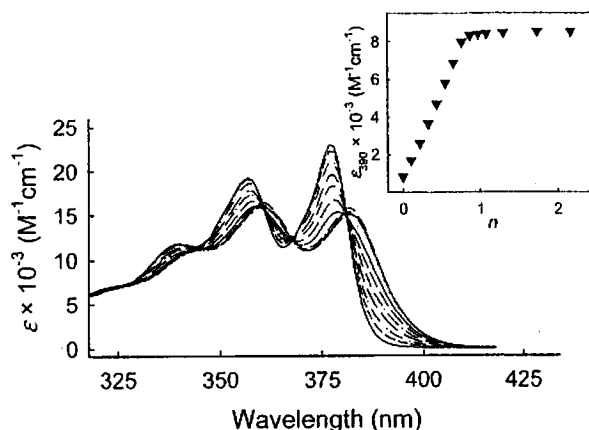


Figure 1. Absorption spectra recorded during the titration of **1** (5×10^{-4} M in MeCN) with Ba(ClO₄)₂ in MeCN. Titration profile is reported in the inset ($n = \text{equiv of Ba}^{2+}/\text{equiv of 1}$).

The reason why Ba²⁺ ions can form sandwich-like [2 +2] complexes

- The hole radii of 15-crown-5 is 1.7~2.2 .
- The atomic radii of Ba²⁺ is 2.70 .

Table V. Ionic Diameters of Cations in Angstrom Units

Group I		Group II		Group III		Group IV	
Li	1.20	Be	0.62				
Na	1.90	Mg	1.30				
K	2.66	Ca	1.98				
Cu(I)	1.92	Zn	1.48				
Rb	2.96	Sr	2.26				
Ag	2.52	Cd	1.94				
Cs	3.34	Ba	2.70	La	2.30		
Au(I)	2.88	Hg(II)	2.20	Tl(I)	2.80	Pb(II)	2.40
Fr	3.52	Ra	2.80				

Li⁺, Na⁺, Mg²⁺, Ca²⁺, (Sr²⁺): too small, [1 + 1] complexes

Rb⁺ and Cs⁺: too large

Although they might be able to form [2 + 2] complexes, the distance of two naphthalenediimides is not enough short (?)

or

Other complexes (ex. metal : ligand = 1 : 3) are more stable (?)

The atomic radii of K⁺ is similar whis the one of Ba²⁺ . . .

Actually it can make sandwich-like complexes whis 15-crown-5 derivatives and they show fluorescence. . .

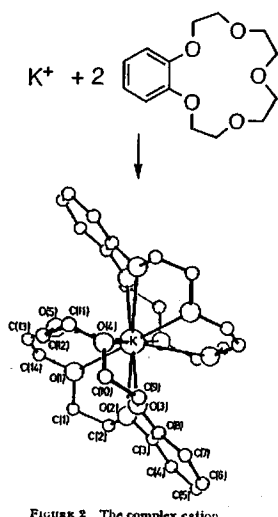


FIGURE 2 The complex cation

J. C. S. Perkin *trans* 2 1972, 1818.

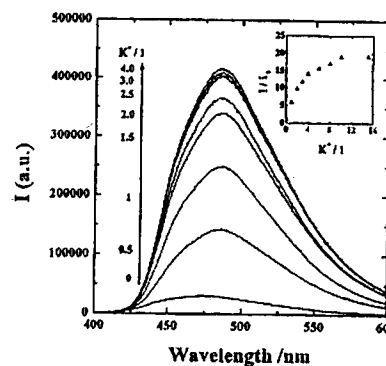
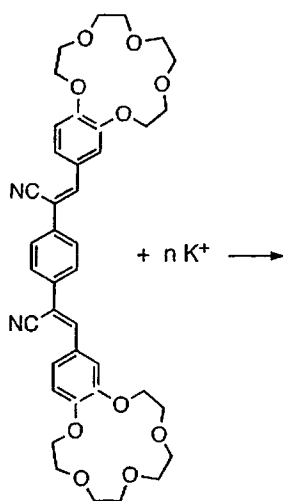


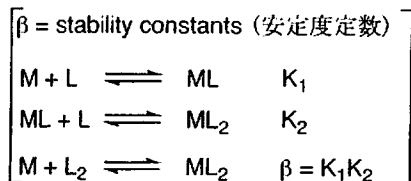
Figure 2. Emission spectra of 1 in the presence of varying amounts of K⁺ in methanolic acetonitrile solutions following 325-nm excitation. Inset: integrated intensity of emission as a function of K⁺ concentration.

JACS 1999, 121, 5599.

In this literature authors doesn't refer to Ba²⁺

Authers (*Org. Lett.*) say 'the [2 + 2] species formed by K⁺ should be reasonably less stable than that formed by Ba²⁺, owing to the different positive charges of the cations'.

$\log \beta = 12.55 \pm 0.59$ (for Ba²⁺) and
 $\log \beta = 10.14 \pm 0.77$ (for K⁺)



Also in the case of K⁺ almost all K⁺ cations make [2 + 2] complexes . . . ??

Conclusion

Interaction between Ba²⁺ and polyethers
 (the factor of self-assembly: electronic interaction)



The distance between naphthalenediimides is shorten

+

The formation of excimers, fluorescence
 (the change in molecular level: aggregation, new function)



Chemosenscer
 (total result)

分子時計

Molecules That Assemble by Sound: An Application to the Instant Gelation of Stable Organic Fluids

Takeshi Naota* and Hiroshi Koori
J. Am. Chem. Soc. 2005, 127, 9324.

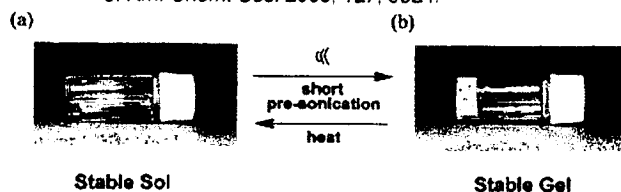


Figure 1. *anti-1a* in acetone at 293 K. (a) A long-lived, stable solution under nonsonication conditions. (b) A gel just after presonication (0.45 W/cm², 40 kHz, 3 s).

Principally sonication cleaves the weak noncovalent interactions between molecules.

Usually it is used to dissolve compounds.
 (except for oversaturated conditions)

ex. N-lauroyl-L-glutamin acid di-n-butylamide (H-bonding gelator)

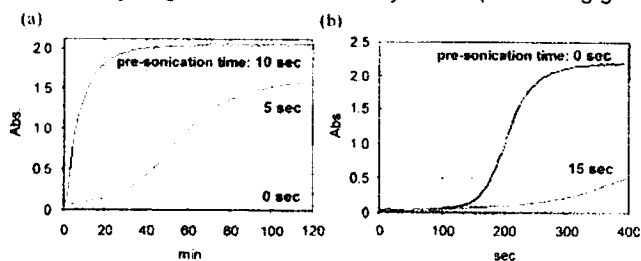


Figure 2. Contrasting gelation profiles of solutions of *anti-1a* (7.23×10^{-3} M (a) and 7.00×10^{-3} M (b)) in acetone at 293 K. evaluated from baseline absorption at 700 nm. Each curve indicates the results just after presonication (0.45 W/cm², 40 kHz, 0–15 s).

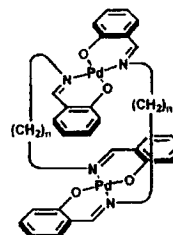
(b) The gelation was considerably retarded.
 The sonication breaks the early stage H-bonded aggregation.

(a) The rate can be controlled over "no gelation" and "instant gelation" simply by tuning the sonication time.

- π - π Stacking (cleavage + regeneration)
- Transform + Aggregation: New Future
- Gelation

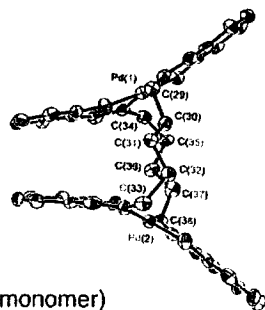
Abstract

An association-inert Pd complex, *anti-1a*, which is stabilized by intramolecular π -stacking interactions, gelatinizes a variety of organic solvents instantly upon brief presonication. This is the first quick, positive, and reversible method for the remote switching of stable sol-gel phase.

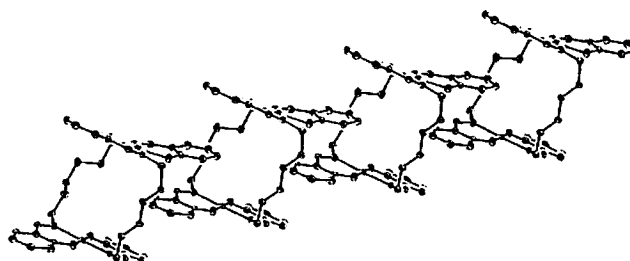


- anti-1 a:* (n = 5)
- b: (n = 6)
- c: (n = 7)
- d: (n = 8)

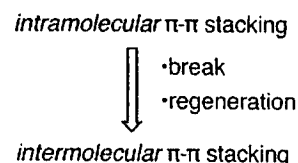
How the Gelation Occur by the Sonication ?
 Structure of monomer(sol) and origomer(gel)



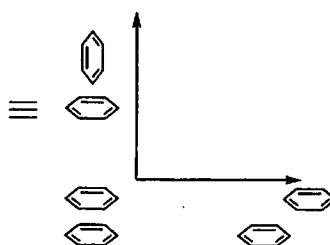
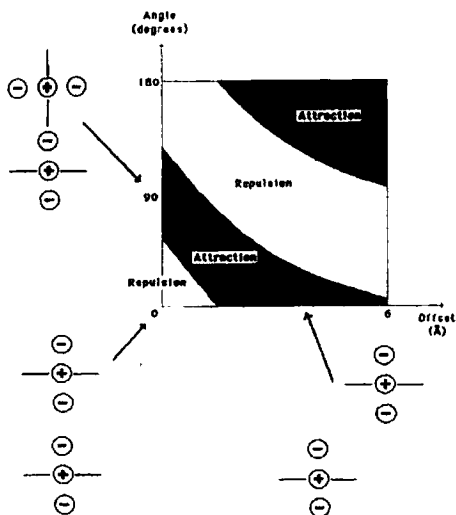
anti-1a (monomer)
 bending structure due to intramolecular π - π stacking



anti-2a (origomer)
 planer structure due to intermolecular π - π stacking



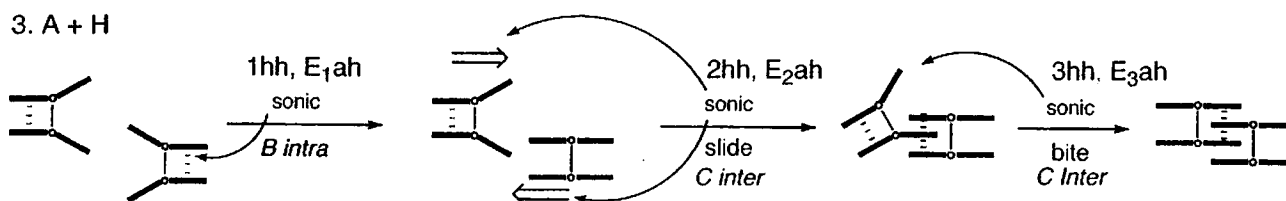
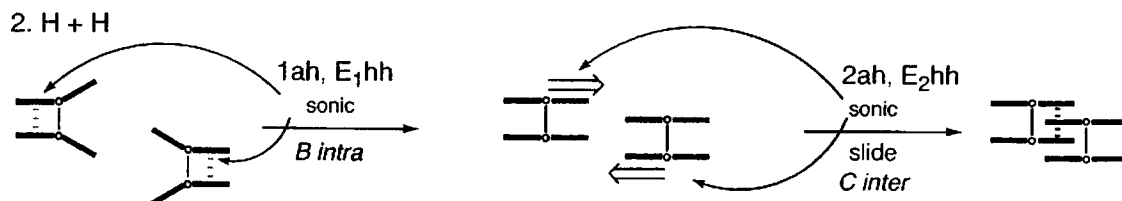
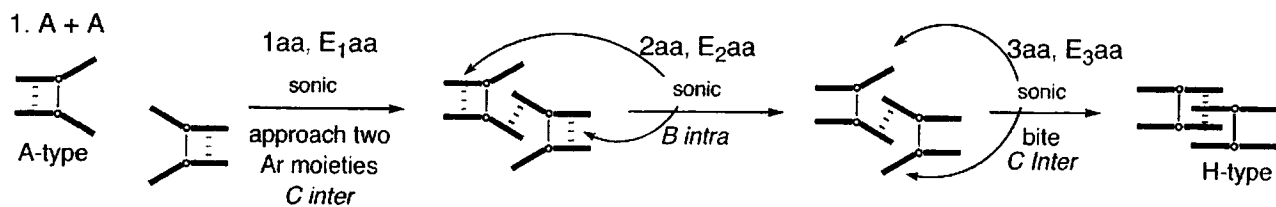
π - π interaction dosen't always stabilize molecules.



Proper relative position is essential.
JACS 1990, 112, 5525.
 Kuma-san's lit. seminar (D1)

Several gelation mechanism can be supposed.

(*B Intra*: break intramolecular π - π stacking
C Inter: construct intermolecular π - π stacking)



- E intramolecular < E intermolecular (frequency)
- E 1 interaction < E 2 interaction (position)

$$E_{1aa} < E_{2aa} \approx E_{1hh} \approx E_{1ah} \times 2 < E_{1aa} + E_{3aa} \approx E_{2hh} \approx E_{2ah} + E_{3ah}$$

- The step having lower E could occur more frequently.
- When external force exists relative ratio (ground state : excited state) should be lower.
- Large E should be shared.

1. A + A: The reaction proceeds along the order of E (small \rightarrow large).
 Remaining the weakest interaction, two steps must proceed.
 At least there are no meaning of sonication in the step 1aa.

2. H + H: The reaction proceeds along the order of E (small \rightarrow large).
 The step having highest E proceed with 1 step.

3. A + H: Provably $E_{3ah} < E_{2ah}$.
 The formation of intermolecular 3-position interaction is shared 2 steps.

← authors' push

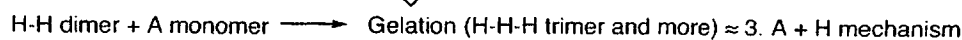
authors comment;
 UV absorbance changes from 235 nm to 268 nm during gelation.

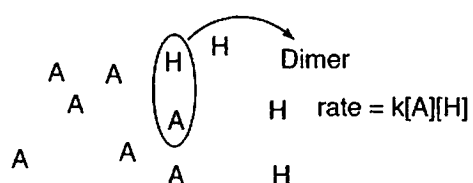
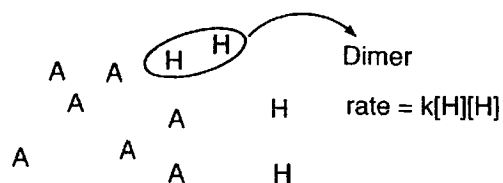
bend planer
 ↓ ↓

[I think this result reflects just structures of monomers and oligomers but not intermediates.]

Although the exact mechanism is now investigated and authors recommend 2. H + H mechanism, I like 3. A + H mechanism.

• After formation of dimers the gelation occurs without the sonication. (authors comment, Figure 2)





Even in the presence of external force
the ratio $[A]:[H]$ is $[A] > [H]$

(no external force $[A] \gg [H]$)

Anyway we must wait experimental evidence to know the correct mechanism.

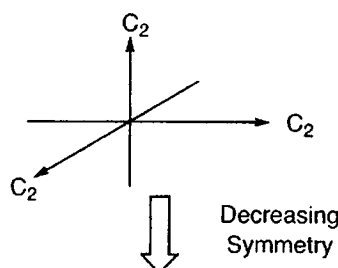
Appendix

Bend Structure in Solution State

1:1 splitting of the ddd signals of NCHaHb occurs at lower temperature (~190K).

|||

The symmetry of molecule decrease.



Three C_2 axis \Rightarrow one pair four equivalent Cs (NCHH) x4

\Rightarrow two pairs four equivalent Hs (NCHa) x4, (NCHb) x4

\Rightarrow two peaks as ddd coupling state

2.87 (ddd, $J = 11.3, 6.8, 4.5$ Hz, 4 H, NCHa)

4.72 (ddd, $J = 11.3, 8.3, 3.8$ Hz, 4 H, NCHb)

One C_2 axis \Rightarrow two pairs two equivalent Cs (NCaHH) x2 + (NCbHH) x2

\Rightarrow four pairs two equivalent Hs (NCaHa) x2 + (NCaHb) x2

+ (NCbHa) x2 + (NCaHb) x2

\Rightarrow four peaks as ddd coupling state
actually two broadening peaks