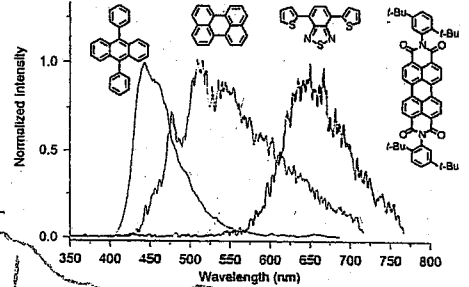
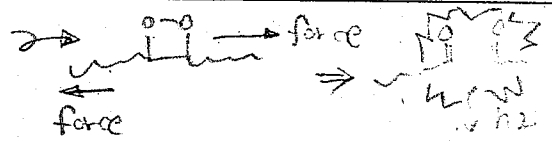
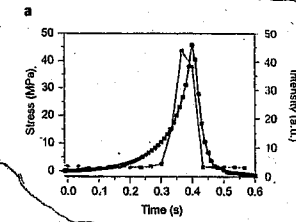
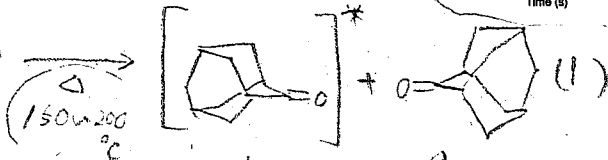
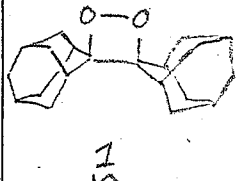


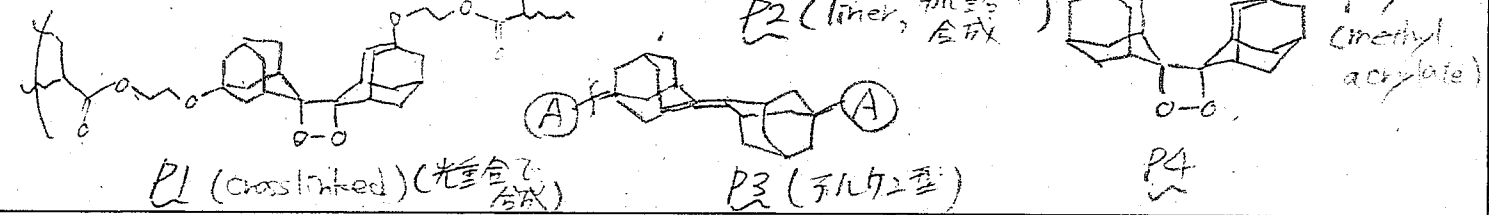
Mechanically Induced Chemiluminescence from Polymers Incorporating a 1,2-Dioxetane Unit in the Main Chain

化学発光 = 化学反応による発光
 工場の分子が基底状態に戻ると、エネルギーを光として放出する現象。
 (例: 1,2-ジオキタン)

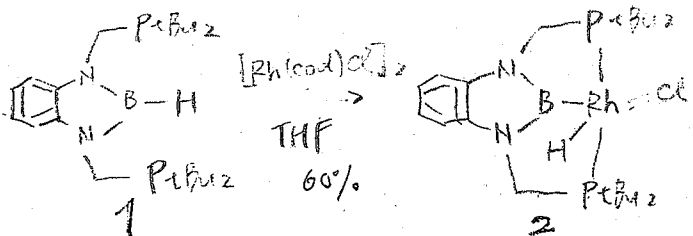


1,2-dioxetane (官能基)
 <This Work>

化学的に結合解裂させて、
 同様の発光をおこなうか?

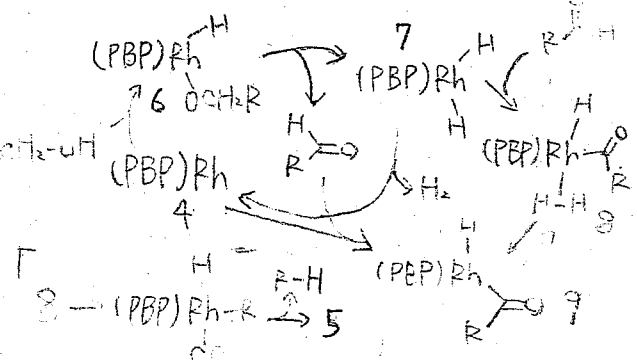
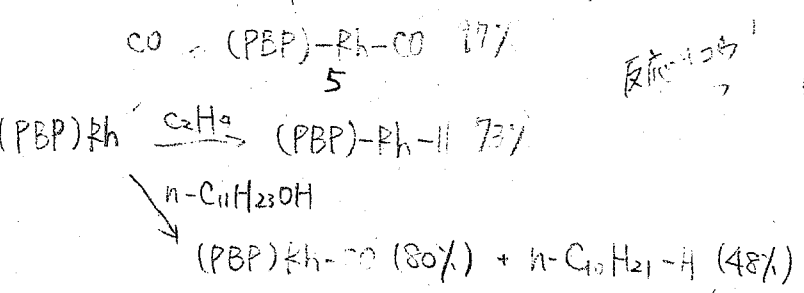
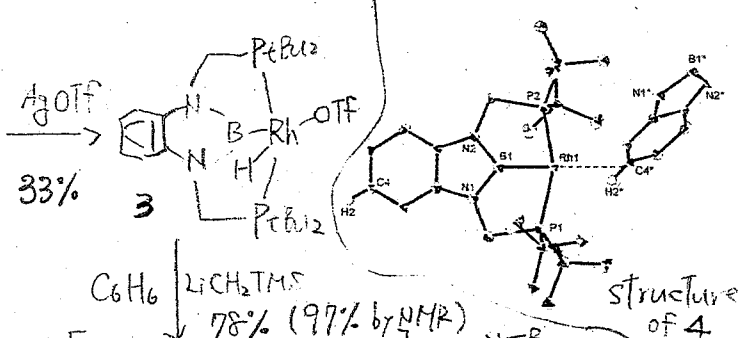


Isolation of a PBP-Pincer Rhodium Complex Stabilized by an Intermolecular C-H σ Coordination as the Fourth Ligand



以前に対応する Ir 錯体を報告している。
 (JACS, 2009, 131, 9201)

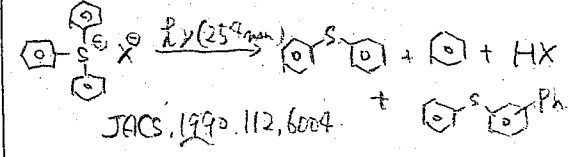
本報告含有 PBP pincer 配位子を用いた
 Rh 錯体の合成。本報告配位子の強
 のドナー性による錯体の安定性を検討。



A photo Lewis Acid Generator (PhLAG): Controlled Photorelease of B(C₆F₅)₃

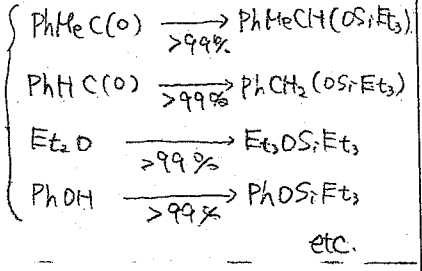
B(C₆F₅)₃: Lewis acid (高)
 揮発性の低い安定な Lewis 酸
 cat. 100°C

photoacid generator (PAGs)

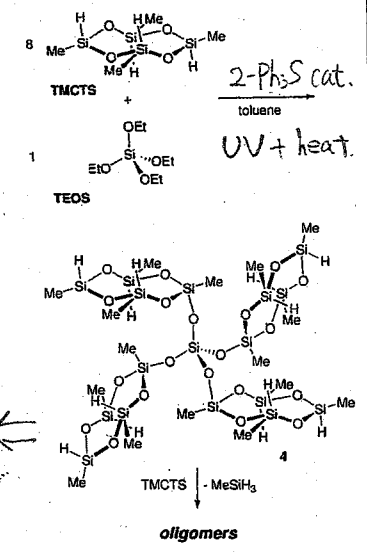
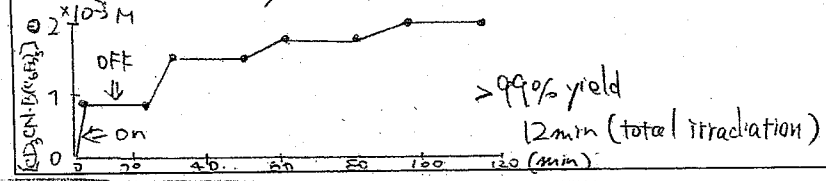
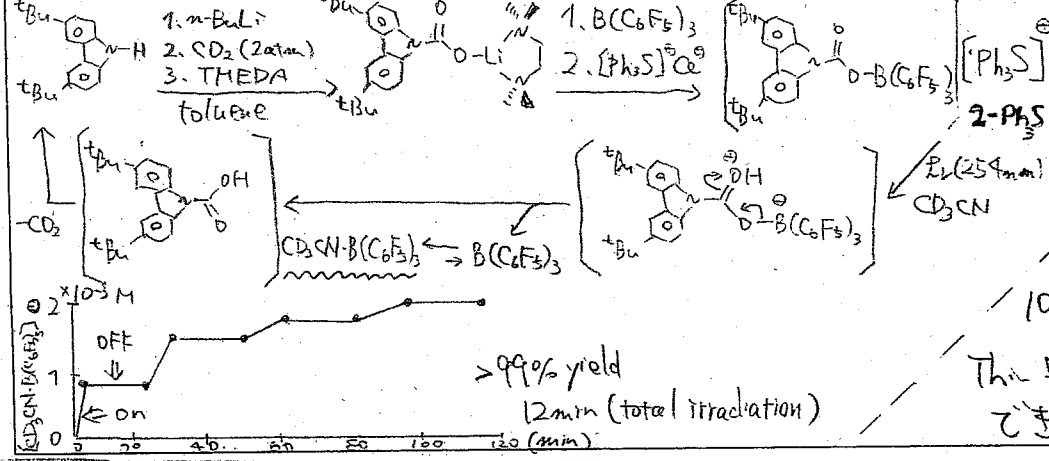


この時 用いた場合 樹脂の 100% 硬化 可能に なる

Photoinduced hydrosilylation reactions:
 $[substrate] + Et_3SiH \xrightarrow[CD_3CN, rt, 15min]{2-Ph_3S (1mol\%), h\nu}$
 Piers-Rubinszajn reaction:
 $R_3SiOR' + HS-R'' \xrightarrow[CH_2Cl_2, rt]{2-Ph_3S (1mol\%), h\nu} R_3SiOR' + H-R''$
 $R_3=Me, R'=H, R''=Et, 100\% (15min)$
 $R_3=Me, R'=Et, PMHS = 100\%$ etc

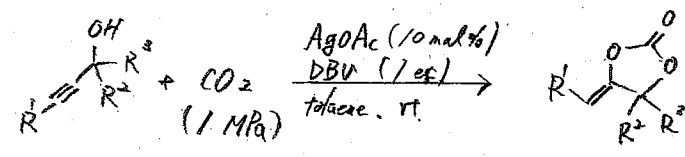


This Work



C-C Bond Formation with Carbon Dioxide Promoted by a Silver Catalyst

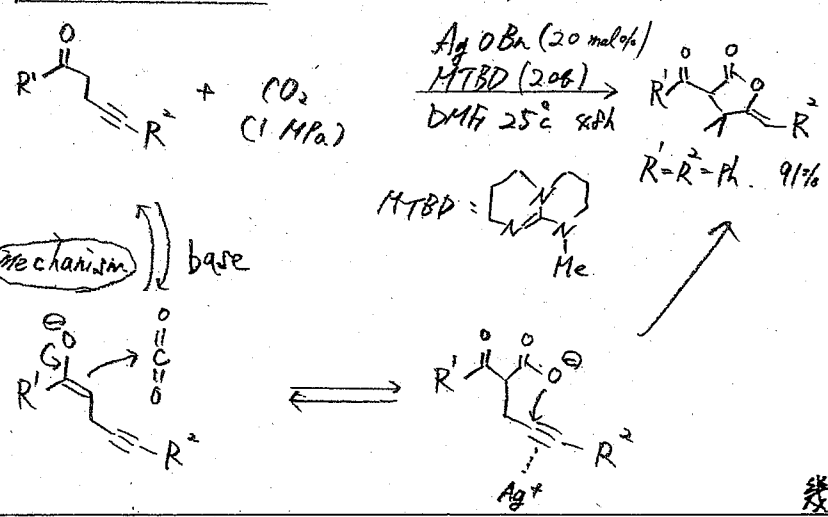
previous work



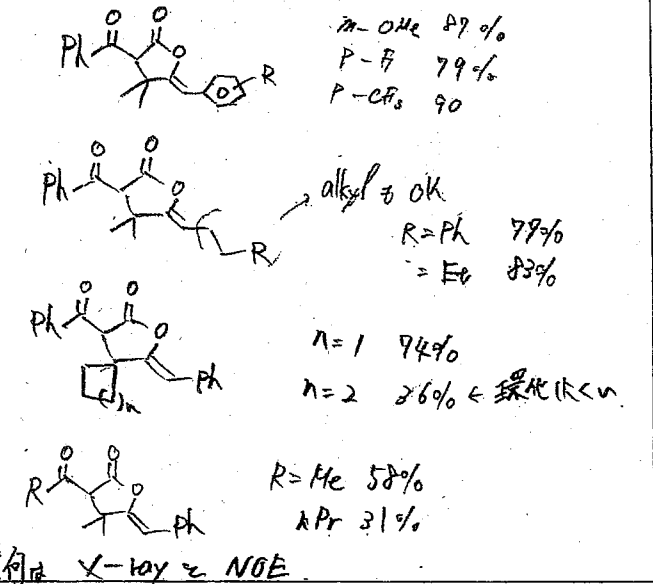
π -Lewis acid

Ag a 100% 進行 (Pd(OAc)₂, Cu(OH)₂, AuCl, AuCl₃ ≠ 90%)
 base は DMAP. Hinrich base 程度は 9X

present work

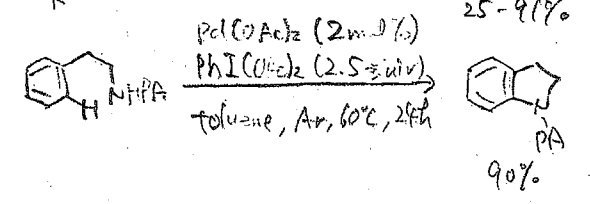
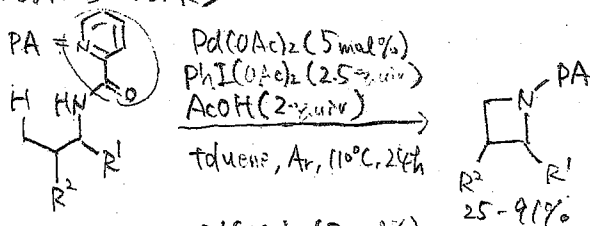


scope (time: 8h ~ 250h)

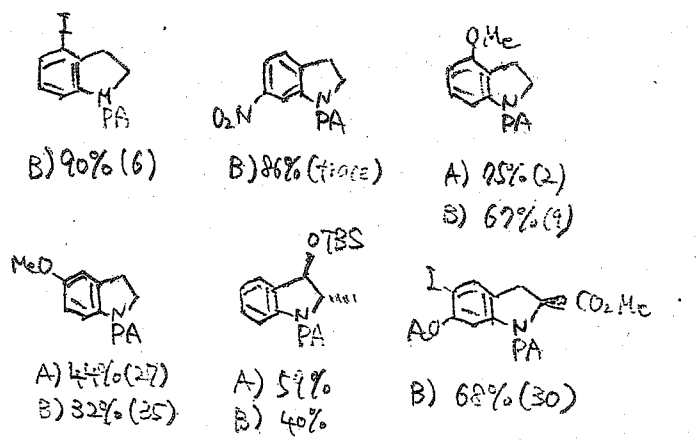


Improved Protocol for Indoline Synthesis via Palladium-Catalyzed Intramolecular C(sp³)-H Amination.

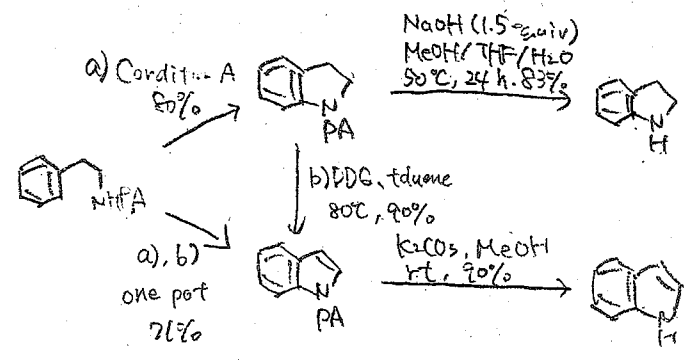
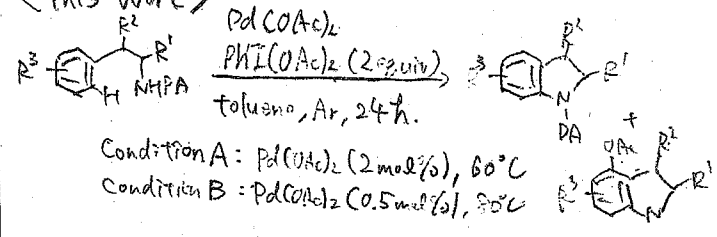
<Previous Work>



Chen, G. JACS, 2012, 134, 3-6.



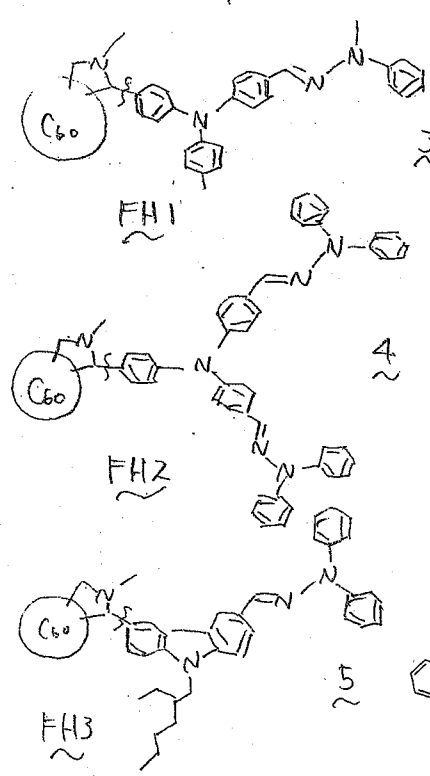
<This Work>



Vytautas Getautis	Kaunas University of Technology (Lithuania)	Chem. Asian J. 2012, 7, 614.	M2 Kawai
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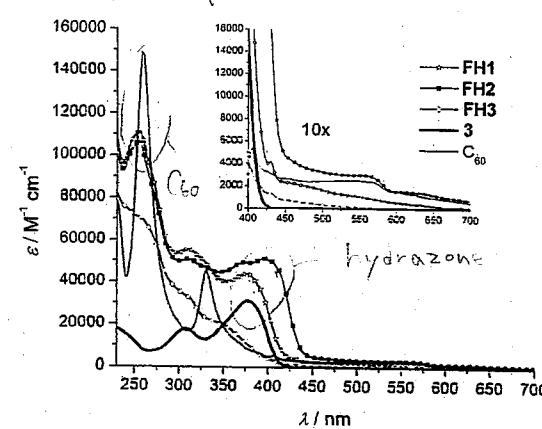
Air-Stable, Narrow-Band-Gap Ambipolar C₆₀ Fullerene-Hydrazone Hybrid Materials

Fullerene-Hydrazone Materials

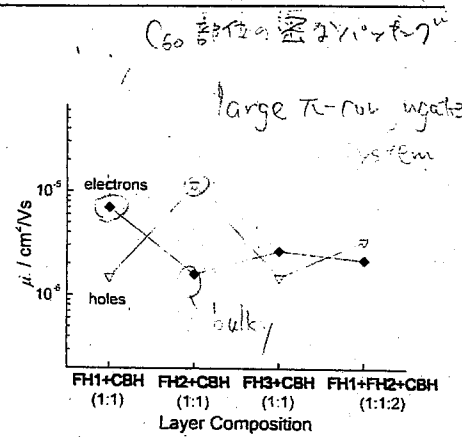


Ambipolar 有機電導材料の開発を目的とした。

3. Absorption spectra



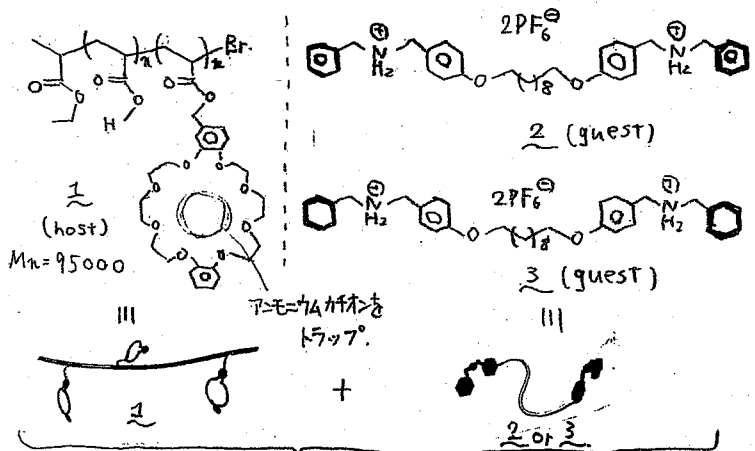
Entry	E _{1/2red} vs. Fc [V]	E _{1/2ox} vs. Fc [V]	E _g ^{CV} [eV]	E _g ^{opt} [eV] ^(b)	I _p [eV] ^(c)	E _{HOMO} [eV] ^(d)	E _{LUMO} [eV]
3	-	0.20	-	2.93	5.40	-5.00	-2.07 ^(e)
4	-	0.24	-	2.76	5.28	-5.04	-2.28 ^(e)
5	-	0.34	-	2.93	5.40	-5.14	-2.21 ^(e)
FH1	-1.12	0.22	1.34	-	5.21	-5.02	-3.68
FH2	-1.11	0.25	1.36	-	5.26	-5.05	-3.69
FH3	-1.12	0.36	1.48	-	5.41	-5.16	-3.68



C₆₀ と hydrazone の相互作用は強くなる。

 今回合成した化合物は、2.0 eV 以下の条件下で、電荷移動体としての性質を示した。

Self-Healing Supramolecular Gels Formed by Crown Ether Based Host-Guest Interactions



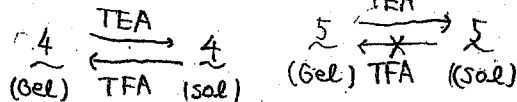
from 1 + 2 → Gel 4 (Ph)
 from 1 + 3 → Gel 5 (reflux, 30 days)
 solvent: CHCl₃/MeCN (v/v=1:1)

3は CyHex基が高いため、厳しい条件が必要!

(F定) ¹H NMR + Dibenzo[24]crown-8 + Dibenzylammonium salt 間の錯体化で見られたのと同傾向を示す。

(物性) ①粘度 Gel 5 > Gel 4 > polymer 1

②刺激応答性



→ 末端置換基に由来する性質が発現。

Gel 4 (Ph): ポリマ-鎖間の架橋が弱い (可逆)

Gel 5 (CyHex): ポリマ-鎖間の架橋が強い (不可逆)

(自己修復力)



Gel 4 or 5 (上面)

弾性率の評價

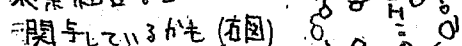
Gel 4 (Ph): 30秒以内 = 傷つた前の状態の95%に戻す

Gel 5 (CyHex): 10,000% 伸びた後10秒以内 = 100% 戻す

★ 自己修復機構の違い。

Gel 4 → 単純な Host-Guest 機構

Gel 5 → 水素結合など



Highly Enantioselective Chlorination of β-Keto Esters and Subsequent S_N2 Displacement of Tertiary Chloride: A Flexible Method for the Construction of Quaternary Stereogenic Centers

• S_N2 反応は立体化学の完全な反転を伴って起きる。

もし、S_N2 反応が起きるならば、光学活性な

第三級キリドは、第四級の立体中心を持つ

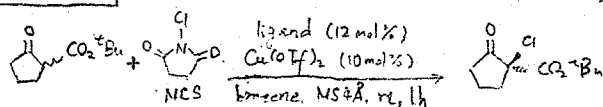
キルな分子を調整する際の中継剤として使用できる。

問題点

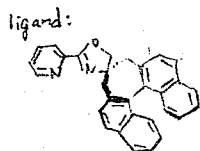
• 第三級キリドは通常 S_N2 反応が起きない

• 比較的少数しか第三級キリドを高エ+24才選択的に合成する例が報告されておらず、基質適用範囲が狭い

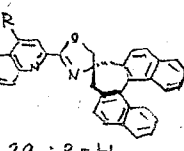
This Work



entry	ligand	yield (%)	ee (%)
1	1	93	78
2	2a	97	95
3	2b	96	95



SPRMOx 1



2a: R=H
 2b: R=OMe

1.5eq NCS was used

Enantioselective Chlorination

n	yield (%)	ee (%)
n=1	90%	95% ee
n=2	92%	98% ee
n=3	92%	98% ee

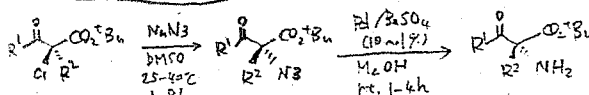
R	yield (%)	ee (%)
R=Me	99%	95% ee
R=Bn	94%	92% ee
R=allyl	96%	94% ee
R=CH ₂ CN	84%	95% ee
R=CH ₂ CO ₂ Ph	90%	91% ee

21 examples

92~99% yields
 80~98% ees

キリド+キリド、二重結合、キリド反応にも対応。

S_N2 Substitution

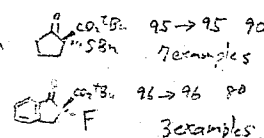


n	yield (%)	ee (%)
n=1	95% ee → 95% ee	85 (91) % yield
n=2	98% ee → 98% ee	92 (95) % yield

condition

RSH, Et₃N, CH₂Cl₂, rt, 12h

CF, 18-crown-6, CH₂CN, rt, 12h



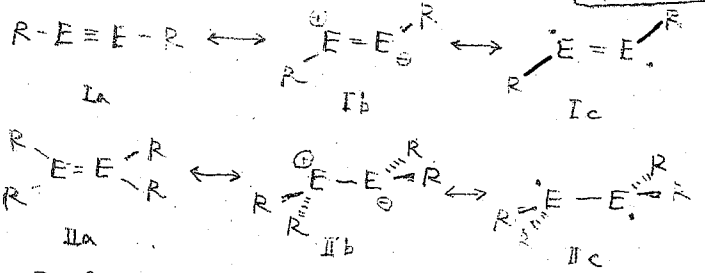
10 examples

95→95 90
 7 examples

96→96 80
 3 examples

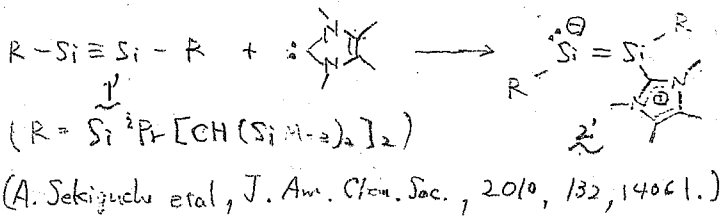
Reversible Base Coordination to a Dicylene

alkene and alkyne analogues of heavier G14 elements

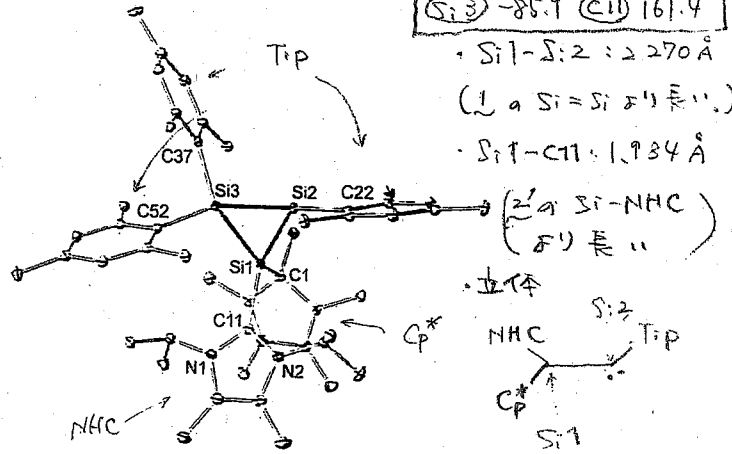
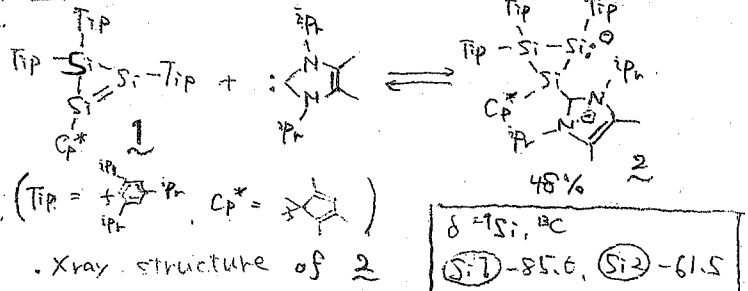


(E = Si, Ge, Sn, Pb; R = sterically demanding substituent)

polar disilyne-NHC complex

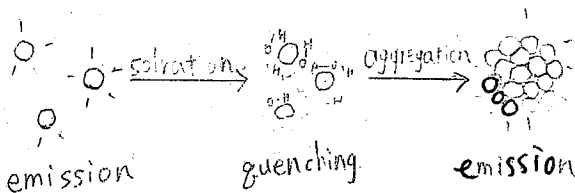


This Work

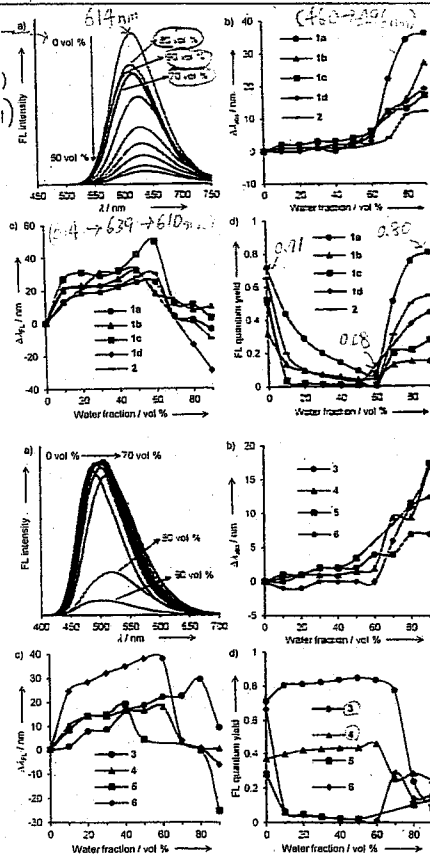
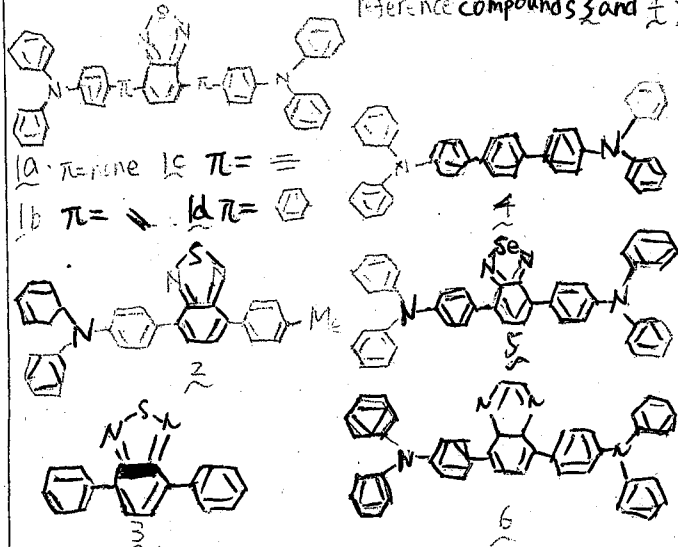


Red-Light-Emitting System Based on Aggregation of Donor-Acceptor Derivatives in Polar Aqueous Media

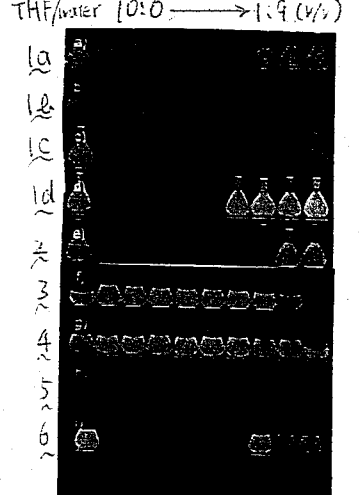
This work



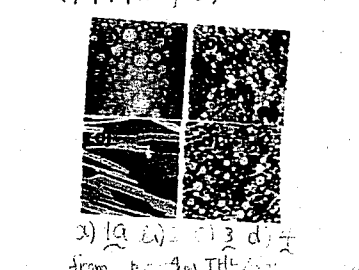
Structures of dyes 1a-d, 2, 5 and 6, and corresponding reference compounds 3 and 4



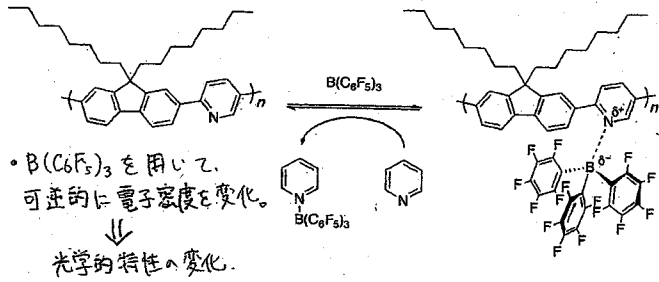
Fluorescence images



AFM images



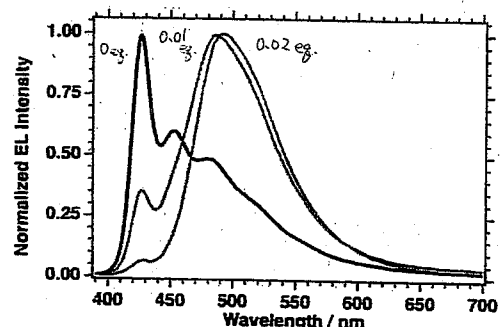
Color Tuning in Polymer Light-Emitting Diodes with Lewis Acids



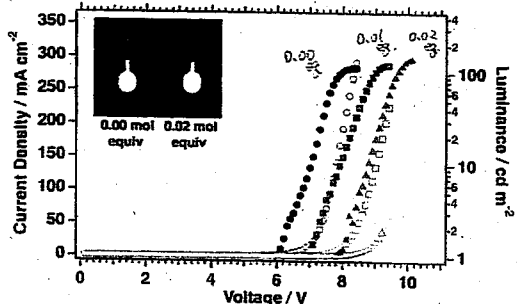
① solution (toluene) と film で Abs. と PL (λ_{ex}=390nm) を測定
いずれの場合も...
B(C₆F₅)₃ の添加量増加に伴い、長波長シフト。

- solution (5 × 10⁻⁶ M)
 - [Abs.] 1.3 eg. の B(C₆F₅)₃ 添加で変化が収束。
 - [PL] B(C₆F₅)₃ 添加でスロートルが大幅に broad (450~600nm) 添加量は量子収率には影響せず (φ_f=0.69~0.71)
- film
 - [Abs.] 0.7 eg. の B(C₆F₅)₃ 添加で変化が収束。
 - [PL] スロートルが大幅に broad (450~700nm) 0.1 eg. の添加で変化が収束。 (φ_f=0.20→0.44)

② EL測定
デバイス中の発光素子として利用



• B(C₆F₅)₃ の添加量の増加に伴い、徐々に red-shift した。
• 添加量 0.02 eg. をこえると、劇的な変化は無く、少しだけ red-shift。

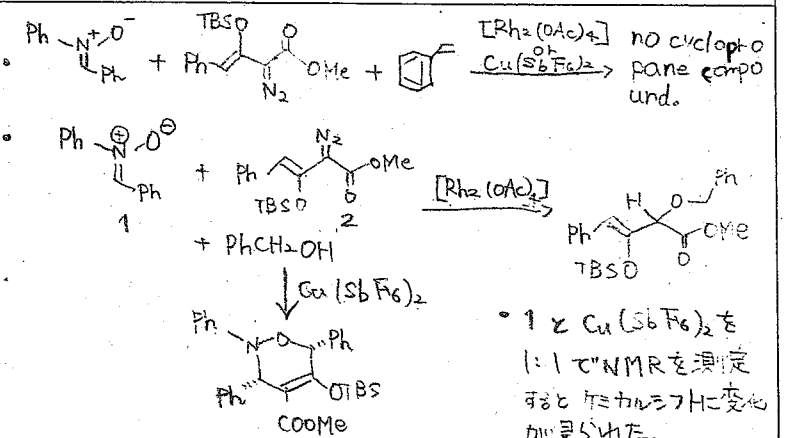
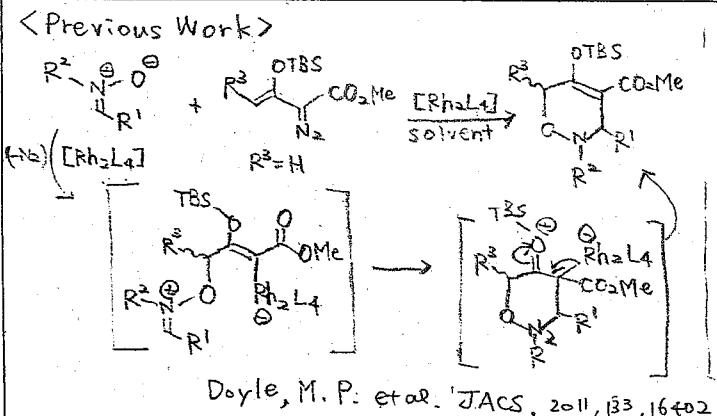


• B(C₆F₅)₃ の添加量が増加すると、高電圧での HOMO (eV) ↓
0.00 eg. -5.74
0.01 eg. -5.86
0.02 eg. -5.92

Fig. デバイス中の電流-電圧特性 (○, □, △) 発光-電圧特性 (●, ■, ▲)

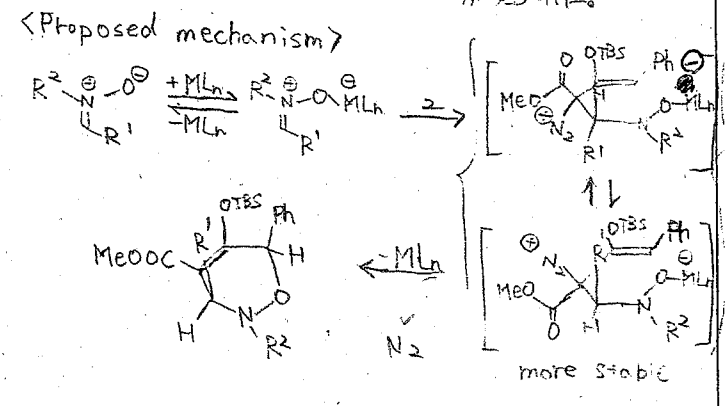
• 添加量が増えれば、正孔輸送材料: PVK の HOMO (-5.9 eV) とのエネルギーギャップが小さくなり、ホールの輸送が促進され、高電圧での効率向上が期待される。

Rhodium (II)- and Copper (II)-Catalyzed Reactions of Enol Diazoacetates with Nitrones: Metal Carbene versus Lewis Acid Directed Pathways



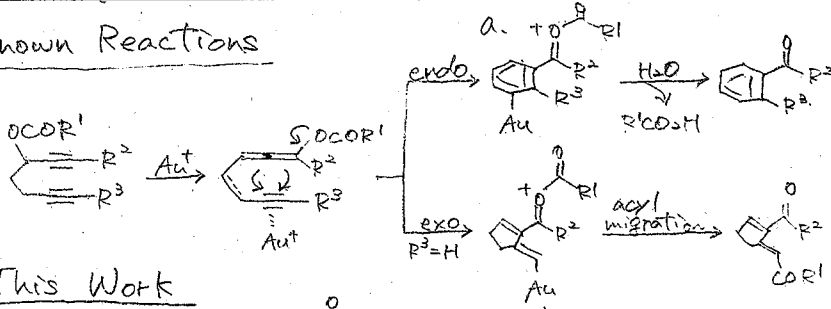
< Present Work >

Entry	ML _n	t	yield (%)	d.r. (syn/anti)
1	[Rh ₂ (OAc) ₄]	1h	none	25:1
2	[Cu(MeCN) ₄](PF ₆) ₆	24h	31	Metal Carbene X
3	Zn(OTf) ₂	24h	6	⇒ Lewis Acid O
4	Cu(OTf) ₂	24h	54	?
5	AgSbF ₆	5min	29	?
6	Cu(SbF ₆) ₂	5min	95	?



Gold-Catalyzed Cascade Cyclizations of 1,6-Diynyl Carbonates to Benzolo[6,5]fluorenes

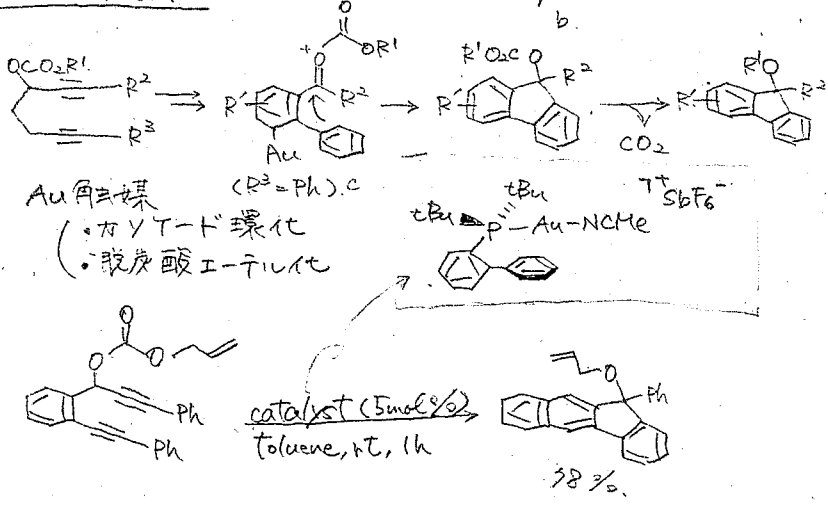
Known Reactions



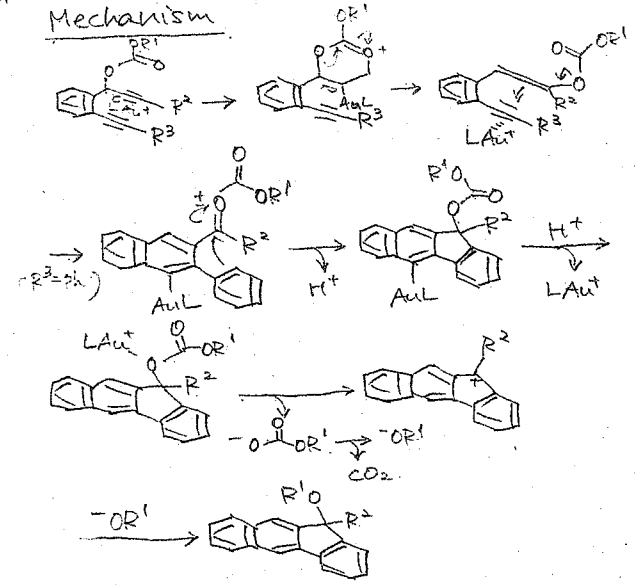
SCOPE

R₁: allyl, alkyl, benzyl 66-85% yield
 R₂: C_6H_5 , $\text{C}_6\text{H}_4\text{R}$ 50~73% yield
 tBu , tBu , H
 69% 76% 47%
 R₃: *p*-MeC₆H₄ 74%, *p*-BrC₆H₄ 34%

This Work



Mechanism

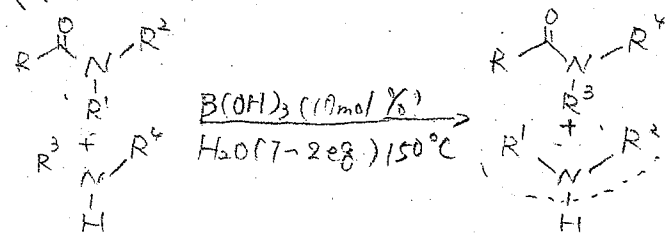


Thank Boris M. Agreus (CNRS (フランス国立科学研究所) France) *Organic Letters* 10 (2012) 3030-3032 B4 黒田

Boronic Acid
 A Highly Efficient Catalyst for Transamidation of Carboxamides with Amines

不活性なアミドの交換反応は...
 ⇒ 7級アミドの報告の対

<This Work>

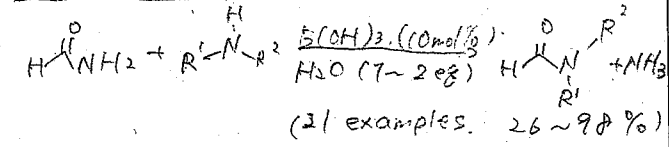


溶媒: Et_2O > 芳香族 > 極性非プロトン性溶媒 > 水
 (H₂O, *p*-TOL) (DMF, DMSO) (PIU-11)
 ⇒ 溶媒を用いる 添加剤は H₂O
 B(OH)₃, H₂O の "5500" の付加は 任意

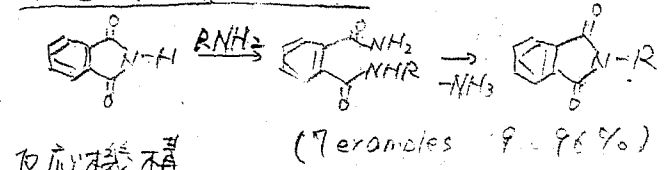
基質展開

R¹=H 脂肪族 > 芳香族 (71~90%) (40%) (2例 3例 5例)
 9 examples. 2 examples
 R²=H 立体障害のないアミド > 立体障害のあるアミド
 BnNH₂ > BnCH₂NH₂
 3例 2例 = 71% 42%

N-アミド化



N-置換アミド化の合成



反応機構

