

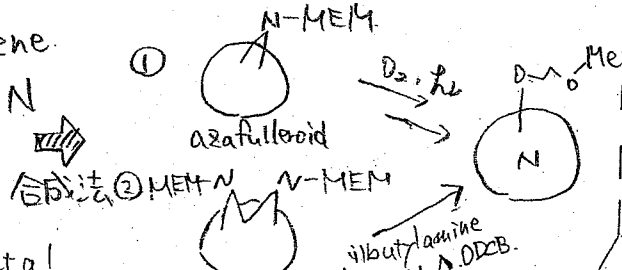
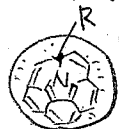
Fullerenes Doping: Preparation of Azafullerene C₅₉NH and Oxafulleroids C₅₉O₃ and C₆₀O₄

Doped fullerenes



X = N, O, As, P, S, B } 11 すべて Gas phase で 合成. Mass の 変化 同様.

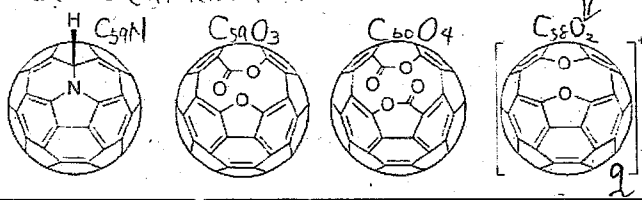
Azafullerene



- ① Wudl, F. et al Science, 1995, 269, 1554
- ② Hirsch, A. et al Chem. Commun., 1996, 1421

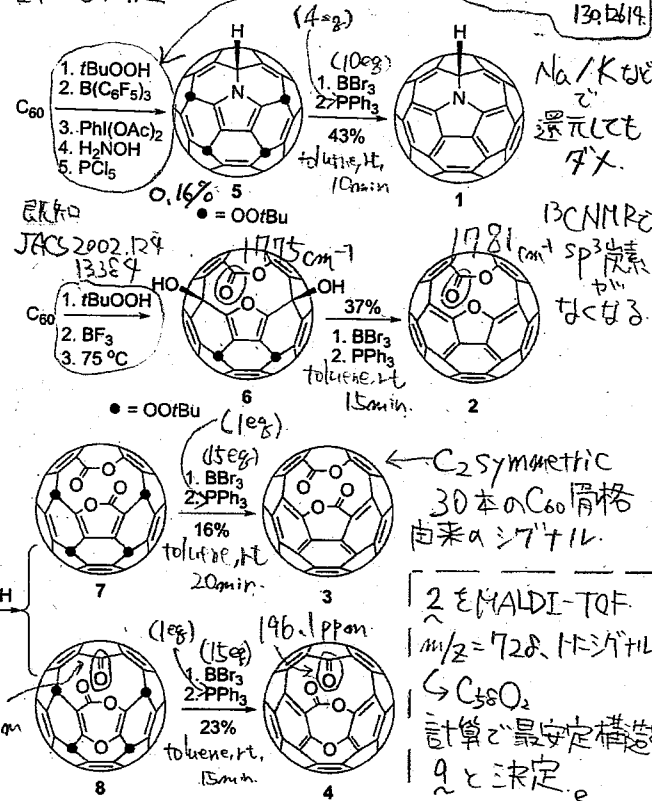
This Work

azafullerene 新規合成法 & oxafulleroid 合成



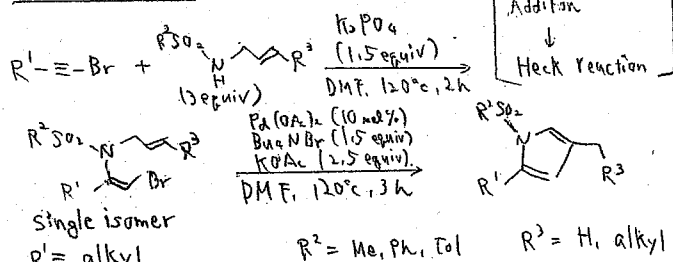
合成と同定

既知 JACS, 2008 130, 1619

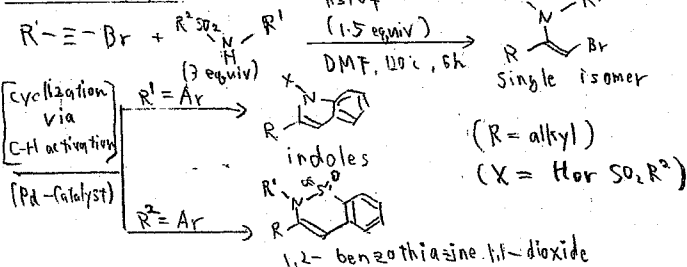


Facile Preparation of Indoles and 1,2-Benzothiazine 1,1-Dioxides: Nucleophilic Addition of Sulfonamides to Bromoacetylenes and Subsequent Palladium-Catalyzed Cyclization

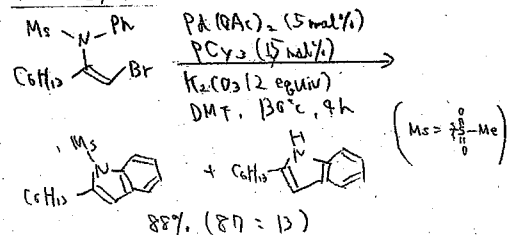
Previous work



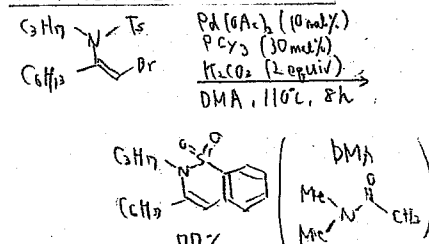
Present work



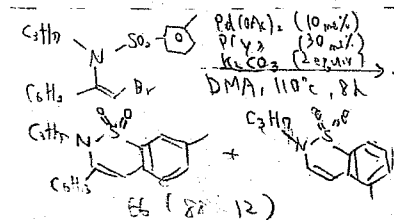
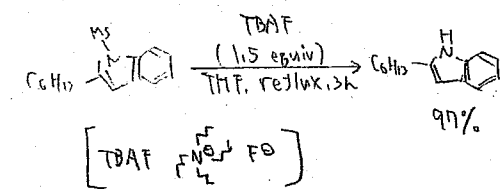
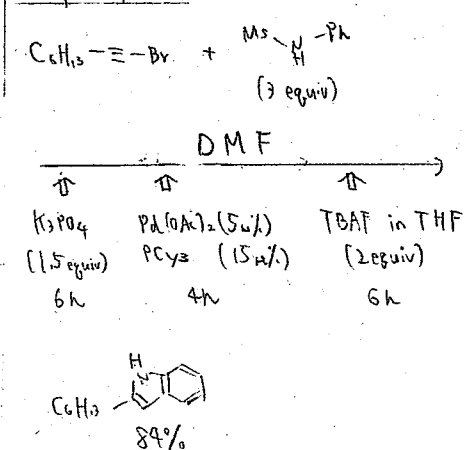
Indole synthesis



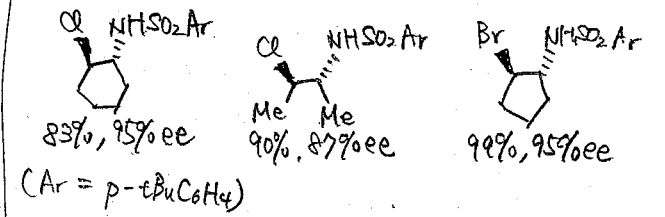
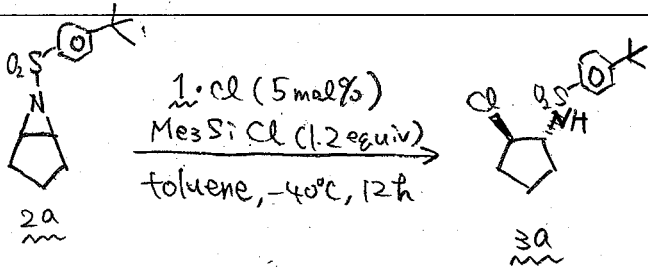
1,2-benzothiazine 1,1-dioxide



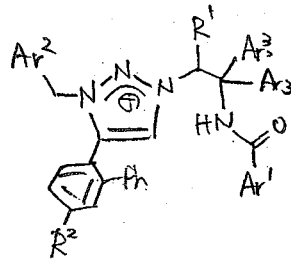
One-pot synthesis



Catalytic Asymmetric Ring Opening of Meso and Terminal Aziridines with Halides Mediated by Chiral 1,2,3-Triazolium Silicates



| 1 | % yield | % ee |
|-----------------|---------|------|
| 1a | 35 | 65 |
| 1b | 24 | 81 |
| 1d | 42 | 87 |
| 1g | 31 | 95 |
| 1g ^a | 85 | 95 |



| | Ar ¹ | Ar ² | Ar ³ | R ¹ | R ² |
|----|---|---|-----------------------------------|-----------------------|-----------------|
| 1a | Ph | Ph | Ph | CH ₂ Ph | H |
| 1b | p-NO ₂ C ₆ H ₄ | Ph | Ph | CH ₂ Ph | H |
| 1d | p-NO ₂ C ₆ H ₄ | p-CF ₃ C ₆ H ₄ | p-ClC ₆ H ₄ | CH ₂ Ph | H |
| 1g | p-NO ₂ C ₆ H ₄ | p-CF ₃ C ₆ H ₄ | p-ClC ₆ H ₄ | CH ₂ iPr | CF ₃ |
| 1f | p-NO ₂ C ₆ H ₄ | p-CF ₃ C ₆ H ₄ | p-ClC ₆ H ₄ | CH ₂ c-Hex | CF ₃ |

²⁹Si NMR
 1a: Cl + Me₃SiCl
 (in toluene-d₆)
 ⇒ single peak TBAF + TMSCl
 at δ = 6.6 ppm

^a with Me₃Si(OH)
 (1 equiv)

Yutaka Matuo
 Eiichi Nakamura

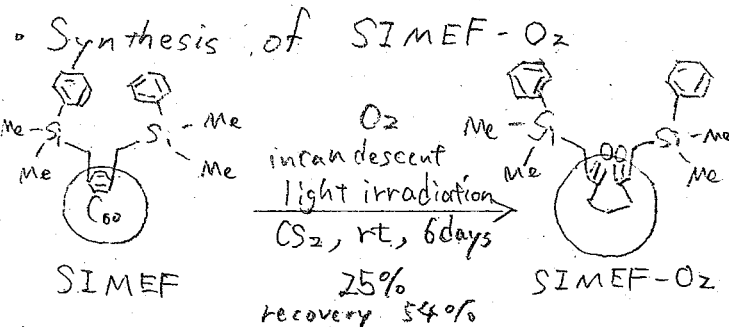
The University of Tokyo (Japan)

Chem, Commun. 2012, 48, 3878.

M2 Kawai

Deterioration of bulk heterojunction organic photovoltaic devices by a minute amount of oxidized fullerene

BHJ型太陽電池の実用化に向け、重要な課題の一つである酸化によるデバイス劣化についての研究。



PCBMではこのような酸化反応は進行しない。

• UV-Vis spectra

SIMEF-O₂では、SIMEFに見られる450nmの吸収極大が消失。

• 溶解性

SIMEF-O₂の各種溶媒に対する溶解性は、SIMEFに比べ良好。

BHJ-Filmでは、SIMEF-O₂を添加することにより、p型のP3HT由来である600nm付近の吸収が減少する。

- electron mobility
 SIMEF-O₂ = 5.8 × 10⁻⁴ cm² V⁻¹ s⁻¹
 SIMEF = 8.0 × 10⁻³ cm² V⁻¹ s⁻¹
- LUMO level

| Compound | E _{1/2} ^{red1} /V | E _{1/2} ^{red2} /V | E _{1/2} ^{red3} /V | LUMO level ^b /eV |
|----------------------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------------|
| SIMEF-O ₂ | -0.96 | -1.53 | -2.11 | -3.84 |
| SIMEF | -1.06 | -1.63 | -2.23 | -3.74 |
| PCBM | -1.00 | -1.59 | -2.21 | -3.80 |

• OPV performance 表面の粗さ (AFMで測定)

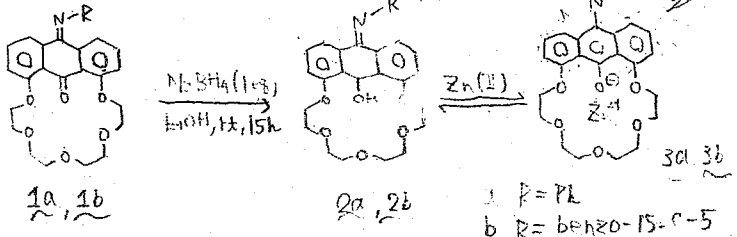
| Device | SIMEFO ₂ x [%] | Ra/nm | V _{oc} /V | J _{sc} /mA cm ⁻² | FF | PCE [%] |
|--------|---------------------------|-------|--------------------|--------------------------------------|------|---------|
| 1 | 0 | 9.8 | 0.67 | 9.2 | 0.52 | 3.2 |
| 2 | 1 | 6.8 | 0.64 | 7.5 | 0.40 | 1.9 |
| 3 | 10 | 4.6 | 0.60 | 6.6 | 0.27 | 1.1 |
| 4 | 25 | 3.8 | 0.36 | 2.4 | 0.22 | 0.19 |
| 5 | 50 | 3.0 | 0.19 | 0.21 | 0.23 | 0.0093 |
| 6 | 75 | 3.6 | 0.16 | 0.15 | 0.24 | 0.0055 |
| 7 | 100 | 2.8 | 0.17 | 0.31 | 0.21 | 0.011 |

SIMEF-O₂の電子特性以外に、高い溶解性も電荷分離、電荷移動の原因となり、PCEが低下している。

Zinc (II) Mediated Imine – Enamine Tautomerization

Zn(II) を選択的に取り込む蛍光センサーの開発
 → Zn(II) の生物学的役割の解明において重要

This Work



2の同定 IR: C=O (1670 cm⁻¹) の消失, C-N (1650-1670 cm⁻¹) の出現
 OH (3400-3500 cm⁻¹) の出現.

¹H NMR, ¹³C NMR, ESI-MS, X線結晶構造解析

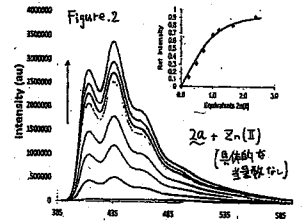
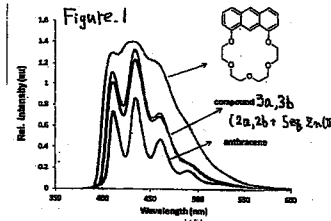
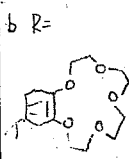
3の同定 ESI-MS: 729 m/z MZn⁺

蛍光 アントラセンと同じ波長の光を示す (Figure. 1)

Zn(II) の定量実験によって 1:1 の complex の

形成が判明 (Figure. 2)

平衡定数 $K = 1.0 \times 10^5 (\pm 10\%) M^{-1}$



Zn(II) に対する蛍光センサーとしての評価

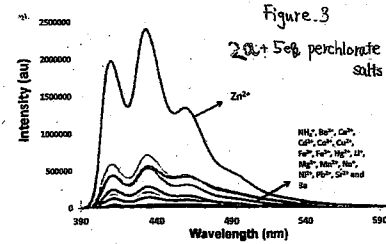


Fig. 3 他の金属イオンとの比較

Fig. 5 の他金属イオンがある場合には, Zn(II) 添加の時よりも, 蛍光強度が上がることは言及されず

Fig. 4 430nm の相対的な蛍光強度の比較

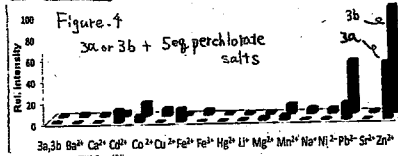
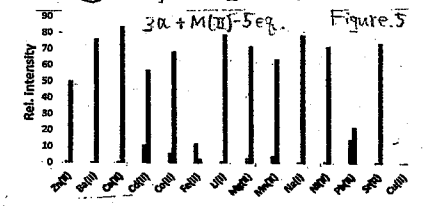
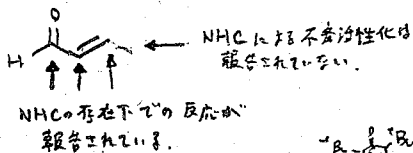


Fig. 5 他の金属イオン共存下での蛍光強度 (左) Zn(II) なし (右) Zn(II) 1 eq.

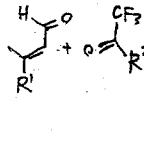


Oxidative α -Addition of Enals to Trifluoromethyl Ketones: Enantioselectivity Control via Lewis Acid/N-Heterocyclic Carbene Cooperative Catalysis

エナルのエタン骨格選択的な C-H 活性化



Scope



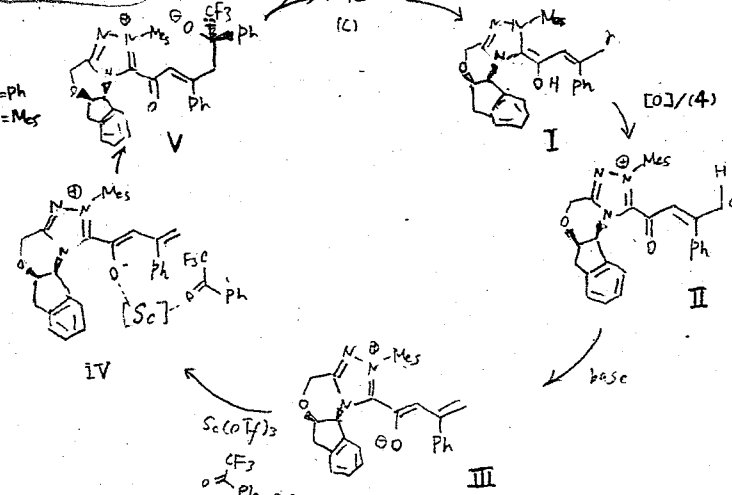
Enal

Ketone

| | | | |
|-------------------------|------------------|------------|---------|
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 61% | ee: 93% |
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 21% | ee: 93% |
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 52% | ee: 80% |
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 13% | ee: 80% |
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 64% | ee: 60% |
| Enal: 2-methyl-2-butene | Ketone: Ph-CO-Me | Yield: 20% | ee: 60% |

| entry | NHC | Lewis acid | base | yield (%) | ee (%) |
|-------|-----|---|---------------------------------|-----------|--------|
| 1 | A | - | CS ₂ CO ₃ | 70 | - |
| 2 | B | - | CS ₂ CO ₃ | 50 | 21 |
| 3 | C | - | CS ₂ CO ₃ | 63 | 29 |
| 4 | B | Sc(O Tf) ₃ | CS ₂ CO ₃ | 52 | 64 |
| 5 | C | Sc(O Tf) ₃ | CS ₂ CO ₃ | 64 | 73 |
| 6 | C | Sc(O Tf) ₃ | K ₂ CO ₃ | 72 | 88 |
| 7* | C | Sc(O Tf) ₃ | K ₂ CO ₃ | 84 | 91 |
| 8* | C | Sc(O Tf) ₃ / Ms(O Tf) ₂ | K ₂ CO ₃ | 81 | 94 |

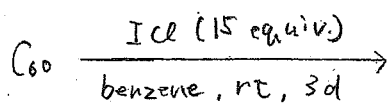
Postulated Pathway



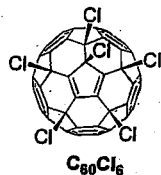
* 0.15 mmol of 1a at 0°C

Highly selective reactions of $C_{60}Cl_6$ with thiols
for synthesis of functionalized [60]fullerene derivatives.

① Synthesis of Chlorofullerene ($C_{60}Cl_6$)



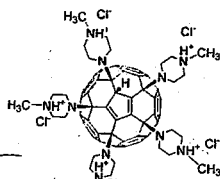
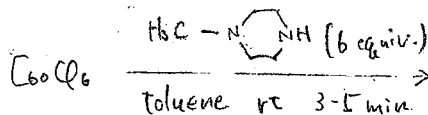
< J Chem Soc Chem Commun.,
1993, 1230 >



100%

② Previous Work

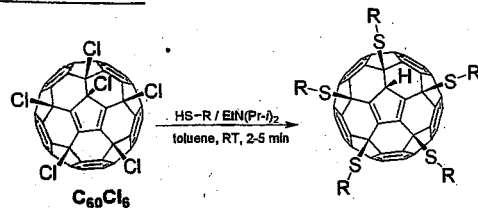
< Chem. Commun. 2012 4P. 5481 >



> 95% yield

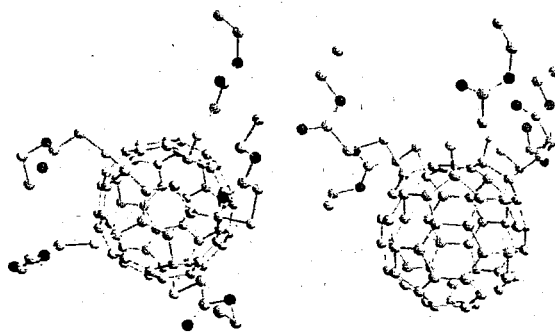
- High solvility in water ($>300 \mu\text{g/mL}$)
- The first easily water-soluble fullerene derivative.

③ This Work



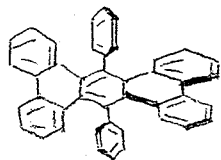
- R = (a) $-C_{12}H_{25}$, 98% (b) $-CH_2COOMe$, 80%
(c) $-CH_2COOEt$, 92% (d) $-CH_2CH_2NH\text{Boc}$, 86%
(e) $-CH_2COOH$, 87% (f) $-(CH_2)_{10}COOH$, 84%

④ X ray molecular structure (c)



Synthesis and Structure Characterization of a Stable Nonatwistacene

< Twistacene >

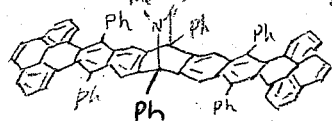
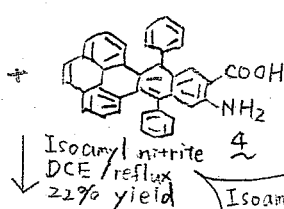
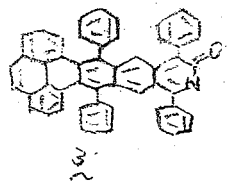


non-bonding interactions
between substituents (π-π)

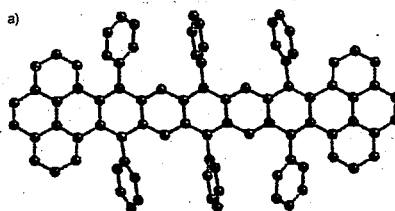
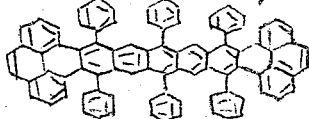
twist

J. Am. Chem. Soc. 1987, 109, 4660.

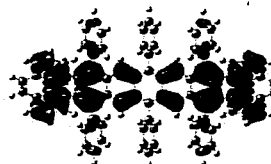
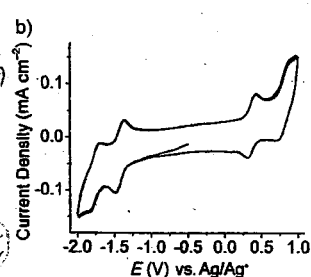
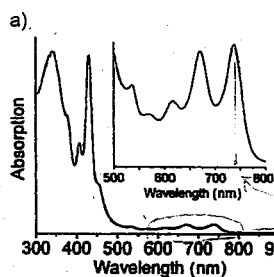
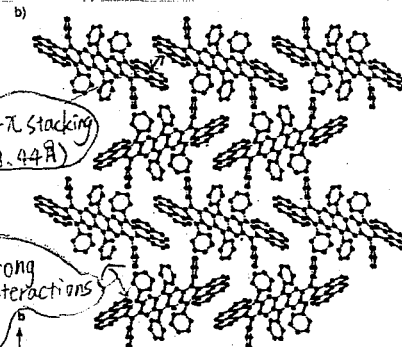
< Synthesis of 1 >



Heat at 330°C
diphenyl ether
98% yield



b) Molecular packing (→)

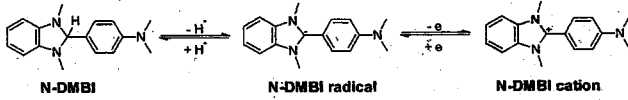


$\Delta E_{HOMO-LUMO} = 1.72 \text{ eV}$
(cf. heptacene 1.36 eV
hexacene 1.84 eV
pentacene 2.1 eV)

no contribution to
the HOMO-LUMO gap

2-(2-Methoxyphenyl)-1,3-dimethyl-1H-benzimidazol-3-ium Iodide as a New Air-Stable n-Type Dopant for Vacuum-Processed Organic Semiconductor Thin Films

previous work (n-type: N-DMBI)

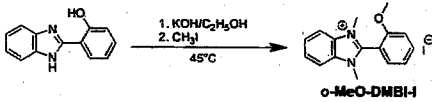


DMBI 誘導体

ラジカル形成を経由することで電子の移動が促進される。

phys let (2010)

This work (n-type: o-MeO-DMBI-I)

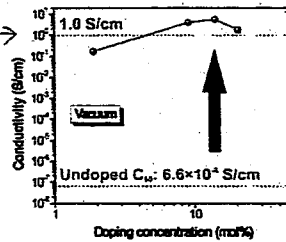


o-MeO-DMBI-I を C60 (TCNQ) にドープすると...

↓

今まで、報告されている n-type 伝導体の内で最も高い伝導性を示す。

(doping concentration of 14 mol% ⇒ 5.5 S/cm)



o-MeO-DMBI-I を C60 にドープ (真空蒸着して作製)

伝導性が飛躍的に向上 (10^7 order)

(濃度が 21 mol% だと... 伝導性が徐々に減少 (1.8 S/cm))

Fig.1 ドープ前後の伝導性の違い

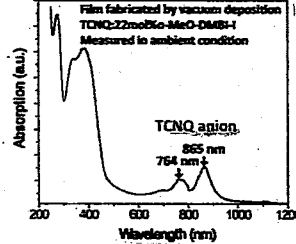


Fig.2 doped TCNQ の UV-Vis-NIR 吸収スペクトル

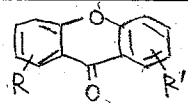
ドープすることで、TCNQ J=ホンの吸収が現れた

o-MeO-DMBI-I が TCNQ への効率的な電子移動を示唆 (C60 にドープした時にも同様のことか) 生じていると判断

o-MeO-DMBI-I の MS 実験...

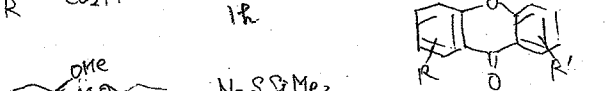
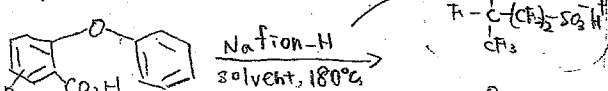
中性的なラジカル・ヒョクが観測されなかった。代わりに、o-MeO-DMBI のヒョクが明確に現れた。高真空下での蒸着で、o-MeO-DMBI-I が C60 の電子移動を伴うか S. o-MeO-DMBI の変化

Palladium-Catalyzed Oxidative Double C-H Functionalization/Carbonylation for the Synthesis of Xanthenes



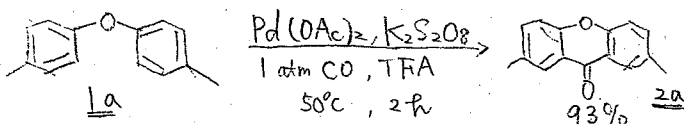
- antibacterial
anti-inflammatory
anticancer
antiviral

popular methods



harsh reaction conditions

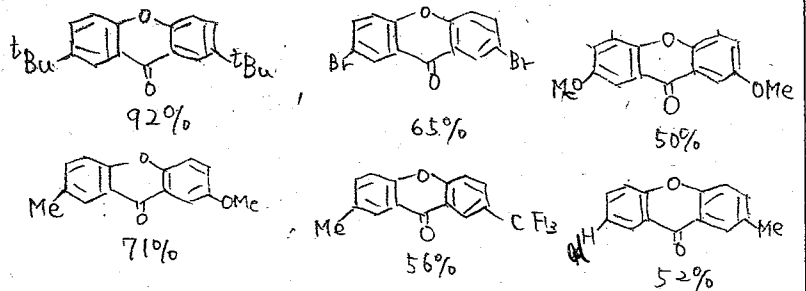
This Work



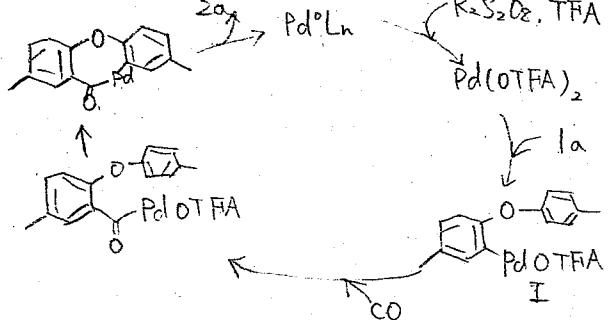
the first Pd-catalyzed double C-H functionalization/carbonylation of diaryl ethers.

- Catalyst: Pd(OAc)2, PdCl2, [Pd(dba)2]
Oxidants: K2S2O8, MnO2, Na2S2O8, Cu(OAc)2

Scope



Proposed mechanism



Metal-Free Ortho C-H Borylation of 2-Phenoxypyridines

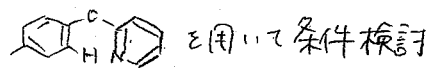
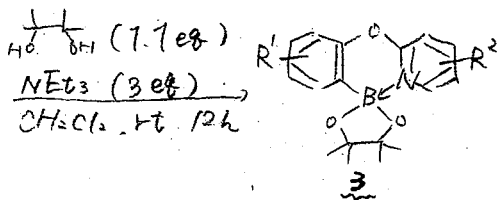
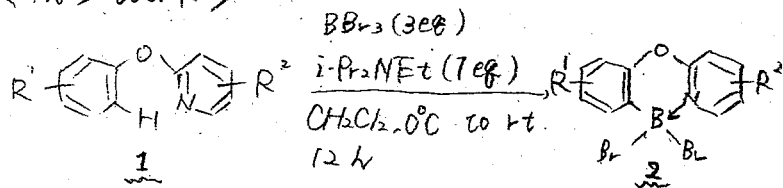
under Mild Conditions

TL-の位置選択的, Metal-Freeの活性化

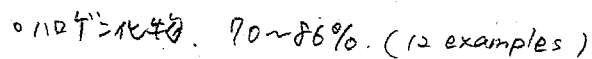
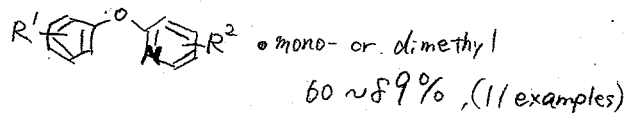


様々な官能基をもつ化合物へ変換可能

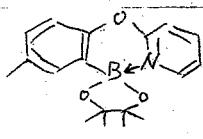
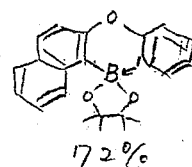
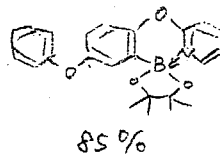
< This Work >



< 基質展開 >



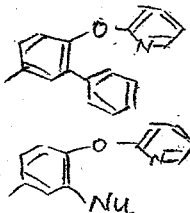
他は0.7%の基や17%に構造上の基質性高収率



(Nu: I⁻, Br⁻, Me)

PhI
 Pd(PPh₃)₄, PhMe,
 or Na₂CO₃, N₂
 reflux, 12 h

NaNu
 Cu₂O (10 mol%),
 NH₄H₂O (2.5 eq)
 EtOH, air, rt, 15 h



(i) MeOTf, PhMe, deprotection;
 100°C, 2 h → 7:1-11 誘導体
 (ii) Na/MeOH, 生成
 reflux, 30 min