

Snapshots of some topics of interest of recent notable advances in chemistry

- Iridium-catalyzed Simultaneous Production of Dicarboxylic Acids and Hydrogen from Aqueous Solutions of Diols
- Large-scale Production of Hydrofluoroethers as Replacement of Chlorofluorocarbons and Hydrochlorofluorocarbons
- Chiral Guest-induced Catalytic Deracemization of a Double-stranded Spiroborate Helicate Containing a Bisporphyrin Unit with Acids
- $B(C_6F_5)_3$ -mediated Tuning of Spatial and Electronic Properties of Lewis Base Molecules

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Snapshots of some topics of interest of recent notable advances in chemistry

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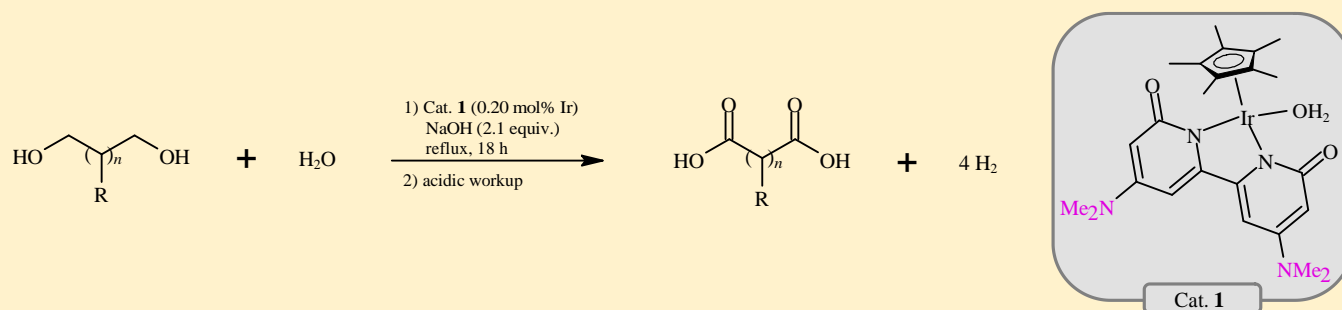
Managing Director / Founder

Iridium-catalyzed Simultaneous Production of Dicarboxylic Acids and Hydrogen from Aqueous Solutions of Diols

The synthesis of industrially important dicarboxylic acids and hydrogen, which is used as an energy carrier, was accomplished from aqueous solutions of diols using an iridium complex containing a functional bipyridonate ligand with *N,N*-dimethylamino substituents. Besides, the selective dehydrogenative oxidation of vicinal diols to afford α -hydroxycarboxylic acids is highlighted.

Dicarboxylic acids constitute industrially important building blocks due to their participation in the synthesis of a wide range of materials such as polymers, plasticizers, and lubricants. Their conventional production methods suffer from many draw backs including low atom efficiency, the employment of harmful oxidants, and the generation of nitrous oxide. Alternatively, the production of dicarboxylic acids from aqueous solutions of diols through a catalytic dehydrogenation reaction is an attractive potential route because of its atom-economical and environmentally benign technique.

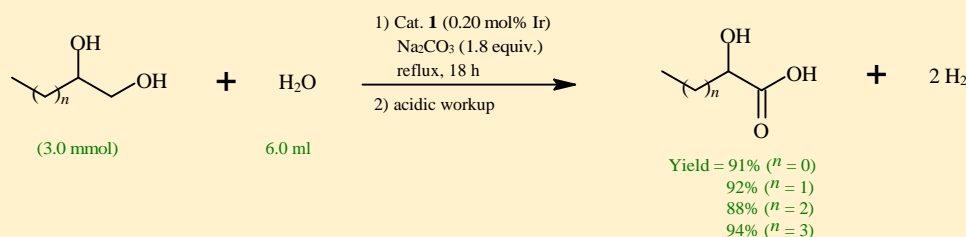
In this context, Toyooka and Fujita reported a novel catalytic system for the synthesis of dicarboxylic acids from aqueous solutions of diols through catalytic dehydrogenation using an iridium complex bearing an extremely electron-rich bipyridonate ligand with *N,N*-dimethylamino groups **1**, which exhibited a high catalytic performance for this type of dehydrogenative reaction (Scheme 1).



Scheme 1. Synthesis of various dicarboxylic acid derivatives from aqueous solutions of diols catalyzed by **1**.

Among the prepared dicarboxylic acids, the sebacic acid was obtained from the reaction of 1,10-decanediol ($n = 8$, $R = H$) and NaOH as a base under reflux in H_2O for 44 h, which is one of the starting materials for the production of nylon-6,10. Furthermore, a diol containing a furan ring was readily converted into 2,5-furandicarboxylic acid, which is considered as a platform molecule for the preparation of bio-based materials for packaging applications such as polyethylene 2,5-furandicarboxylate (PEF), an alternative to polyethylene terephthalate (PET).

In the dehydrogenative reactions of vicinal diols, α -hydroxycarboxylic acid derivatives, important as building blocks prevalent in biologically active compounds, were selectively obtained in high yields accompanied by the evolution of two equivalents of hydrogen (Scheme 2).



Scheme 2. Dehydrogenative oxidation of vicinal diols to α -hydroxycarboxylic acid derivatives catalyzed by **1**.

Among the resulted compounds in Scheme 2, the high-yield synthesis of α -hydroxyhexanoic acid is of particular importance because this compound is a synthetic precursor of lipoxazolidinone A, prostaglandin analogues, and a series of neutral thrombin inhibitors.

The advantages of the present catalytic system are oxidant-free, organic solvent-free, no generation of toxic waste, and highly atom efficiency, which can be implemented in a large scale industrial production, accompanied by the evolution of hydrogen as a byproduct.

Review

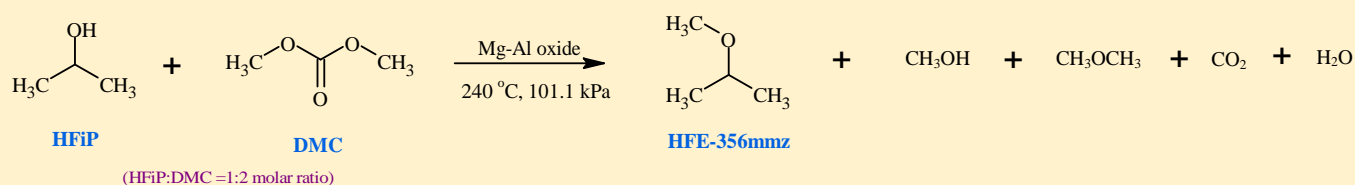
G. Toyooka, K. Fujita, *ChemSusChem*, **2020**, *13*, 3820 – 3824.

Large-scale Production of Hydrofluoroethers as Replacement of Chlorofluorocarbons and Hydrochlorofluorocarbons

Mixed oxides of Mg and Al with various Mg/Al₂ ratios were employed as catalysts for the pollution-free and large-scale production of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether through the vapor-phase methylation of 1,1,1,3,3,3-hexafluoroisopropanol. These hydrofluoroethers are considered as replacement of the harmful chlorofluorocarbons and hydrochlorofluorocarbons that cause high ozone-depletion and global-warming.

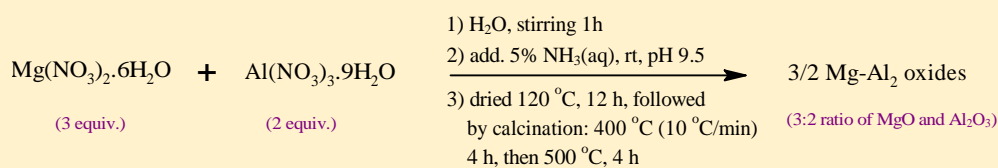
According to the Montreal and Kyoto protocols, the phasing-out of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) is an insistent request to protect the stratospheric ozone layer and tackle global warming issues. As alternatives, hydrofluoroethers (HFEs) are considered to be promising substituents for CFCs and HCFCs. HFEs are featured by their zero-depletion and low global-warming potentials, short atmospheric lifetimes, and wide applicability. However, the pollution-free and large-scale preparation of HFEs has been a quite challenge. In this regard, Li *et. al.* previously developed a new synthetic method for the large-scale production of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether (HFE-356mmz), a member of the HFE family, through the vapor-phase catalytic methylation of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) with dimethyl carbonate (DMC) using metal fluorides as catalysts.¹

Further, the authors extended their work and developed a new procedure for synthesized HFE-356mmz through the vapor-phase methylation of HFIP with DMC using Mg-Al mixed oxide catalysts as alternative to metal fluoride catalysts, which are less expensive, easier to synthesize, and have readily adjustable acid-base properties (Scheme 1).²



Scheme 1. Synthesis of HFE-356mmz through the vapor-phase methylation of HFIP using DMC over a Mg-Al-oxide catalyst.

The Mg-Al mixed oxides were prepared by the co-precipitation method. Among various mixed Mg-Al oxides, the (MgO:Al₂O₃) with a molar ratio of 3:2 ratio (3/2Mg-Al₂ oxide) showed the highest catalytic activity (0.94 mmol h⁻¹m⁻²) due to its moderate Lewis acidity and basicity (Scheme 2). The prepared catalysts were used directly in the vapor-phase methylation reaction, which the 3/2 Mg-Al₂ oxide promoted the reaction efficiently with 100% selectivity of HFE-356mmz and 89.5% conversion of HFiP. Furthermore, 3/2Mg-Al₂ oxide gave good activity and stability in 500 h.



Scheme 2. Synthesis of the Mg-Al mixed oxides by the co-precipitation method.

The applicability of metal oxides makes the reaction very suitable for the industrial-scale mass production of HFE-356mmz as well as more universal and operable, particularly, in heat-pump and cleaning-agent applications.

Review

- 1) W. Li, G. Yang, F. Lu, X. Zhang, *Appl. Catal. A Gen.*, **2020**, *594*, 117416.
- 2) W. Li, F. Lu, X. Zhang, *J. Fluorine Chem.*, **2021**, *241*, 109673.

Chiral Guest-induced Catalytic Deracemization of a Double-stranded Spiroborate Helicate Containing a Bisporphyrin Unit with Acids

A deracemization technique is described, in which the deracemization of a racemic double-stranded spiroborate helicate containing a bisporphyrin unit in the middle assisted by optically-active guests was achieved in the presence of strong acid below room temperature. The strong acid triggered the partial B-O bond cleavage/reformation of the spiroborate groups, affording a highly enantio-enriched helicate with up to 93% ee.

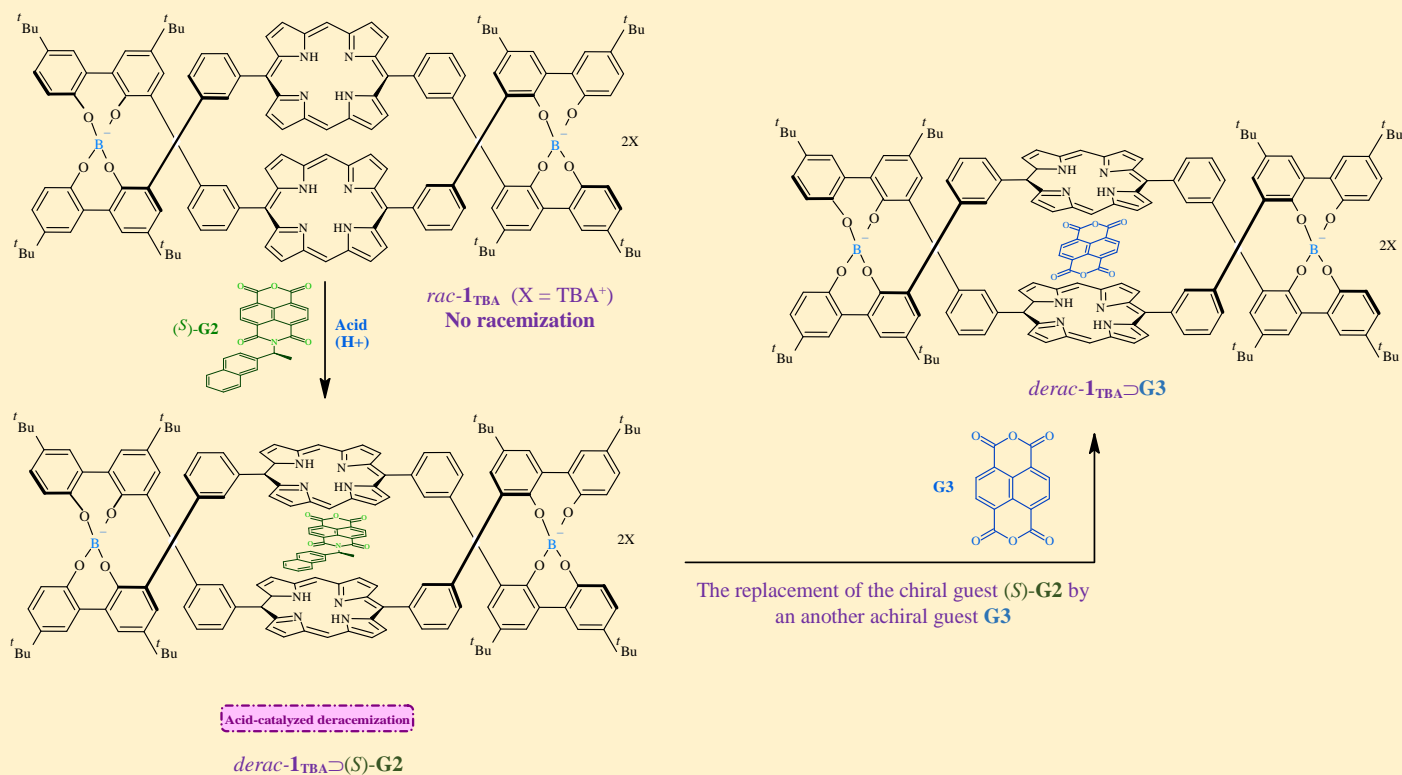
Inspired by the biological multi-stranded helical structures as manifested by the right-handed DNA double helix, many studies have been made to design artificial multi-stranded helical oligomers and polymers for use in different purposes. Such helicates are described as metal-directed self-assemblies in which organic molecular strands with a coordination ability are complexed with two or more metal ions in a helical manner.

To develop advanced chiral materials, it is important to control the helicity of helicates. In this regard, the team of Yashima reported a number of optically-active helicates with a controlled helix-sense. They are composed of two achiral oligophenol strands with a variety of linkers in the middle, which are intertwined with each other through two spiroborate bridges. These racemic double-stranded spiroborate helicates contain a bisporphyrin unit in the middle, which forms an inclusion complex with an electron-deficient planer guest in the bisporphyrin cavity, resulting in unidirectional dual rotary and twisting motions.

Aiming to produce an optically-active helicate with a higher helix-sense excess using this deracemization technique, they reported the resolution of racemic **1**TBA (TBA = tetra-*n*-butylammonium) complexed with (*S*)-**G2** molecule (**1**TBA \supset (*S*)-**G2**) into the enantiomeric (*P*)- and (*M*)-**1**TBA below room temperature using acids as a proton source.

The deracemization reaction of *rac*-**1**TBA complexed with (*S*)-**G2** in the presence of *p*-toluenesulfonic acid (TsOH) ($pK_a = 0.9$ in DMSO) with ([TsOH]/[**1**TBA] = 0.5) in DMSO at 25 °C was performed. Furthermore, to determine the helical sense excesses of the resulting *derac*-**1**TBA and its helical handedness (*P* or *M*), the chiral guest included in *derac*-**1**TBA was exchanged with the achiral guest, **G3**, to afford the corresponding enantiomeric *derac*-**1**TBA \supset **G3** complexes (Scheme 1). The results showed that the acids accelerated the interconversion between the (*P*)- and (*M*)-helicates through the trigger of partial B-O bond cleavage of the spiroborate groups by a proton addition and reduced the activation energy for the racemization of the helicate. The circular dichroism (CD) intensity of the resulting *derac*-**1**TBA \supset **G3** increased with time and the helix-sense excess reached a plateau value (75% ee, *M*-rich) within 8 h. Changing the solvent with decreasing temperature during the deracemization process, the results indicated that both the most rapid equilibration between the (*P*)-

and (*M*)-helicates and the highest helix-sense selectivity (93% ee, *M*-rich) were achieved in DMF at $-20\text{ }^{\circ}\text{C}$ after 48 h.



Scheme 1. Acid-catalyzed deracemization of $rac-1_{TBA}$ upon inclusion complex formation with (*S*)-**G2** and the replacement of the chiral guest by an achiral **G3** to give $derac-1_{TBA} \supset G3$. TBA = tetra-*n*-butylammonium.

This contribution has the potential to develop spiroborate helicate-based chiral functional materials, such as asymmetric catalysts, chirality sensors, and circularly polarized luminescence materials, that can be prepared in 100% theoretical yield from the corresponding optically inactive racemic helicates.

Review

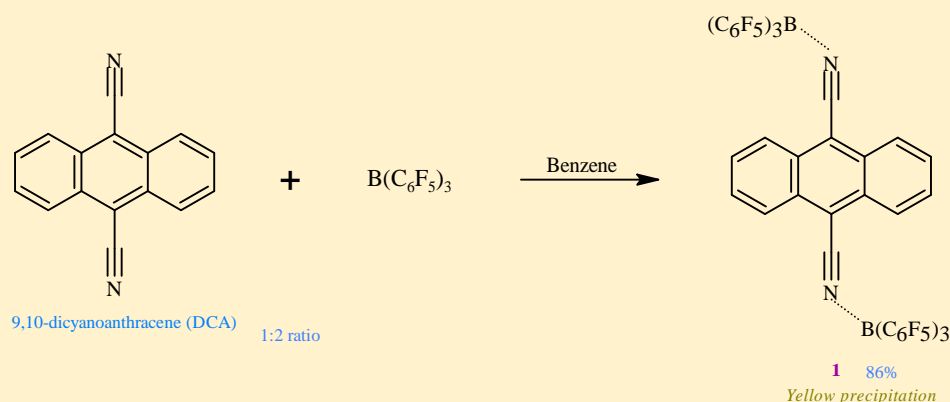
M. Ito, T. Ikai, S. Yamamoto, D. Taura, N. Ousaka, E. Yashima, *Chem. Lett.*, **2020**, *49*, 1030–1033.

B(C₆F₅)₃-mediated Tuning of Spatial and Electronic Properties of Lewis Base Molecules

The complexation of the solid-state light-emitting Lewis adduct of 9,10-dicyanoanthracene with two equivalents of B(C₆F₅)₃ induced a substantial improvement of the quantum yield of the anthracene-based Lewis molecule by preventing π - π stacking.

Some of the solid-state light-emitting materials suffer from intermolecular interaction leading to quenching of the concentration and, consequently, a reduction in their luminescence efficiency. For instance, anthracene, an important class of organic fluorophore, exhibits a poor quantum yield in the solid-state, in contrast to its performance in solution, which shows a high quantum yield. Such a poor performance in the solid-state is related to its highly planar structure, which induces strong intermolecular π -stacking.

In order to obtain solid-state materials with good emission property, a bulky B(C₆F₅)₃ is used with Lewis basic fluorescent substrates as a robust method. Indeed, the strong Lewis acidity of B(C₆F₅)₃ makes it easily accept a valence electron pair from a Lewis basic moiety in π -conjugated systems which drastically lowers the LUMO energy levels of the conjugated systems, resulting in a red-shifted absorption. In a study of the hidden properties of Lewis adducts of B(C₆F₅)₃, Imagawa *et. al.* reported a facile method to tune the optical properties of the anthracene-based Lewis complex **1** through preventing π - π stacking using B(C₆F₅)₃, which showed a high quantum yield in the solid-state relative to the parent 9,10-dicyanoanthracene (DCA) (Scheme 1).



Scheme 1. Preparation of solid-state light-emitting Lewis adduct of DCA with B(C₆F₅)₃.

The X-ray crystallographic study and the comparison of the photophysical behavior between in solution and as solids revealed the effective prohibition of intermolecular π - π stacking. Furthermore, the theoretical calculations indicated coordination of the $B(C_6F_5)_3$ decreases the π - π^* transition energy (Figure 1).

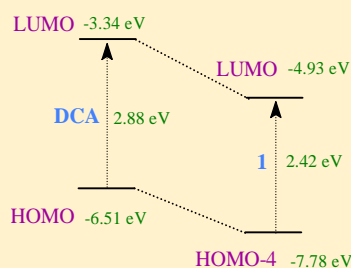


Figure 1. Energy level of selected molecular orbitals of DCA (left) and **1** (right).

Such complexation of conjugated nitrile and $B(C_6F_5)_3$ is quite simple and easy to use for the fabrication of highly planarized nitrile-containing chromophores.

Review

T. Imagawa, M. Nakamoto, R. Shang, Y. Adachi, J. Ohshita, N. Tsunoji, Y. Yamamoto, *Chem. Lett.*, **2020**, *49*, 1022–1025.