

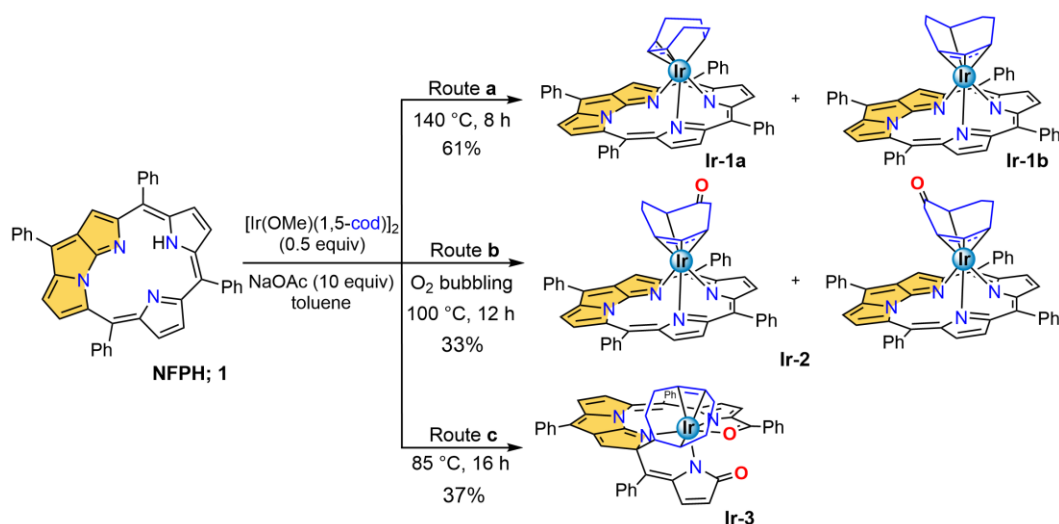
## Synthesis and Characterization of N-Fused Porphyrin Iridium Complexes

(Graduate School Engineering, Kyushu University) ○Jibin Alex Abraham, Masatoshi Ishida, Hiroyuki Furuta

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N-fused porphyrin (NFpH) is a class of porphyrin analogs containing an inner fused tri-pentacyclic pyrrole unit, which serves as a unique monovalent N3 tridentate ligand (Scheme 1).<sup>1</sup> To date, several sitting atop metal complexes of NFp with ruthenium(II), manganese(I), iron(II), ruthenium(II), and tungsten(VI) ions at the inner core have been reported.<sup>2</sup> In this work, we have investigated the iridium(I) (1,5-cyclooctadiene: cod) complexation of NFp to understand the metal effect on the coordination mode, reactivity, and optical properties.

Complexation with an  $[\text{Ir}(\text{I})(\text{cod})(\text{OMe})_2]$  afforded a sitting atop iridium complex (**Ir-1**) supported by a transformed  $\eta^3$ -allylic and  $\sigma$ -bonded cod ligand (Scheme 1). The resulting complex has two independent ancillary cod rotational isomers (i.e., **Ir-1a** and **Ir-1b**), and under aerobic conditions, a methylene-oxygenated cod analog (**Ir-2**) was formed. During the study, a unique octahedral Ir complex possessing a cod-fused and ring-broken dioxo-analog of NFp (**Ir-3**) was obtained. We have further studied their optical and electrochemical properties of these Ir complexes.



**Scheme 1.** Synthesis of N-Fused Porphyrin Iridium Complexes

1) H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc.* **1999**, *121*, 2945–2946.

2) M. Togano, H. Furuta, *Chem. Lett.* **2019**, *48*, 615–622.