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Reaction mechanism with indano[60]fullerene bromide for evaporable fullerene derivatives

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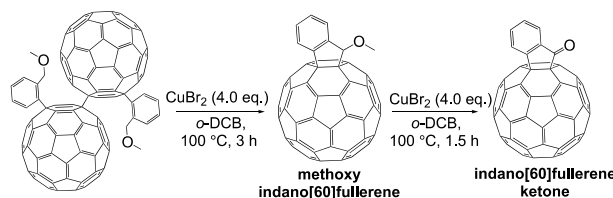
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Indano[60]fullerene bromide was isolated as a key intermediate in the synthesis of indano[60]fullerene ketone, an evaporable fullerene derivative. Based on the identified reaction mechanism, aqueous hydrobromic acid was used to achieve reproducible and high-yielding reactions. A scalable one-pot reaction from aryl[60]fullerenyl dimer to indano[60]fullerene ketone was also demonstrated.

Chemically modified fullerene derivatives have been developed for applications in fields such as organic electronics^{1–5} and biomedical science.^{6–10} In particular, organic photovoltaics have garnered significant attention in recent years due to their potential to contribute to the realization of a sustainable society.^{11–13} However, existing fullerene derivatives such as phenyl-C61-butyric acid methyl ester (PC₆₁BM)^{14–16} can only be formed into films by solution-coating method, as vacuum deposition cannot be applied due to their thermal instability. To address this challenge, we have developed evaporable fullerene derivatives, indano[60]fullerene ketones, which have five-membered carbon rings with ketone structure on the rings.^{17,18} Our previous research¹⁷ demonstrated a high yield in the oxidation reaction from methoxy indano[60]fullerene to indano[60]fullerene ketone via fullerene-cation-intermediate^{19–24} generating from the single electronic transfer (SET) with the help of CuBr₂. Although a high yield can be achieved, it was found the difficult to scale up the reaction and inert gas requirements. In this study, we used the aqueous hydrobromic acid improving the reaction based on Ref 17. We achieved a one-pot synthesis of hundreds of milligrams of indano[60]fullerene ketone and identified

indano[60]fullerene bromide as a key intermediate in the copper(II) bromide-mediated synthesis of indano[60]fullerene ketone (H-FIDO) (Fig. 1) providing an alternative way to synthesis the FIDO in a large-scale comparing to retro Baeyer–Villiger reaction^{25–26}. Scalable synthesis of evaporable fullerene derivatives has the potential to propel advancements in the field of organic electronics research, including organic photovoltaics, perovskite solar cells,^{18,27–29} organic light-emitting diodes,^{30–32} and organic photodiodes.³³

Previous work: single electronic transfer reaction



This work: oxidation-reduction reaction

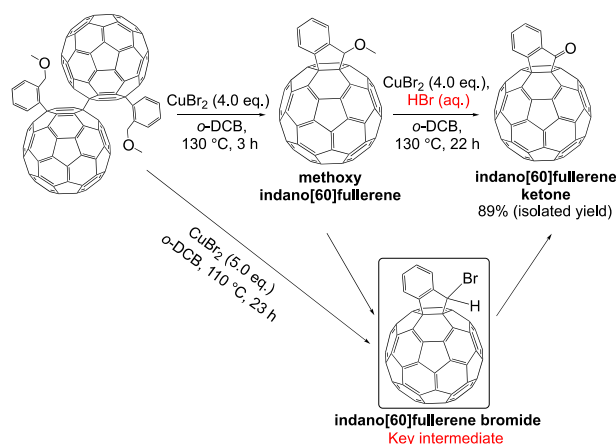


Fig. 1 Research outline: Finding of an indano[60]fullerene bromide intermediate and investigation of the reaction mechanism have resulted a reliably reproducible reaction for one-pot synthesis.

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While synthesizing methoxy indano[60]fullerene in the presence of CuBr_2 from aryl[60]fullerenyl dimers as the starting material, we observed the formation of an unidentified byproduct. Subsequently, the same byproduct was observed when we conducted CuBr_2 -mediated synthesis of the evaporable fullerene derivative indano[60]fullerene ketone from aryl[60]fullerenyl dimers. Although the same reaction condition between aryl[60]fullerenyl dimers to methoxy indano[60]fullerene and methoxy indano[60]fullerene to indano[60]fullerene ketone it is, this byproduct was not found in the reaction from methoxy indano[60]fullerene to indano[60]fullerene ketone¹⁷. This led us to hypothesize that this byproduct may be an intermediate in the reaction for indano[60]fullerene ketone. Therefore, we conducted ^1H -NMR, ^{13}C -NMR and high-resolution mass spectrometry (HRMS) measurements of this byproduct and identified it as indano[60]fullerene bromide. The ^1H -NMR spectrum displayed five signals for five hydrogen atoms. Specifically, a singlet observed at 7.37 ppm was assigned to a benzyl hydrogen atom. Four signals at lower magnetic field were attributed to the four hydrogen atoms on the benzene ring. The ^{13}C -NMR provided the signal of benzyl carbon at 60.86 ppm clearly. The small peak at 430 nm in the absorption spectrometry indicate the 1,2-addition pattern of fullerene (Fig.S1). HRMS data confirmed that the molecular formula was $\text{C}_{67}\text{H}_5\text{Br}$. In particular, a peak at $m/z = 887.9588$ (calc. 887.9569) with a characteristic isotope pattern for ^{79}Br and ^{81}Br was observed.

Next, the reaction mechanism involving indano[60]fullerene bromide was considered. Considering the indano[60]fullerene bromide was not found in the reaction from methoxy indano[60]fullerene to indano[60]fullerene ketone (Ref 17), we believe that the bromide in indano[60]fullerene bromide came from the leaving hydrobromic acid when forming the 5-membered ring of methoxy indano[60]fullerene¹⁹ after checking the mechanism of formation methoxy indano[60]fullerene from aryl[60]fullerenyl dimers.

For confirmation, the indano[60]fullerene chloride was synthesized in the presence of CuBr_2 and HCl (aq.). In the experimental procedure, methoxy indano[60]fullerene dissolved in *ortho*-dichlorobenzene (*o*-DCB) was heated at 130 °C for 15 min after adding CuBr_2 and HCl (aq.). Subsequently, HRMS measurements were performed on the obtained product, confirming it had a molecular formula of $\text{C}_{67}\text{H}_5\text{Cl}$. This result provided evidence that indano[60]fullerene halogen formed from the free ions in solution rather than the anions in the copper salt. Once the fact that the generation of indano[60]fullerene bromide was mainly determined by the majority anion in the solution was confirmed, we speculated that CuBr_2 may not play a role in the generation of indano[60]fullerene bromide. Thus, we gave the reaction mechanism simply (Fig.2). First, the methoxy group was protonated, followed by the bromide ion attacking the benzyl carbon, leaving the methanol molecule to afford the indano[60]fullerene bromide. To prove the mechanism, an

experiment was performed in the absence of CuBr_2 . Methoxy indano[60]fullerene dissolved in *ortho*-dichlorobenzene (*o*-DCB) was heated at 130 °C was reacted with the aqueous hydrobromic acid (47%). The production was detected by HPLC giving the strong peak of indano[60]fullerene bromide after 1.5-hour reaction (Fig.S2).

After confirming the indano[60]fullerene bromide as an important intermediate, we considered that there are two reaction paths from methoxy indano[60]fullerene to indano[60]fullerene ketone. In the absence of HBr (aq.), methoxy indano[60]fullerene reacted with CuBr_2 forming indano[60]fullerene ketone by single electronic transfer (SET) mechanism (Fig.2) as previously reported¹⁷. On the other hand, in the presence of HBr (aq.), methoxy indano[60]fullerene was reacted with HBr to form the indano[60]fullerene bromide first. Then the transformation of indano[60]fullerene bromide to indano[60]fullerene ketone was considered via both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ pathway. For $\text{S}_{\text{N}}1$ pathway the Br of indano[60]fullerene bromide was eliminated under acid environment to afford the fullerene benzyl cation. Finally, it is capped by a hydroxy group provided by H_2O giving the hydroxy indano[60]fullerene. For $\text{S}_{\text{N}}2$ pathway under the acid environment, the interaction between Br of indano[60]fullerene bromide and HBr was formed, then the hydroxy indano[60]fullerene Intermediate was formed by attached by H_2O and eliminating the HBr . The hydroxy indano[60]fullerene Intermediate was then oxidized by O_2 or CuBr_2 quickly to afford indano[60]fullerene ketone (Fig.2b).

The key intermediate hydroxy indano[60]fullerene was separated and characterized to prove our hypothesis with the reaction condition in an inert atmosphere, with no oxidizing agent such as O_2 and CuBr_2 . The ^1H -NMR spectrum gives the clear and sharp peak of the hydroxyl group at 3.04 ppm, which shifted to the low field due to the formation of hydrogen bonds with water after adding one drop of D_2O (Fig. S3). HRMS confirmed the structure by showing a clear peak at $m/z = 826.0415$ (calc. 826.0419).

The introduction of the Br-intermediate provides a reaction pathway with a faster reaction rate than the single-electron transfer (SET) pathway using only CuBr_2 when synthesizing indano[60]fullerene ketone. To test our hypothesis, a time-course experiment was conducted to synthesize indano[60]fullerene ketone from methoxy indano[60]fullerene, employing CuBr_2 as the oxidant and hydrobromic acid as the mediator. In contrast, CuBr_2 was used alone for the control group (Fig. 3). The specific synthesis procedures for hydrobromic acid usage were as follows. First, methoxy indano[60]fullerene (10.0 mg) was dissolved in *o*-DCB (10.0 mL). Then, CuBr_2 (4.0 equiv) was added as an oxidant. Subsequently, 0.1 mL of aqueous hydrobromic acid (47%) were added as a reaction mediator. The mixture was stirred thoroughly at 130°C, and HPLC measurements were performed every couple of hours to monitor the progress of the reaction. At 1.0 h after the start of the reaction, methoxy indano[60]fullerene was completely converted to indano[60]fullerene bromide and indano[60]fullerene ketone when the presence of hydrobromic acid. Subsequently, the amount of indano[60]fullerene bromide

decreased, while that of indano[60]fullerene ketone increased over time. When the experiment was terminated at 18 h, the peak area ratio of indano[60]fullerene ketone was calculated to be 90%, while the group with only CuBr_2 as an oxidant only shows a 60% conversion yield. These results confirmed that the series of reactions occurred sequentially,^{36–38} proving that indano[60]fullerene bromide is a key intermediate to accelerate the reaction.

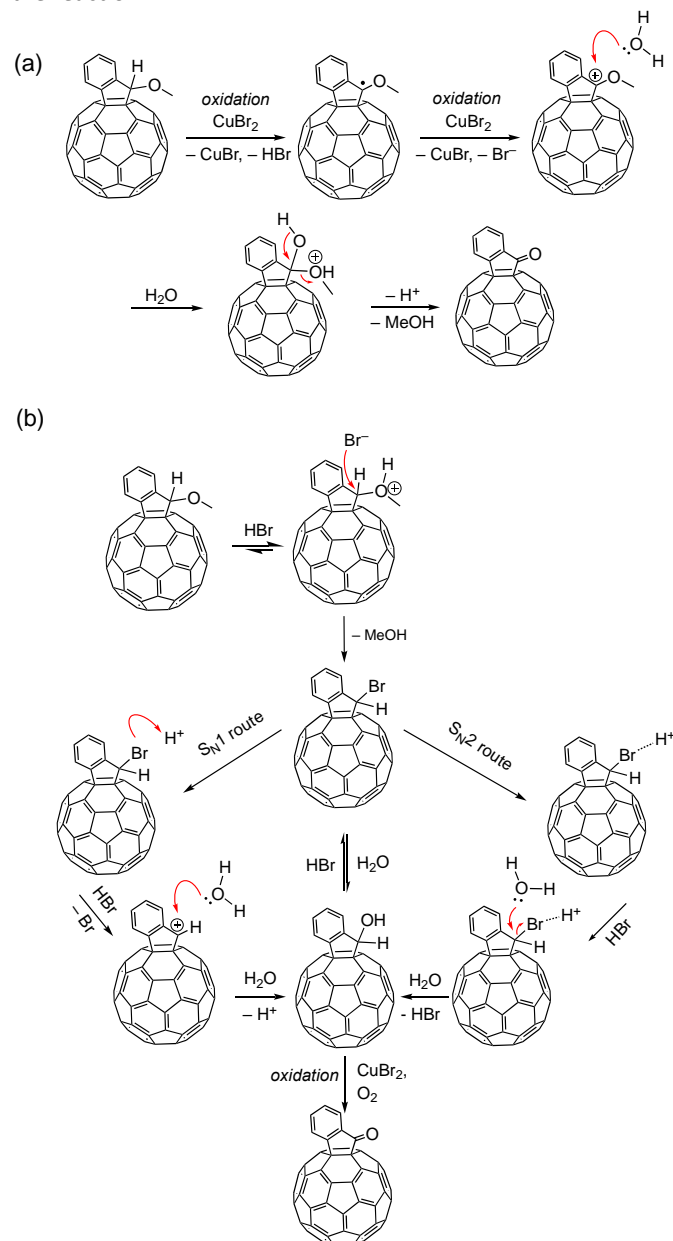


Fig. 2 Plausible reaction mechanism: (a) Formation of indano[60]fullerene ketone with CuBr_2 . (b) Production of indano[60]fullerene ketone with air from indano[60]fullerene bromide.

To be more specific, the optimization reaction condition from methoxy indano[60]fullerene to indano[60]fullerene ketone with different copper salt and different equivalents of aqueous hydrobromic acid were performed (Table S1). It was found that the HBr only affected the formation of the

indano[60]fullerene bromide and the excess HBr will not have a negative effect on the reaction. Considering the higher reaction condition and the evaporation of water and HBr, it was recommended to add excessive amount of aqueous hydrobromic acid.

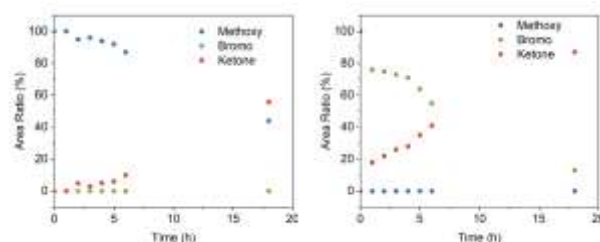


Fig. 3 HPLC peak area ratio of each compound vs reaction time (Left CuBr_2 as oxidant, right hydrobromic acid and CuBr_2 as oxidant and mediator). Blue, green, and red circles represent methoxy indano[60]fullerene, indano[60]fullerene bromide, and indano[60]fullerene ketone.

Based on the proposed reaction mechanism and the optimization condition, we demonstrated that indano[60]fullerene ketone can be synthesized from aryl[60]fullerenyl dimer in a one-pot reaction using CuBr_2 and hydrobromic acid (Fig. 4). Subsequently, indano[60]fullerene ketone was directly obtained from aryl[60]fullerenyl dimer in the presence of both CuBr_2 and HBr (aq.) in the open air. This reaction enables a remarkably simple synthesis process to prepare evaporable indano[60]fullerene ketones for industry. The *tert*-Bu-substituted indano[60]fullerene ketone was also synthesized on a scale of several hundreds of milligrams, thus demonstrating the versatility of the reaction mechanism proposed in this paper.

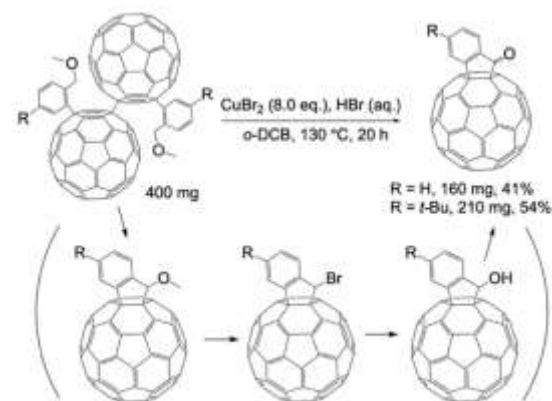


Fig. 4 Scalable one-pot synthesis of indano[60]fullerene ketone and its derivative.

In conclusion, we identified indano[60]fullerene bromide as a key intermediate in the oxidation from methoxy indano[60]fullerene to indano[60]fullerene ketone using CuBr_2 as an oxidant. The bromide intermediate was characterized by NMR and HRMS, which showed the characteristic isotope pattern of Br. Based on the identified reaction mechanism, the reaction from methoxy indano[60]fullerene to

indano[60]fullerene ketone was made reproducible by adding aqueous HBr as an acid. Furthermore, we demonstrated the one-pot synthesis of indano[60]fullerene ketone from aryl[60]fullerenyl dimer on a large scale with various substituents. The synthesized products obtained from this optimized reaction will serve as an important class of evaporable fullerene derivatives with various substituents available to control sublimation temperature and thin-films morphology.^{18,39}

Data availability

All relevant data are within the manuscript. The data that support the findings of this study are available in the ESI† of this manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Data availability statements

The data supporting this article have been included as part of the Supplementary Information.