

π -Extended Iodoarene as an Electrochemical Mediator for Oxidative C-N Coupling: Reactions, Mechanism, and Kinetics

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ABSTRACT: Herein, we present the design and application of π -extended iodoarenes for electrocatalytic C-N bond coupling reactions. The extended π -systems of such compounds lower the oxidation potentials and stabilize the radical cation states, thus facilitating the selective and efficient electrochemical generation of hypervalent iodine. The electrocatalytic C-N coupling reactions of various *N*-protected aminobiphenyl derivatives were achieved, including those of substrates with the *tert*-butoxycarbonyl protecting group, which has never been applied to electrochemical C-N coupling reactions. A mechanistic study suggests the presence of halogen-bonding interactions of the radical cation state of the iodoarene with Lewis bases, and the coordination of Lewis bases evidently promotes electrochemical oxidation to generate hypervalent iodine species. A kinetic study using foot-of-the-wave analysis (FOWA) was also employed for the first time to examine electrochemical hypervalent iodine catalysis.

Hypervalent iodine compounds comprise a class of reagents with significant utility in terms of promoting selective oxidative transformations in organic syntheses.¹⁻⁶ The explosive nature of these compounds as well as their expense when used as stoichiometric oxidants has led to interest in the application of catalytic amounts of iodoarenes in the presence of terminal oxidants.⁷⁻⁹ Electrochemical processes have also gained attention as a means of achieving sustainable hypervalent iodine catalysis.¹⁰⁻¹² Electrochemistry enables the direct use of electrons/holes as safe, inexpensive and green reductants/oxidants, thus eliminating the need for stoichiometric redox reagents.¹³⁻¹⁸ Fuchigami and co-workers reported pioneering work regarding the use of iodobenzene derivatives as electrochemical mediators.¹⁹ Since then, successful electrocatalytic systems using iodoarene mediators have been reported.²⁰⁻²² Even so, studies concerning the electrocatalytic use of hypervalent iodine remain rare and the associated substrates are limited to relatively electron-deficient molecules.

We considered two major reasons for this limited use of hypervalent iodine in electrocatalytic systems. The first is the high oxidation potentials that are typical of monocyclic iodoarenes and that result in the less selective anodic oxidation of iodoarenes in the presence of various reactants. The high oxidation potential of the mediator will also limit the applicability of electron-rich substrates. The second issue is the instability of the radical cation intermediates produced by the one-electron oxidation of iodoarenes. The electrochemical oxidation of iodoarenes is thought to proceed via an ECEC mechanism in which an initial electron transfer at the electrode generates radical cation species. If the radical cation intermediate is unstable, it may induce side reactions such as the homocoupling of iodoarenes.

To address these challenges, we propose the utilization of π -extended iodoarenes in electrocatalytic systems (Figure 1). The extended π -systems in these compounds delocalize both the charge and the spin of radical cations, thus increasing the

stability of such species and lowering the oxidation potential. These stabilized radical cations can react with donor molecules, following which a second electron transfer occurs to form hypervalent I(III) species. The present research produced a novel iodoarene, 9-iodo-10-mesitylanthracene (**1**), and investigated the electrocatalytic C-N coupling reaction of *N*-protected aminobiphenyl derivatives (**2**). In-depth mechanistic and kinetic studies were also performed.

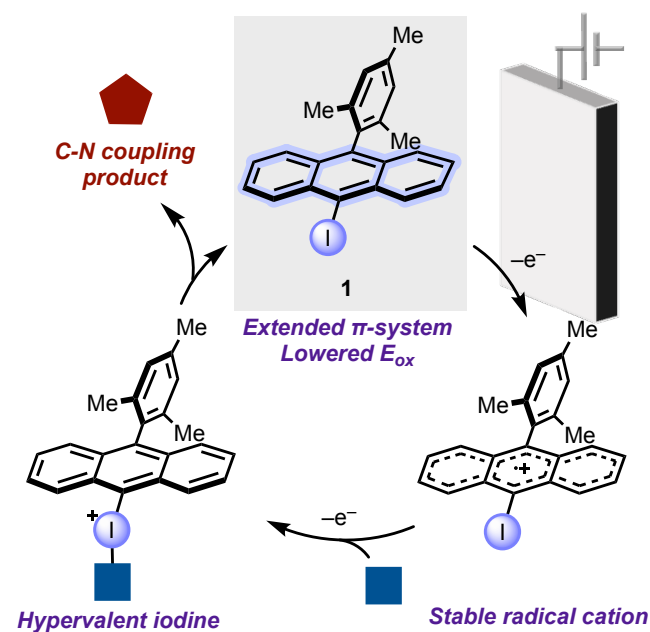


Figure 1. The concept of this study.

The redox behaviors of various π -extended iodoarenes were initially assessed using the cyclic voltammetry (CV) technique. The compounds 9-iodoanthracene (**Anth-I**), 9-iodophenanthrene (**Phen-I**), and 1-iodopyrene (**Pyr-I**) were analyzed in $\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4/\text{CH}_2\text{Cl}_2$ (Figure 2a). The oxidation onset potentials for **Anth-I** and **Pyr-I** were observed at *ca.* 1.0 V vs. Ag/AgNO_3 , whereas **Phen-I** showed a relatively high oxidation onset potential of 1.4 V. Notably, **Anth-I** showed a fully reversible voltammetric feature and so evidently had the structural motif most suitable for use as an electrochemical mediator. However, when CV analyses of **Anth-I** were performed with trifluoromethanesulfonate (TfO^-) as an anion in the supporting electrolyte, the voltammetry became irreversible (Figure S2). This result suggested that the radical cation obtained from **Anth-I** was susceptible to further chemical reactions in the presence of a slightly donating anion such as TfO^- . Therefore, it was necessary to substitute a bulky substituent at the reactive 10-position of this molecule.

Based on this concept, the mesityl-substituted iodoanthracene **1** was prepared. This compound exhibited an oxidation onset potential of 0.9 V (Figure 2b). **1** displayed a fully reversible redox response even in the presence of TfO^- , meaning that the stability of the radical cation state had evidently been improved. I^{++} was successfully generated and accumulated by bulk electrolysis under ambient conditions, confirmed by electron paramagnetic resonance spectroscopy (Figures S9). To highlight the redox stability of **1**, CV measurements were also performed on monocyclic iodoarenes, *i.e.*, iodobenzene and 4-iodoanisole, under identical conditions (Figure 2b). As expected, the voltammograms of monocyclic iodoarenes displayed irreversible oxidation waves at higher oxidation potentials, demonstrating the generation of unstable intermediates and the concomitant occurrence of irreversible chemical processes.

We next investigated the voltammetric response of **1** in the presence of *N*-acetyl-aminobiphenyl (**2a**). The addition of **2a** to an electrolytic solution containing **1** resulted in an increased oxidation current and decreased reduction current compared with that obtained in the absence of **2a**, which corresponded to a typical catalytic current (Figure 2c, blue line). The oxidation current even increased in the presence of bases such as 2,6-di-*tert*-butylpyridine (tBu_2Py) (Figure 2c, black line). CV data were also acquired from **1** with various pyridine derivatives and in the absence of **2a**. Irreversible responses were obtained with pyridine and 2,6-lutidine while the addition of tBu_2Py did not produce a change (Figures S3-5). These results suggest that pyridine and 2,6-lutidine coordinated to the iodine center of I^{++} to facilitate additional chemical/electrochemical reactions. In contrast, the sterically hindered reagent tBu_2Py did not interact with I^{++} .

Based on these assessments, we next carried out electrocatalysis on a bulk scale (Table 1). After passing 2 F mol^{-1} of charge at 25°C , the desired product, *N*-acetyl-carbazole (**3a**), was obtained when using either tBu_2Py or 2,6-lutidine, in 25% and 23% yields, respectively (Table 1, entries 1 and 2). Interestingly, **3a** was not produced in the case that pyridine was used as the base, indicating that a base capable of strong coordination did not promote the reaction (entry 3). Consequently, tBu_2Py was selected as the optimal base for subsequent work. The application of a higher reaction temperature of 50°C and passage of a larger amount of charge increased the product yield (entries 4-6). Specifically, passing 5 F mol^{-1} of charge gave **3a** in a 52% yield, representing the optimal condition for this reaction (entry 6). The necessity of employing an excess of charge for the reaction was attributed to the use of an undivided cell, in which radical cations generated during the reaction could be partially reduced at the counter electrode.

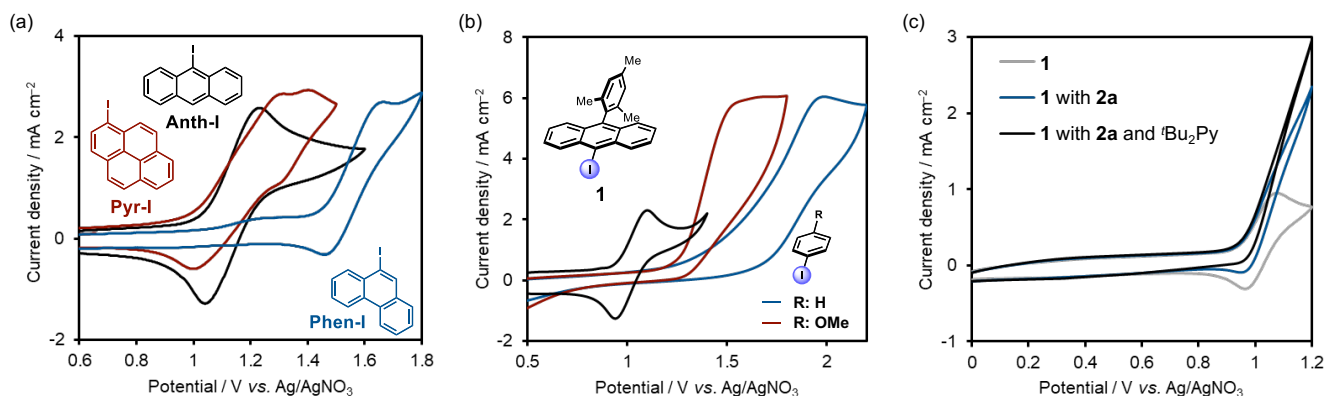


Figure 2. Redox behavior of iodoarenes. (a) CVs of 5 mM **Anth-I** (black), **Phen-I** (blue), and **Pyr-I** (red) in 0.1 M $\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4/\text{CH}_2\text{Cl}_2$ at a scan rate of 0.1 V s^{-1} . (b) CVs of 5 mM **1** (black), 4-iodoanisole (red), and iodobenzene (blue) in 0.1 M $\text{LiTfO}/\text{MeCN}+\text{CH}_2\text{Cl}_2$ (6:4 in vol.) at a scan rate of 0.1 V s^{-1} . (c) CV of **1** (gray), **1** with **2a** (blue), and **1** with **2a** and tBu_2Py (black) recorded in 0.1 M $\text{LiTfO}/\text{MeCN}+\text{CH}_2\text{Cl}_2$ (6:4 in vol.) at a scan rate of 0.1 V s^{-1} (**1**: 1 mM, **2a**: 20 mM, tBu_2Py : 8 mM).

The compatibility of various protecting groups for amines with this system was subsequently investigated with applying the optimized reaction conditions. When a trifluoroacetyl group was used (**2b**), the C-N coupling product was not obtained (Table 1, entry 7). On the other hand, carbamate groups such as methoxycarbonyl (Moc) and *tert*-butoxycarbonyl (Boc) were found to be compatible and the Boc-protected substrate **2d** gave the highest yield of 82% (entries 8,9). To the best of our knowledge, there have been no reports on the electrochemical C-N coupling reactions using Boc-protected amines, despite the usefulness of Boc as a protecting group. CV data showed that the oxidation potentials of these compounds decreased in the order of **2b** > **2a** > **2c** > **2d** (Figure S6), in good agreement with the order of the yield. Thus, catalytic efficiency was greatly affected by the difference between the oxidation potentials of **1** and the substrate. Additional control experiments are summarized in Table S2.

Table 1. Optimization of electrocatalytic Intramolecular C-N coupling reaction using **1**.

Entry	PG ^a	Base	T/°C ^b	Q/F mol ⁻¹ ^c	Yield ^d
1	Ac (2a)	^t Bu ₂ Py	25	2	23 (3a)
2	Ac (2a)	2,6-Lutidine	25	2	25 (3a)
3	Ac (2a)	Pyridine	25	2	0 (3a)
4	Ac (2a)	^t Bu ₂ Py	50	2	30 (3a)
5	Ac (2a)	^t Bu ₂ Py	50	4	40 (3a)
6	Ac (2a)	^t Bu ₂ Py	50	5	52 (3a)
7	CF ₃ CO (2b)	^t Bu ₂ Py	50	5	0 (3b)
8	Moc (2c)	^t Bu ₂ Py	50	5	60 (3c)
9	Boc (2d)	^t Bu ₂ Py	50	5	82 (3d)

^aProtecting group of amine, ^bReaction temperature, ^cCharge passed, ^dDetermined by ¹H NMR.

Next, the substrate scope of the present system was evaluated (Figure 3). The reaction proceeded with substrates containing electron-withdrawing groups such as Cl, Br, CHO, Ph and COOMe. In particular, the installation of a Br at the 5-position (**2d-3**) gave a C-N coupling product in high yield (96%). No reaction was observed in the case of substrates having a nitro group (**2d-7,10**) due to the excessively high oxidation potentials of these compounds. The reaction also failed to proceed with methoxy-containing substrates (**2d-6,9**) having lower oxidation potentials. In these trials, direct oxidation of the substrate was favored.

The mechanistic aspects of the present system were evaluated by first investigating the extent of halogen bonding interactions.²³ A preliminary assessment was performed via the computationally simulated electrostatic potential mapping of **1**⁺. These calculations confirmed that a σ -hole is indeed formed at the iodine center (Figure S10). An experimental evaluation of halogen-bonding interactions using square wave voltammetry (SWV) was then carried out (Figure S11b).²⁴⁻²⁶ SWV data were obtained from **1** in conjunction with successive addition of ClO₄⁻ and negative shifts of the oxidation potential were noted. Based on these data, the binding enhancement factor was

calculated to be 1.87, showing that **1**⁺ is capable of functioning as a halogen-bonding acceptor.

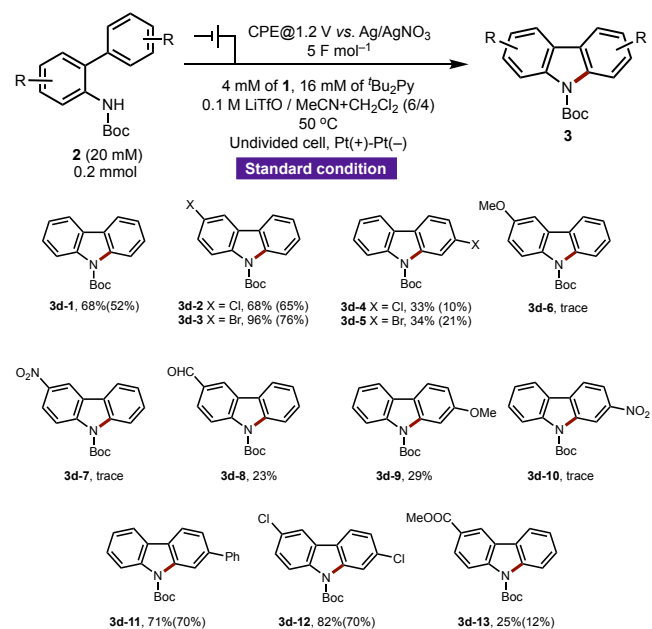


Figure 3. Substrate scope with *N*-Boc-aminobiphenyl derivatives. Yields were determined by ¹H NMR. Isolated yields are in parentheses.

We next investigated the authenticity of the reaction intermediates (*i.e.*, hypervalent iodine species) by CV analysis, employing an electrolyte containing AcO⁻ and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).²⁰ The voltammogram of **1** recorded in the presence of 2 equiv. of AcO⁻ showed an almost doubled oxidation current compared to the original oxidation wave of **1**, as well as the disappearance of the reduction current (Figure S8). In addition, further increases in the amount of AcO⁻ did not lead to increases in the oxidation current. These data strongly suggested that AcO⁻ anions coordinated with the iodine centers to promote 2e⁻-oxidation via the ECEC process, resulting in the formation of I(III) species.

On the basis of these findings, we propose an ECEC mechanism for the present electrocatalysis (Figure 4). Initially, **1** is oxidized at the anode to give **1**⁺. The persistent nature of **1**⁺ and halogen-bonding interactions enable effective coordination of amines, where deprotonation of N-H is facilitated by ^tBu₂Py. These neutral radicals are then oxidized at the anode to generate hypervalent iodine species. Finally, intramolecular cyclization gives carbazole **3** to close the catalytic cycle. The rate-determining step (RDS) was identified through voltammetric studies of **1** in the presence of **2d** and its deuterated analogs (Figure 5a). The use of deuterated compounds, **2d-d₁** and **2d-d₅**, produced no change in the oxidation current compared with that obtained from the protio analogue **2d**, suggesting that deprotonation was not the RDS. Thus, the coordination of the substrate to **1**⁺ appears to have been the RDS.

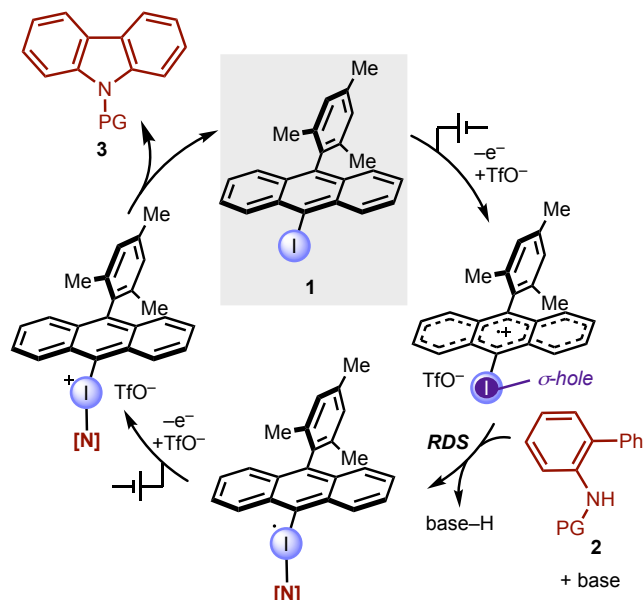


Figure 4. Plausible reaction mechanism.

A quantitative kinetic analysis of the catalytic process was also carried out using a foot-of-the-wave analysis (FOWA) as developed by Savéant, Costentin.^{27–30} FOWA allows the extraction of kinetic data from CV results even in case of a system in which side reactions such as catalyst degradation occur. Notably, there are no prior reports of the application of FOWA to the kinetic analysis of hypervalent iodine. This is presumably because FOWA requires the catalyst to undergo reversible redox reactions in the absence of the substrate. FOWA was performed for the catalytic system using **2d** (Figure 5b see SI for a more detailed discussion). The rate constant, k_{obs} , was estimated to be $21.8 \text{ M}^{-1} \text{ s}^{-1}$ and the catalyst turnover frequency (TOF_{max}) for the reaction was determined to be 0.437 s^{-1} .

In conclusion, 9-iodo-10-mesitylanthracene (**1**) was found to function as a novel hypervalent iodine electrocatalyst. The key to the design of an electrochemical mediator in the present study was stabilization of the radical cation intermediate via an extension of the π -system. The development of such strategies is expected to assist in the future design of iodoarene-based electrochemical mediators for sustainable oxidative chemical transformations.

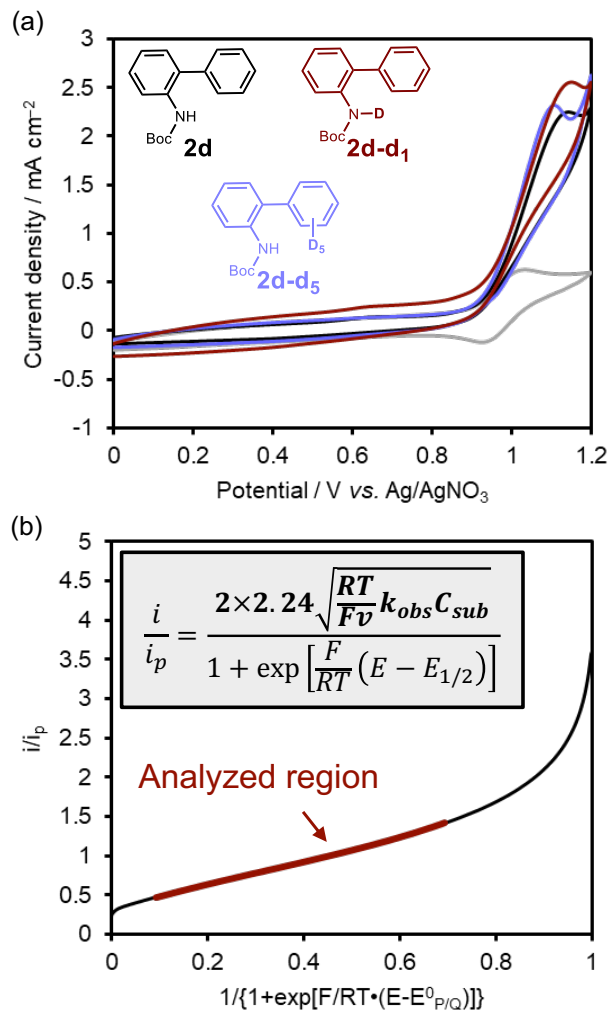


Figure 5. Kinetic studies of electrocatalytic reaction. (a) CVs of 1 mM **1** (gray line), 1 mM **1** with 20 mM **2d** or 20 mM deuterated substrates (**2d-d**₁, **2d-d**₅) (red and purple lines, respectively) in 0.1 M LiTfO/MeCN+CH₂Cl₂ (6:4 in vol.) with 4 mM ^tBu₂Py at a scan rate of 0.1 V s⁻¹. (b) FOWA of 1 mM **1** with 20 mM **2d**.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/xxxxxxxxxxxxxxxxxx>. Materials, synthetic procedure, detailed discussion regarding the FOWA process, single crystal X-ray diffraction data for **1**, ¹H and ¹³C NMR spectra for various compounds.

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Funding Sources

This work was supported by Kakenhi Grants-in-Aid (nos. JP20K15241 and 22H02118) from the Japan Society for the Promotion of Science (JSPS) and by the Murata Science Foundation.

Notes

The authors declare no competing financial interest.

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