Electrochemical Synthesis of Pyridinium-Conjugated Assembly based on Nucleophilic Substitution of Pyrene/Perylene π-Radical Cation

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Efficient and selective N-arylation of pyridine derivatives was demonstrated as nucleophilic substitution reaction of electrochemically generated π-radical cations such as pyrene and perylene. 1-Methylimidazole also worked as a nucleophile toward pyrene π-radical cation to give the imidazolium. This reaction provides a widely applicable and powerful method for pyridinium-conjugated assembly in which the redox-active pyridinium moieties can be integrated through π-conjugated system. Preparative scale synthesis was demonstrated successfully by using perylene π-radical cation prepared by chemical oxidation with I2/AgClO4. The resulting pyridinium-conjugated assembly shows both one-electron reduction assigned to the pyridinium moiety and one-electron oxidation of the pyrene and perylene moieties. UV-visible absorption and fluorescence spectra indicated intramolecular charge transfer character from the pyrenyl and perylenyl moieties to the pyridinium ones of the pyridinium-conjugated assembly.

Key Words: Anodic Pyridination, Pyridinium-Conjugated Assembly, π-Radical Cation, N-Arylpyridinium

1 Introduction

Organic radical cations have been of fundamental interest in a variety of contexts for both organic and physical chemists. Especially, aromatic π-radical cations are prone to suffer further transformations such as nucleophilic attack, deprotonation, rearrangement, fragmentation, polymerization, and so on.1-3 Recently, we have developed a series of electrochemical synthetic reactions of pyridinium-conjugated assembly based on nucleophilic substitution of electrochemically generated oligothiophene π-radical cations.4-6 This efficient pyridination can be regarded as an easy and widely applicable N-arylation method of pyridine derivatives, which has been little achieved except for some special arylated reagents such as 2,4-dinitrohalogenobenzene, 2-halogenopyridazine, and so on.5-9 This success also stimulated us to apply this anodic nucleophilic substitution reaction to various kinds of π-conjugated functional molecules including conducting polymers.7) Along this line, we reported here the syntheses of pyridinium-conjugated pyrene and perylene derivatives (Scheme 1) based on the anodic nucleophilic substitution and their electrochemical and spectroscopic properties.

2 Experimental

The potentiostatic electrolysis and the isolation procedure of the products were carried out according to our previous report.8) Typically, 50 mM pyrene in 50 ml CH2CN solution containing 0.5 M NaClO4 and 0.5 M pyridine (Py) or 1-methylimidazole (Im) was oxidized at 1.20 V vs. Ag/Ag+ by using a Pt plate electrode.8) In the case of perylene, 5 mM perylene substrate and 50 mM nucleophiles was used and electrolysis potential was 1.00 V. A home-made Ag/Ag+ electrode (0.24 V vs. SCE) was used as reference electrode. The electrolysis was controlled by the passed charges of 0.4 F/mol substrate, which corresponds to 20% of theoretical charges based on two-electron oxidation process of the total reaction.9) The preparative-scale synthesis based on chemical oxidation of perylene with I2/AgClO4, was performed according to the reported procedure.9,10) Under N2 atmosphere, to a solution of 50.5 mg (0.2 mmol) of perylene in a 10 ml dry CH2Cl2 was added a solution of 41.5 mg (0.2 mmol) of dry AgClO4 in 0.5 ml CH2CN. To this mixture was added a solution of 25.4 mg (0.1 mmol) I2 in 5 ml CH2Cl2.
A deep-blue precipitate of perylene π-radical cation formed immediately. After stirring for 20 min, the mixture was directly transferred to 10 ml CH₃CN solution containing 4 mmol nucleophile without isolating the π-radical cation as solid. After stirring for 2 h, the mixture was filtered to remove AgI precipitate. The filtrate was then filtered to remove AgI precipitate. The filtrate was collected and purified by recrystallization from CH₃CN.

The identification data of the products were summarized in Table 1.

### 3 Results and Discussion

As pyridinium-conjugated assemblies, N-pyrenyl- and N-perylenylypyridinium were prepared by potentiostatic oxidative electrolysis of pyrene and perylene (ArH), respectively, with pyridine derivatives as nucleophiles (Nu). The nucleophilic attack of the pyridine derivatives took place at the positions with high electron population. The preparative results are summarized in Table 2.

The potentiostatic electrolysis at 1.20 V of pyrene in the presence of pyridine and methyl imidazole afforded quantitatively Ia and Ib, respectively, when 20% of theoretical charges (0.4 F/mol pyrene) were passed. After further electrolysis with 1.1 times theoretical charges (2.2 F/mol pyrene), the compounds Ia and Ib were isolated in 95% and 90% yields based on the amount of the feed pyrene. Similarly, the case of perylene at 1.00 V in the presence of pyridine (Py) gave Ia in a quantitative yield. When bipyridine (Bpy) and 1-methyl-4-(4′-pyridyl)-pyridinium perchlorate (MPP₂ClO₄⁻) were used as nucleophiles, the reaction gave Ib and Ic in 55% and 20% yield, respectively, which may be explained by their lower nucleophilicity than the parent pyridine.

Due to the electron-withdrawing property of pyridinium and imidazolium moieties, the oxidation potentials of Ia and Ib assigned to the oxidation of aromatic units shift anodically by 340 mV and 390 mV with respect to non-substituted pyrene, respectively. As for N-perylenylypyridinium derivatives, the oxidation potentials of IIa, IIb, and IIIc shift anodically by 150 mV, 260 mV, and 560 mV, respectively (Table 2). By setting the electrolysis potential, not enough anodically to oxidize the resulting mono-substituted product, the second substitution was unlikely to take place. Therefore, one can obtain selectively the mono-substituted products, which has been achieved in the anodic pyridination of oligothiophenes.

### Table 1 Identification data of the pyridinium-conjugated assembly.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>¹H-NMR δ (ppm)</th>
<th>EA</th>
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<tbody>
<tr>
<td>Ia</td>
<td>9.56 (d, J = 5.40 Hz, 2H), 9.16 (t, J = 8.10 Hz, 1H), 8.70-8.39 (m, 9H), 8.27 (t, J = 7.56 Hz, 1H), 7.77 (d, J = 9.18 Hz, 1H)</td>
<td>Calcd: C, 66.41; H, 3.72; N, 3.69. Found: C, 66.76; H, 3.77; N, 3.76.</td>
</tr>
<tr>
<td>Ib</td>
<td>9.69 (s, 1H, NCHN), 8.53-8.19 (m, 9H), 8.08 (s, 1H)</td>
<td>Calcd: C, 62.75; H, 3.05; N, 7.32.</td>
</tr>
<tr>
<td>C₂H₅N₃⁺ClO₄⁻</td>
<td>9.41 (d, J = 6.7 Hz, 2H), 8.99 (t, J = 7.83 Hz, 1H), 8.66-8.50 (m, 4H), 8.03-7.92 (m, 3H), 7.72-7.61 (m, 3H), 7.17 (d, J = 8.37 Hz, 1H)</td>
<td>Calcd: C, 69.82; H, 3.75; N, 3.26.</td>
</tr>
<tr>
<td>Ia</td>
<td>9.57 (d, J = 7.02 Hz, 2H), 8.96 (d, J = 5.94 Hz, 2H), 8.91 (d, J = 7.02 Hz, 2H), 8.70-8.52 (m, 4H), 8.20 (d, J = 5.94 Hz, 2H), 8.07-7.93 (m, 3H), 7.74-7.62 (m, 3H), 7.33 (d, J = 8.37 Hz, 1H).</td>
<td>Calcd: C, 71.08; H, 3.78; N, 5.53.</td>
</tr>
<tr>
<td>IIb</td>
<td>9.75 (d, J = 7.02 Hz, 2H), 9.37 (d, J = 6.75 Hz, 2H), 9.07 (d, J = 7.02 Hz, 2H), 8.91 (d, J = 6.75 Hz, 2H), 8.73-8.54 (m, 4H), 8.09-7.94 (m, 3H), 7.76-7.63 (m, 3H), 7.34 (d, J = 8.37 Hz, 1H), 4.48 (s, 3H, -CH₃).</td>
<td>Calcd: C, 59.92; H, 3.57; N, 4.51.</td>
</tr>
</tbody>
</table>

### Table 2 Preparation and electrochemical characterization of pyridinium-conjugated assembly.

<table>
<thead>
<tr>
<th>Products</th>
<th>Electrolysis Potential (V vs. SCE)</th>
<th>Current efficiency (%)b</th>
<th>Oxidation of aromatic ring (V vs. SCE)c</th>
<th>Reduction of Pyridinium ring (V vs. SCE)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>1.20</td>
<td>100</td>
<td>1.54</td>
<td>-1.17</td>
</tr>
<tr>
<td>Ib</td>
<td>1.00</td>
<td>100</td>
<td>1.59</td>
<td>-1.22</td>
</tr>
<tr>
<td>IIa</td>
<td>1.00</td>
<td>100</td>
<td>1.05</td>
<td>-1.15</td>
</tr>
<tr>
<td>IIb</td>
<td>55</td>
<td>55</td>
<td>1.16</td>
<td>-0.46, -0.85d</td>
</tr>
<tr>
<td>Ic</td>
<td>20</td>
<td>20</td>
<td>1.46</td>
<td>-0.46, -0.85d</td>
</tr>
</tbody>
</table>

a) 270 MHz, DMSO-d₆, TMS; b) Isolated by Al₂Os preparative thick-layer chromatography (Merck, 150 F₂₅⁴⁰) with CH₃OH-CH₂Cl; Cl: (10: 90) as eluent.

The reaction was done at 0.1 F mol⁻¹ substrate (20% of theoretical charge); b) Current efficiency (%) calculated from ¹H-NMR measurement (see ref. i); c) Peak potentials were determined by cyclic voltammetry (CV) in CH₃CN containing 0.1 M tetrabutylammonium perchlorate (TBAP) with respect to the Fe³⁺ / Fe²⁺ couple as internal standard (see ref. i); d) Half-wave potentials (E₁/₂).
Cyclic voltammograms of the pyridinium-conjugated compounds show quasi-reversible reduction processes, which were attributable to the reduction of pyridinium derivatives. Compound IIc, which is an analogue of viologen, shows two sets of reversible redox peaks at −0.46 and −0.85 V.

The preparative-scale reaction of perylene π-radical cation generated by L/AgClO4, with several pyridine derivatives were also performed, as shown in Table 3. The reaction of perylene with Py gave IIa in high yield, as reported previously. When Bpy and MPP+ were used as nucleophiles, the reaction gave IIb and IIc with isolated yield of 50% and 28%, respectively. The product IIb, having similar structure to MPP+ nucleophile, can also act as a nucleophile. Furthermore, the reaction of the perylene π-radical cation with 20 times excess of IIb (molar ratio) afforded 4,4'-bis(3'-perylenyl)bipyrindinium bisperchlorate (IIId) in 30% yield. The reaction of perylene with excess amount of Bpy only gave IIb with no IIId, indicating that Bpy is stronger nucleophile than IIb.

In order to elucidate electronic structure of the pyridinium-conjugated assembly, the UV-visible absorption and fluorescence spectra of Ia were measured. The absorption maximum of Ia is red-shifted in comparison with perylene, as shown in Fig. 1. The Ia shows a broad absorption band with no vibrational structure in 350 to 450 nm. The solvent effect on the UV-visible absorption spectra of Ia indicated weak negative solvatochromism due to an intramolecular charge-transfer (IMCT) from the pyrene part to the pyridinium one (Fig. 1, inset).

The compound Ia shows two emission bands in both CHCl3 and CH3CN. The higher energy fluorescence band (Ia) with vibrational structure appears in the similar wavelength region to that of pyrene, while the lower energy one (Ia) has no structure. The latter fluorescence with maxima of 575 and 587 nm in CHCl3 and CH3CN, respectively, may be assigned to the emission from intramolecular charge transfer (IMCT) state. Compared to the emission spectra in both CHCl3 and CH3CN, the emission bands intensity of Ia increased with increasing the polarity, while the one of Ia is inverse. X-ray crystal structure of Ia reveals that the pyridinium plane is twisted against the pyrene one by torsion angle of about 70°, because of the steric repulsion between two hydrogen atoms on the N-adjacent carbons of pyridine and peri-position of pyrene. The charge-transfer character can be varied as a function of the dihedral angle between pyrene and pyridinium planes. Since a less twisted conformation strengthens the conjugation between pyrene and pyridinium moieties, the fluorescence intensity of pyrene would be reduced and that of the emission from the IMCT state might be enhanced. Thus the dihedral angle and the extent of conjugation between pyrene and pyridinium unit might be tunable by the solvent polarity in the excited state.

Compounds IIa, IIb and IIc also show red-shifted absorption maxima in comparison with perylene and IMCT band in the long wavelength region. The onset of absorption tail is red-shifted in the order of IIa<IIb<IIc. The fluorescence spectra revealed very weak emission band in comparison with perylene, which shows that the pyridinium substituents act as efficient fluorescence quencher.

### 4 Conclusion

We have demonstrated an efficient preparative method

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**Table 3** Preparation of pyridinium-conjugated perylene derivatives by chemical method.a

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Productb</th>
<th>Yield%c</th>
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<tbody>
<tr>
<td>Py</td>
<td>IIA</td>
<td>87</td>
</tr>
<tr>
<td>Bpy</td>
<td>IIb</td>
<td>50</td>
</tr>
<tr>
<td>MPP⁺</td>
<td>IIc</td>
<td>28</td>
</tr>
<tr>
<td>IIb</td>
<td>IIId</td>
<td>30d</td>
</tr>
</tbody>
</table>

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a The reaction was done as described in the text.
b All the products were isolated as ClO4⁻ salts.
c Isolation yield based on the perylene substrate.
d Calculation based on ¹H NMR with ethanol as internal standard in DMSO-d₆ without isolation.

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**Fig. 1** UV-vis absorption and fluorescence spectra of the pyridinium-conjugated compound Ia at room temperature. The excitation wavelength (λ-ex) is 342 nm. Inset: the dependence of λ-absct in UV-visible absorption spectra on the relative permittivity of solvent (εr) for compound Ia.

**Fig. 2** (a) ORTEP plot of Ia. Thermal ellipsoids are drawn at the 50% probability level. (b) Molecular structure of complex Ia. The torsion angle (τC21, N1, C1, C7) between pyridinium plane and pyrene plane is 68.7(2)°.
of a series of pyridinium-conjugated compounds based on the nucleophilic substitution reaction of pyrene and perylene \( \pi \)-radical cation generated electrochemically and chemically. These N-arylpyridinium salts show specific redox properties and solvent-dependent charge transfer character. Further investigation on fluorescence properties of these new molecules is currently underway.

Acknowledgement

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References

8) In this study, the anodic peaks in cyclic voltammograms of pyrene and perylene in CH\(_3\)CN solutions containing 0.1 M NaClO\(_4\) were observed at 1.20 V and 0.90 V vs. SCE, respectively. These values seem consistent with previously reported half-wave potentials of 1.16 and 0.85 V vs. SCE in CH\(_3\)CN for pyrene and perylene, respectively. To see: S. L. Murov, I. Carmichael, and G. L. Hug, Handbook of Photochemistry, 2nd ed., M. Dekker, New York, p.271 (1993).
10) 1-Methyl-4-(4'-pyridyl)-pyridinium perchlorate (MPP\(^{+}\)ClO\(_4\)\(^-\)) was synthesized and characterized according to the literature (1) and followed ion exchange with NaClO\(_4\). White powder. \(^1\)H NMR (270 MHz, DMSO-d$_6$, TMS): \(\delta\) 9.11 (d, J = 6.75 Hz, 2H), 8.87 (d, J = 5.98 Hz, 2H), 8.59 (d, J = 6.75 Hz, 2H), 8.03 (d, J = 5.94 Hz, 2H), 4.38 (s 3H, -CH$_2$). FAB-MS (NBA): \(m/e = 171\) (C$_{14}$H$_{15}$N$_2$). Anal. calc. for C$_{14}$H$_{15}$N$_2$ClO$_4$: C, 48.81; H, 4.10; N, 10.35. Found: C, 48.70; H, 4.35; N, 10.17.
13) The crystal data of 1-(4'-Pyrenyl)-pyridinium Perchlorate (Ia) are as follows: C$_{21}$H$_{15}$ClO$_4$N, Mw = 379.80. Triclinic, Space group P\(\alpha\), \(a = 7.688(2)\), \(b = 9.716(3)\), \(c = 11.981(3)\), \(\alpha = 93.955(8)\)\(^\circ\), \(\beta = 89.879(7)\)\(^\circ\), \(\gamma = 78.959(9)\)\(^\circ\), \(D_{c} = 1.458gcm^{-3}\), \(V = 849.24(4)\) \(\AA^3\), \(Z = 2\), \(R = 0.032\), \(R_w = 0.045\) for 3053 reflections with \(I > 3\sigma(I)\).