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Highly electron-deficient 1-propyl-3,5-dinitropyridinium: evaluation of electron-accepting ability and application as an oxidative quencher for metal complexes†

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Impacts of the nitro groups on the electron-accepting and oxidizing abilities of *N*-propylpyridinium were evaluated quantitatively. A 3,5-dinitro derivative has efficiently quenched emission from photosensitizing Ru(II) and Ir(III) complexes owing to the thermodynamically-favored electron transfer to the pyridinium whose LUMO is greatly lowered by the presence of electron-withdrawing nitro groups.

Introduction

Pyridines are typical electron-deficient heterocyclic compounds that can be seen all around us as substructures of functional materials such as pharmaceuticals, ligands, and optical and electronic devices.¹ The nucleophilic ring nitrogen, furthermore, undergoes *N*-alkylation, resulting in pyridinium salt. Owing to their highly electron-deficient aromatic character, pyridinium skeletons have been utilized in a variety of natural/artificial systems as electron acceptors as represented by NAD⁺,² methyl viologen³ and so forth.⁴ On the other hand, a nitro group exhibits strong electron-withdrawing ability due to both resonance and inductive effects, with the latter effect equivalent to two chloro groups.⁵ Therefore, a combination of the highly electron-deficient pyridinium and strong electron-withdrawing nitro group is expected to significantly increase the oxidation or electron-accepting abilities.

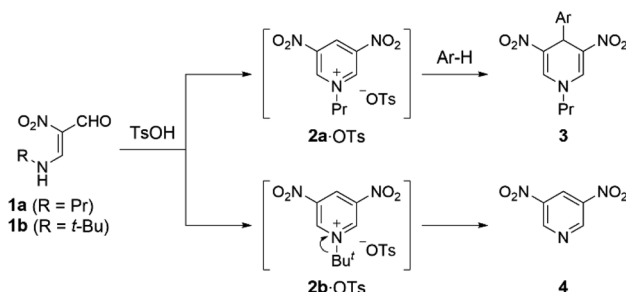
In our previous work, we have demonstrated that 1-propyl-3,5-dinitropyridinium salt **2a**·OTs is formed *in situ* upon treatment of *N*-propyl-β-formyl-β-nitroenamine **1a** (R = Pr) with *p*-toluenesulfonic acid (TsOH), and formation of the salt **2a**·OTs is confirmed by trapping as 4-arylated 1,4-dihydropyridine derivatives **3** with electron-rich benzenes.⁶ On the other hand, 3,5-dinitropyridine **4** was obtained when *N*-*tert*-butylenamine

1b (R = *t*-Bu) was subjected to the same reaction, which is because a stable *tert*-butyl cation is readily eliminated (Scheme 1). The easy access to 3,5-dinitropyridine **4** facilitates the *N*-modification to afford versatile *N*-alkyl-3,5-dinitropyridinium salts **2**. Indeed, treatment of **4** with propyl triflate (PrOTf) proceeded at room temperature to furnish **2a**·OTf. This easily modifiable feature prompted us to evaluate the electron-acceptability of its *N*-alkylated form (**2a**⁺) by comparing with 3-nitro and unsubstituted pyridinium relatives (**5**⁺ and **6**⁺) that are prepared from commercially available pyridines by *N*-propylation.

Experimental

Preparation of **2a**·OTf

A mixture of 3,5-dinitropyridine **4** (86 mg, 0.5 mmol) and PrOTf (122 mg, 0.63 mmol) was stirred without solvent at room temperature for 2 d. Colorless precipitates were collected and washed with CH₂Cl₂ to afford **2a**·OTf (95 mg, 0.28 mmol, 56%) as colorless powder, mp 217.0–217.8 °C. ¹H NMR (400 MHz, CD₃CN) δ 1.03 (t, *J* = 7.6 Hz, 3H), 2.12 (tq, *J* = 7.6, 7.6 Hz, 2H),



Scheme 1 Generation of 1-alkyl-3,5-dinitropyridinium salts **2**·OTs *in situ* from *N*-alkyl-β-formyl-β-nitroenamines **1**.

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† Electronic supplementary information (ESI) available: Cyclic voltammograms of the metal complexes and emission quenching data by **5**⁺ and **6**⁺. See DOI: <https://doi.org/10.1039/d4ra00845f>

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4.80 (t, $J = 7.6$ Hz, 2H), 9.78 (t, $J = 2.0$ Hz, 1H), 9.94 ppm (d, $J = 2.0$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 10.2 (CH_3), 25.3 (CH_2), 66.5 (CH_2), 121.8 (q, $J = 318.0$ Hz, CF_3), 135.9 (CH), 147.3 (CH), 147.9 ppm (C); ^{19}F NMR (376 MHz, CD_3CN) δ 79.36 ppm; HRMS (ESI-TOF) calcd for $\text{C}_8\text{H}_{10}\text{N}_3\text{O}_4$ (M^+): 212.0666, found: 212.0676.

Characterization of 5·OTf

mp 102.3–102.7 °C. ^1H NMR (400 MHz, CD_3CN) δ 1.00 (t, $J = 7.2$ Hz, 3H), 2.06 (tq, $J = 7.2, 7.2$ Hz, 2H), 4.66 (t, $J = 7.2$ Hz, 2H), 8.30 (dd, $J = 8.4$ Hz, 6.2 Hz, 1H), 9.01 (dd, $J = 6.2, 2.0$ Hz, 1H), 9.18 (ddd, $J = 8.4, 2.0, 1.2$ Hz, 1H), 9.63 ppm (d, $J = 1.2$ Hz 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 10.3 (CH_3), 25.2 (CH_2), 65.2 (CH_2), 125.1 (q, $J = 319$ Hz, CF_3), 130.4 (CH), 141.0 (CH), 142.7 (CH), 147.8 (C), 150.1 ppm (CH); ^{19}F NMR (376 MHz, CD_3CN) δ 79.31 ppm; HRMS (ESI-TOF) calcd for $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2$ (M^+): 167.0815, found: 167.0819.

Characterization of 6·OTf

^1H NMR (400 MHz, CD_3CN) δ 1.00 (t, $J = 7.6$ Hz, 3H), 2.06 (tq, $J = 7.6, 7.6$ Hz, 2H), 4.49 (t, $J = 7.6$ Hz, 2H), 8.03 (br, 2H), 8.51 (t, $J = 7.6$ Hz, 1H), 8.70 ppm (d, $J = 5.6$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 9.3 (CH_3), 24.0 (CH_2), 62.9 (CH_2), 120.9 (q, $J = 318$ Hz, CF_3), 128.1 (CH), 144.2 (CH), 145.5 ppm (CH); ^{19}F NMR (376 MHz, CD_3CN) δ 79.30 ppm; HRMS (ESI-TOF) calcd for $\text{C}_8\text{H}_{12}\text{N}$ (M^+): 122.0964, found: 122.0966.

Other chemicals

$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) is the same sample which has been used in the earlier literatures.⁷ $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ (ppyH = 2-phenylpyridine) was synthesized and purified similarly to the reported procedure.⁸ Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆, Wako Pure Chemical Industries) was purified by repeated recrystallizations from ethanol. Ferrocene (Wako Pure Chemical Industries) was used as supplied. Anhydrous or spectroscopic-grade CH_3CN (Wako Pure Chemical Industries) was used without further purification for the electrochemical or spectroscopic measurements, respectively.

Electrochemical measurements

Cyclic voltammetry of the complexes in CH_3CN at 298 K was performed by using a BAS ALS-1202A electrochemical analyzer with a three-electrode system using glassy-carbon working, Ag auxiliary, and Ag/AgNO₃ reference electrodes (~ 0.01 mol dm⁻³ (=M) in CH_3CN containing ~ 0.1 M TBAPF₆) supplied by BAS Inc. The sample solutions containing a pyridinium salt or metal complex (~ 1.0 mM) and TBAPF₆ as a supporting electrolyte (~ 0.1 M) in the absence or presence of ferrocene as an internal standard were deaerated by purging an argon-gas stream over 20 min prior to measurements. The potential sweep rate was 100 mV s⁻¹.

Emission quenching study

Emission spectra were recorded and emission quantum yields (Φ_{em}) were determined by the absolute method using

a Hamamatsu Photonics Quantaaurus-QY Plus C13534-02. Emission intensity at each wavelength was corrected for system spectral response so that the vertical axis of a spectrum corresponds to the photon number at each wavelength. Emission decay profiles of $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ was measured by using a Hamamatsu C4334 streak camera with a C5094 polychromator by exciting at 400 nm using second harmonics of a femtosecond-pulse mode-locked Ti:sapphire laser (MKS Instruments Spectra-Physics Tsunami® 3941-M1BB and 3980 frequency doubler/pulse selector, 1 MHz) and analyzed by a single exponential decay function. Sample solutions were deaerated by purging with an argon-gas stream for over 30 min.

Free energy changes for the electron-transfer processes ($-\Delta G$) were calculated by:⁹

$$-\Delta G = nF[E_{1/2}(\text{Q}^{+/0}) - E_{1/2}(\text{M}^*)] + Z_{\text{Q}}Z_{\text{M}}e^2/D_{\text{s}}d = nF[E_{1/2}(\text{Q}^{+/0}) - E_{1/2}(\text{M})] + E_0(\text{M}^*) + Z_{\text{Q}}Z_{\text{M}}e^2/D_{\text{s}}d \quad (1)$$

In eqn (1), $E_{1/2}(\text{Q}^{+/0})$ is the reduction potential of Q^+ , and $E_{1/2}(\text{M})$ is the oxidation potential of the complex (1.32 and 1.63 V vs. SCE for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, respectively, see Fig. S1†). $E_0(\text{M}^*)$ is the excited-state zeroth energy and has been determined to be 16 360 and 16 850 cm⁻¹ for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, respectively, by the Franck–Condon analysis.¹⁰ Z_{Q} and Z_{M} are the charges of Q^+ and complex. d is the sum of effective radii of Q^+ and complex estimated for the optimized geometries by DFT calculations (4.7, 4.6, 4.4, 6.2 and 6.2 Å for 2a^+ , 5^+ , 6^+ , $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, respectively). D_{s} , n , F and e are the static dielectric constant of the solvent (relative dielectric constant of CH_3CN : 37.5), the number of electrons transferred, the Faraday constant and the formal charge, respectively. It should be noted that, in eqn (1), an electrostatic work term for the electron-transfer products was omitted since the reduced pyridiniums are charge-neutral.

Theoretical calculations

Theoretical calculations for the compounds were conducted with Gaussian 09W software (Revision C.01).¹¹ The ground-state geometries of the pyridinium cations were optimized by using density functional theory (DFT) using the restricted B3LYP functional with 6-31+G(d,p) basis set. All the optimized geometries did not gave any negative frequencies under identical methodologies. Lowest-energy unoccupied molecular orbitals were plotted using GaussView 5.¹² All the calculations were carried out as in acetonitrile by using a polarizable continuum model (PCM).

Results and discussion

Down-field shifts of the ring protons in the ^1H NMR spectra in CD_3CN were observed as the number of nitro groups increased (Fig. 1), indicating a decrease in the electron density of the pyridine ring. All the pyridiniums 2a^+ , 5^+ and 6^+ in CH_3CN exhibited an irreversible reduction wave as shown in Fig. 2. Half reduction potential ($E_{1/2}$) was shifted to a positive potential region with increasing the nitro group ($E_{1/2} = -0.061$ (2a^+), -0.41 (5^+) and -0.80 V (6^+) vs. saturated calomel electrode



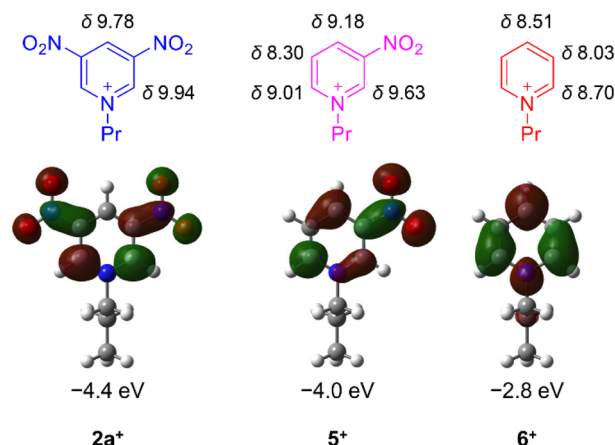


Fig. 1 Chemical shifts of ^1H NMR in CD_3CN (given in ppm) and LUMO distributions/energies of pyridiniums 2a^+ , 5^+ and 6^+ .

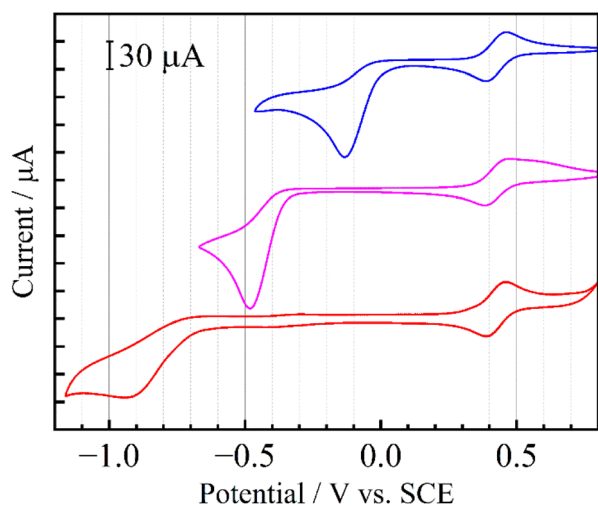


Fig. 2 Cyclic voltammograms of $2\text{a}^+\cdot\text{OTf}$ (blue), $5^+\cdot\text{OTf}$ (pink) and $6^+\cdot\text{OTf}$ (red) in deaerated CH_3CN containing 0.1 M TBAPF_6 . Reversible waves at around $+0.43$ V represent redox couples of ferrocene as an internal standard.

(SCE)). These tendencies were supported by DFT calculations, as the LUMO energy of 2a^+ was lowered to -4.4 eV (see Fig. 1). It is, furthermore, worth emphasizing that the $E_{1/2}$ value of 2a^+ is surprisingly positive even by comparing with that of methyl viologen (-0.44 V vs. sodium saturated calomel electrode (SSCE)¹³). In contrast to fully reversible redox behavior of methyl viologen and resulting applications as a redox shuttle,³ the highly-positive reduction potential of 2^+ is advantageously utilizable as a sacrificial electron acceptor in the various photochemical systems.

The strong electron-accepting ability of 2a^+ is utilizable as an oxidative quencher in photoinduced electron-transfer reactions. As shown in Fig. 3(a), emission from a famous photosensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$ (ref. 14) in CH_3CN (3.8×10^{-5} M) was reduced upon addition of 2a^+ ($(0.0\text{--}4.0) \times 10^{-3}$ M), and emission quantum yield (Φ_{em}) of $[\text{Ru}(\text{bpy})_3]^{2+}$ was decreased from 0.096 to

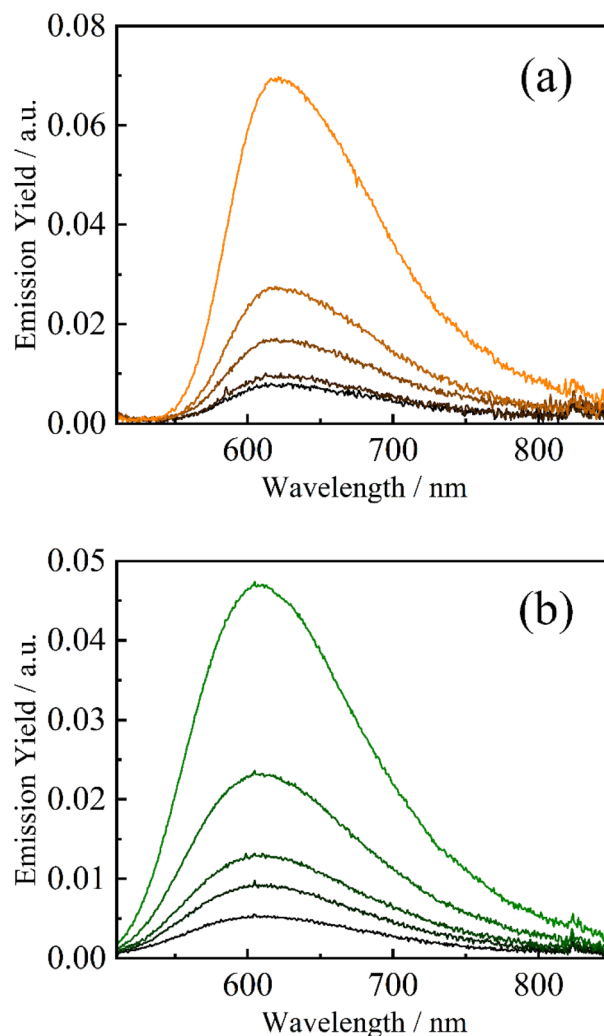


Fig. 3 Emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ (a, 3.8×10^{-5} M, $\lambda_{\text{ex}} = 500$ nm) and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (b, 3.8×10^{-4} M, $\lambda_{\text{ex}} = 470$ nm) in the absence and presence of dinitropyridinium salt $2\text{a}^+\cdot\text{OTf}$ ($(0.0\text{--}4.0) \times 10^{-3}$ M: orange/green \rightarrow black) in deaerated CH_3CN .

0.014 in the presence of 2a^+ (4.0×10^{-3} M). Emission from a cyclometalated iridium(III) complex $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ in CH_3CN (3.8×10^{-4} M) was also quenched when 2a^+ coexisted in a solution ($\Phi_{\text{em}} = 0.085$ and 0.017 in the absence and presence (4.0×10^{-3} M) of 2a^+ , respectively) as shown in Fig. 3(b). Stern–Volmer plots for emission quenching of the complexes by 2a^+ are shown in Fig. 4, together with those by 5^+ and 6^+ (emission spectra are shown in Fig. S2–S5[†]). The plots exhibited good linear dependences, irrespective of the complex and pyridinium, as expressed by the Stern–Volmer equation: $\Phi_{\text{em},0}/\Phi_{\text{em}} = 1 + k_q\tau_0[\text{Q}^+]$ with $\Phi_{\text{em},0}$ and Φ_{em} the emission quantum yields in the absence and presence of the quencher (i.e., 2a^+ , 5^+ or 6^+), respectively, k_q the quenching rate constant, τ_0 the excited-state lifetime of the complex in the absence of the quencher (890 and 300 ns for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, respectively), and $[\text{Q}^+]$ the quencher concentration. As clearly seen in Fig. 4 and Table 1, emission quenching by 2a^+ ($k_q = 1.6 \times 10^9$ and $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, respectively)



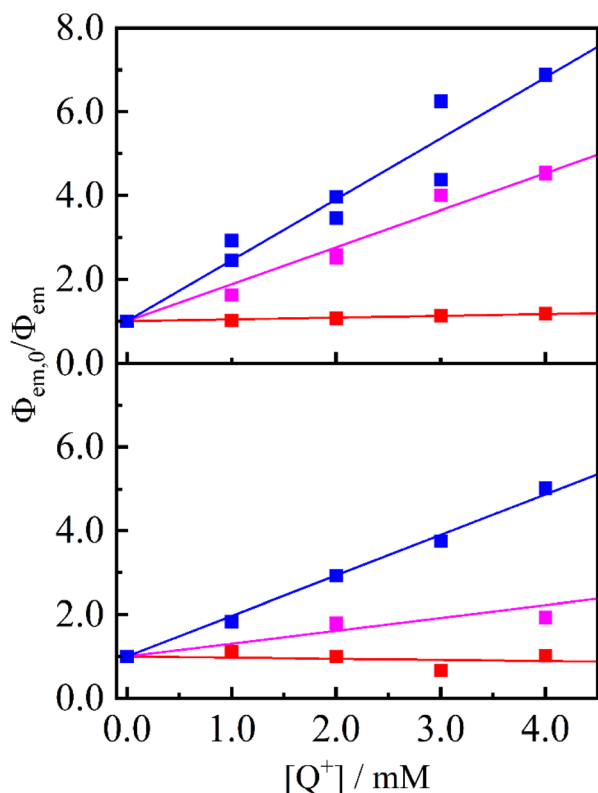


Fig. 4 Stern–Volmer plots for $[\text{Ru}(\text{bpy})_3]^{2+}$ (top panel) and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (bottom panel) quenching by 2a^+ (blue), 5^+ (pink) and 6^+ (red) in deaerated CH_3CN . Solid lines represent linear regressions with the intercept fixed at 1.

Table 1 Reduction potentials, driving forces for electron transfer and quenching rate constants of pyridiniums 2a^+ , 5^+ and 6^+

| Q^+ | $E_{1/2}/\text{V}$ | $[\text{Ru}(\text{bpy})_3]^{2+}$ | | $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ | |
|---------------|--------------------|----------------------------------|--|---|--|
| | | $-\Delta G/\text{eV}$ | $k_q/10^9 \text{ M}^{-1} \text{ s}^{-1}$ | $-\Delta G/\text{eV}$ | $k_q/10^9 \text{ M}^{-1} \text{ s}^{-1}$ |
| 2a^+ | −0.061 | +0.72 | 1.6 | +0.43 | 3.2 |
| 5^+ | −0.41 | +0.37 | 0.99 | +0.084 | 1.0 |
| 6^+ | −0.80 | +0.016 | 0.048 | −0.30 | <0.01 |

was more efficient than those by 5^+ and 6^+ ($k_q \leq 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), indicating that the more nitro group, the stronger the quenching ability.

The efficient emission quenching by 2a^+ can be discussed in terms of a driving force of the electron-transfer process ($-\Delta G$, Table 1), which is calculated from the reduction potentials of the pyridinium, the oxidation potentials of the excited-state complexes and so forth. The k_q value correlates well with the $-\Delta G$ value, suggesting that the observed emission quenching originates in the electron transfer from the metal complex (*i.e.*, $[\text{Ru}(\text{bpy})_3]^{2+}$ or $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$) in the excited state to pyridinium (*i.e.*, 2a^+ , 5^+ or 6^+). It is worth noting that the electron transfer between $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ to 6^+ is highly an endergonic process ($-\Delta G = -0.30 \text{ eV}$) and, therefore, no emission quenching has been observed. Thus, an introduction of a nitro

group(s) into a pyridinium skeleton improves the electron-accepting ability.

Conclusions

A combination of an electron-deficient pyridinium and electron-withdrawing nitro group(s) enhanced electron-accepting and oxidizing abilities. Each nitro-group introduction lowered the LUMO by several tenths of an electron volt, and dinitropyridinium 2a^+ especially served as an excellent oxidative quencher in photoinduced electron-transfer reactions. Since pyridinium derivatives have attracted increasing interest and utilized in a variety of photochemical systems such as natural/artificial photosynthesis, these nitropyridiniums are possible candidates as a new class of electron acceptors.

Author contributions

A. Ito: conceptualization, data curation, writing – original draft, and supervision. Y. Kuroda, K. Iwai and S. Yokoyama: investigation. N. Nishiwaki: supervision and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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