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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 viologen[3] 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.
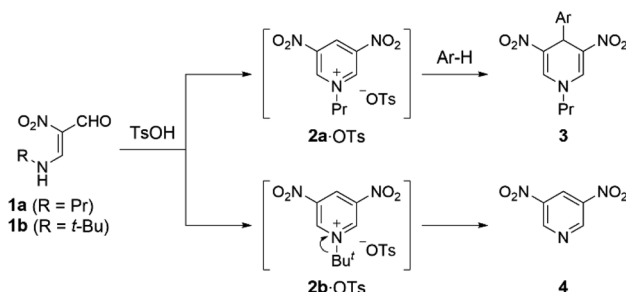
In our previous work, we have demonstrated that 1-propyl-3,5-dinitropyridinium salt **2a**·OTs is formed *in situ* upon treatment of *N*-propyl-β-formyl-β-nitroenamine **1a** (R = Pr) with *p*-toluenesulfonic acid (TsOH), and formation of the salt **2a**·OTs is confirmed by trapping as 4-arylated 1,4-dihydropyridine 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 CH$_2$Cl$_2$ to afford **2a**·OTf (95 mg, 0.28 mmol, 56%) as colorless powder, mp 217.0–217.8 °C. ^{1}H NMR (400 MHz, CD$_3$CN) δ 1.03 (t, *J* = 7.6 Hz, 3H), 2.12 (tq, *J* = 7.6, 7.6 Hz, 2H),

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

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$_3$CN) 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$_3$CN) δ 79.36 ppm; HRMS (ESI-TOF) calcd for C$_8$H$_{10}$N$_3$O$_4$ (M$^+$): 212.0666, found: 212.0676.

Characterization of 5·OTf

mp 102.3–102.7 °C. ^{1}H NMR (400 MHz, CD$_3$CN) 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$_3$CN) δ 10.3 (CH$_3$), 25.2 (CH$_2$), 65.2 (CH2), 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$_3$CN) δ 79.31 ppm; HRMS (ESI-TOF) calcd for C$_8$H$_{11}$N$_2$O$_2$ (M$^+$): 167.0815, found: 167.0819.

Characterization of 6·OTf

^{1}H NMR (400 MHz, CD$_3$CN) 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$_3$CN) 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$_3$CN) δ 79.30 ppm; HRMS (ESI-TOF) calcd for C$_8$H$_{12}$N (M$^+$): 122.0964, found: 122.0966.

Other chemicals

[Ru(bpy)$_3$](PF$_6$)$_2$ (bpy = 2,2′-bipyridine) is the same sample which has been used in the earlier literatures.[7] [Ir(ppy)$_2$(bpy)]PF$_6$ (ppyH = 2-phenylpyridine) was synthesized and purified similarly to the reported procedure.[8] Tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$, 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$_3$CN (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$_3$CN 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/AgNO$_3$ reference electrodes ($\sim$0.01 mol dm^{-3} (=M) in CH$_3$CN containing $\sim$0.1 M TBAPF$_6$) supplied by BAS Inc. The sample solutions containing a pyridinium salt or metal complex ($\sim$1.0 mM) and TBAPF$_6$ as a supporting electrolyte ($\sim$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 Quantaurus-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 [Ir(ppy)$_2$(bpy)]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]

$$-\Delta G = nF[E_{1/2}(Q^{+/0}) - E_{1/2}(M^*)] + Z_Q Z_M e^2/D_s d = nF[E_{1/2}(Q^{+/0}) - E_{1/2}(M)] + E_0(M^*) + Z_Q Z_M e^2/D_s d \quad (1)$$

In eqn (1), $E_{1/2}(Q^{+/0})$ is the reduction potential of Q$^+$, and $E_{1/2}(M)$ is the oxidation potential of the complex (1.32 and 1.63 V $vs.$ SCE for [Ru(bpy)$_3$]$^{2+}$ and [Ir(ppy)$_2$(bpy)]$^+$, respectively, see Fig. S1†). $E_0(M^*)$ is the excited-state zeroth energy and has been determined to be 16 360 and 16 850 cm^{-1} for [Ru(bpy)$_3$]$^{2+}$ and [Ir(ppy)$_2$(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$^+$**, [Ru(bpy)$_3$]$^{2+}$ and [Ir(ppy)$_2$(bpy)]$^+$, respectively). D_s, n, F and e are the static dielectric constant of the solvent (relative dielectric constant of CH$_3$CN: 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 ^{1}H NMR spectra in CD$_3$CN 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$_3$CN 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
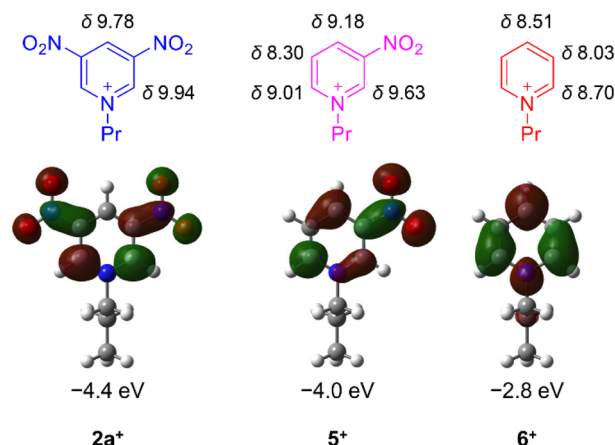
Fig. 1 Chemical shifts of ^{1}H NMR in CD$_3$CN (given in ppm) and LUMO distributions/energies of pyridiniums **2a$^+$**, **5$^+$** and **6$^+$**.
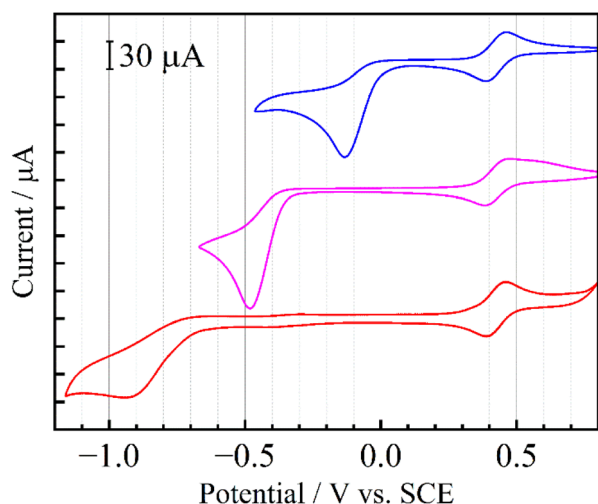

Fig. 2 Cyclic voltammograms of **2a·OTf** (blue), **5·OTf** (pink) and **6·OTf** (red) in deaerated CH$_3$CN containing 0.1 M TBAPF$_6$. Reversible waves at around +0.43 V represent redox couples of ferrocene as an internal standard.

Fig. 3 Emission spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ (a, 3.8 × 10^{-5} M, λ_{ex} = 500 nm) and [Ir(ppy)$_2$(bpy)]PF$_6$ (b, 3.8 × 10^{-4} M, λ_{ex} = 470 nm) in the absence and presence of dinitropyridinium salt **2a·OTf** ((0.0–4.0) × 10^{-3} M: orange/green → black) in deaerated CH$_3$CN.

(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 [Ru(bpy)$_3$]$^{2+}$ (ref. 14) in CH$_3$CN (3.8 × 10^{-5} M) was reduced upon addition of **2a$^+$** ((0.0–4.0) × 10^{-3} M), and emission quantum yield ($\Ph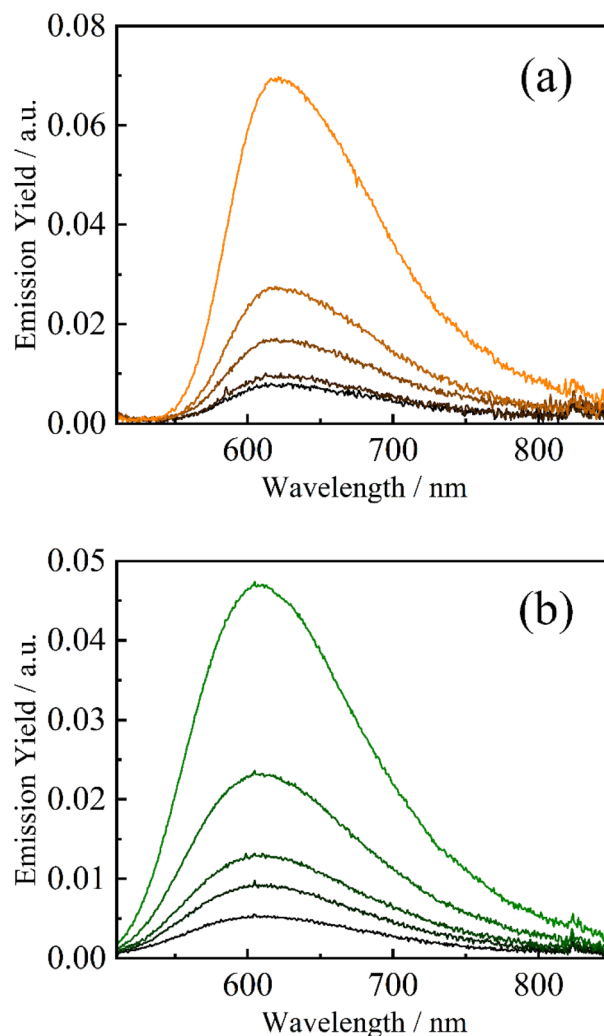i_{em}$) of [Ru(bpy)$_3$]$^{2+}$ was decreased from 0.096 to 0.014 in the presence of **2a$^+$** (4.0 × 10^{-3} M). Emission from a cyclometalated iridium(III) complex [Ir(ppy)$_2$(bpy)]$^+$ in CH$_3$CN (3.8 × 10^{-4} M) was also quenched when **2a$^+$** coexisted in a solution (Φ_{em} = 0.085 and 0.017 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: $\Phi_{em,0}/\Phi_{em}$ = 1 + $k_q\tau_0$[Q$^+$] with $\Phi_{em,0}$ 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 [Ru(bpy)$_3$]$^{2+}$ [15] and [Ir(ppy)$_2$(bpy)]$^+$, respectively), and [Q$^+$] the quencher concentration. As clearly seen in Fig. 4 and Table 1, emission quenching by **2a$^+$** (k_q = 1.6 × 10^9 and 3.2 × 10^9 M^{-1} s^{-1} for [Ru(bpy)$_3$]$^{2+}$ and [Ir(ppy)$_2$(bpy)]$^+$, respectively)

Fig. 4 Stem−Volmer plots for $[Ru(bpy)_3]^{2+}$ (top panel) and $[Ir(ppy)_2(bpy)]^+$ (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$^+$ | $E_{1/2}$/V | $[Ru(bpy)_3]^{2+}$ | | | $[Ir(ppy)_2(bpy)]^+$ | |
		$-\Delta G$/eV	$k_q/10^9$ M^{-1} s^{-1}		$-\Delta G$/eV	$k_q/10^9$ M^{-1} 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

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: conceptulization, 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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was more efficient than those by **5$^+$** and **6$^+$** ($k_q \leq 1.0 \times 10^9$ M^{-1} 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.*, $[Ru(bpy)_3]^{2+}$ or $[Ir(ppy)_2(bpy)]^+$) in the excited state to pyridinium (*i.e.*, **2a$^+$**, **5$^+$** or **6$^+$**). It is worth noting that the electron transfer between $[Ir(ppy)_2(bpy)]^{+*}$ to **6$^+$** is highly an endergonic process ($-\Delta G = -0.30$ eV) and, therefore, no emission quenching has been observed. Thus, an introduction of a nitro

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