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## Highly electron-deficient 1-propyl-3,5dinitropyridinium: evaluation of electron-accepting ability and application as an oxidative guencher for metal complexes<sup>†</sup>

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

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whose LUMO is greatly lowered by the presence of electron-withdrawing nitro groups.

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## 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.<sup>1</sup> 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<sup>+</sup>,<sup>2</sup> methyl viologen<sup>3</sup> and so forth.<sup>4</sup> 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.<sup>5</sup> 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- $\beta$ -formyl- $\beta$ -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** ( $\mathbf{R} = t$ -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-3,5dinitropyridinium salts 2. Indeed, treatment of 4 with propyl triflate (PrOTf) proceeded at room temperature to furnish  $2a \cdot OTf$ . 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  $(5^+ \text{ and } 6^+)$  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  $CH_2Cl_2$  to afford  $2a \cdot OTf$  (95 mg, 0.28 mmol, 56%) as colorless powder, mp 217.0-217.8 °C. <sup>1</sup>H NMR (400 MHz,  $CD_3CN$ )  $\delta$  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- $\beta$ -formyl- $\beta$ -nitroenamines 1.

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<sup>†</sup> Electronic supplementary information (ESI) available: Cyclic voltammograms of the metal complexes and emission quenching data by  $\mathbf{5}^{*}$  and  $\mathbf{6}^{*}.$  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); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN)  $\delta$  10.2 (CH<sub>3</sub>), 25.3 (CH<sub>2</sub>), 66.5 (CH<sub>2</sub>), 121.8 (q, J = 318.0 Hz, CF<sub>3</sub>), 135.9 (CH), 147.3 (CH), 147.9 ppm (C); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN)  $\delta$  79.36 ppm; HRMS (ESI-TOF) calcd for C<sub>8</sub>H<sub>10</sub>N<sub>3</sub>O<sub>4</sub> (M<sup>+</sup>): 212.0666, found: 212.0676.

#### Characterization of 5 · OTf

mp 102.3–102.7 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>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); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN) δ 10.3 (CH<sub>3</sub>), 25.2 (CH<sub>2</sub>), 65.2 (CH<sub>2</sub>), 125.1 (q, J = 319 Hz, CF<sub>3</sub>), 130.4 (CH), 141.0 (CH), 142.7 (CH), 147.8 (C), 150.1 ppm (CH); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN) δ 79.31 ppm; HRMS (ESI-TOF) calcd for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>): 167.0815, found: 167.0819.

#### Characterization of 6 · OTf

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>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); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN) δ 9.3 (CH<sub>3</sub>), 24.0 (CH<sub>2</sub>), 62.9 (CH<sub>2</sub>), 120.9 (q, J = 318 Hz, CF<sub>3</sub>), 128.1 (CH), 144.2 (CH), 145.5 ppm (CH); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN) δ 79.30 ppm; HRMS (ESI-TOF) calcd for C<sub>8</sub>H<sub>12</sub>N (M<sup>+</sup>): 122.0964, found: 122.0966.

#### Other chemicals

 $[Ru(bpy)_3](PF_6)_2 (bpy = 2,2'-bipyridine) is the same sample which$  $has been used in the earlier literatures.<sup>7</sup> [Ir(ppy)_2(bpy)]PF_6 (ppyH$ = 2-phenylpyridine) was synthesized and purified similarly to thereported procedure.<sup>8</sup> Tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Wako Pure Chemical Industries) waspurified by repeated recrystallizations from ethanol. Ferrocene(Wako Pure Chemical Industries) was used as supplied. Anhydrous or spectroscopic-grade CH<sub>3</sub>CN (Wako Pure ChemicalIndustries) was used without further purification for the electrochemical or spectroscopic measurements, respectively.

#### **Electrochemical measurements**

Cyclic voltammetry of the complexes in CH<sub>3</sub>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<sub>3</sub> reference electrodes (~0.01 mol dm<sup>-3</sup> (=M) in CH<sub>3</sub>CN containing ~0.1 M TBAPF<sub>6</sub>) supplied by BAS Inc. The sample solutions containing a pyridinium salt or metal complex (~1.0 mM) and TBAPF<sub>6</sub> 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<sup>-1</sup>.

#### Emission quenching study

Emission spectra were recorded and emission quantum yields  $(\Phi_{em})$  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<sup>®</sup> 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:<sup>9</sup>

$$-\Delta G = nF[E_{1/2}(Q^{+/0}) - E_{1/2}(M^*)] + Z_Q Z_M e^2 / D_s d = nF[E_{1/2}(Q^{+/0}) - E_{1/2}(M)] + E_0(M^*) + Z_Q Z_M e^2 / D_s d$$
(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<sup>+</sup>).  $E_0(M^*)$  is the excited-state zeroth energy and has been determined to be 16360 and 16850 cm<sup>-1</sup> for  $[Ru(bpy)_3]^{2+}$  and [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup>, respectively, by the Franck–Condon analysis.<sup>10</sup>  $Z_{\rm O}$  and  $Z_{\rm M}$  are the charges of  $Q^+$  and complex. *d* is the sum of effective radii of Q<sup>+</sup> and complex estimated for the optimized geometries by DFT calculations (4.7, 4.6, 4.4, 6.2 and 6.2 Å for  $2\mathbf{a}^+, \mathbf{5}^+, \mathbf{6}^+, [\operatorname{Ru}(\operatorname{bpy})_3]^{2+} \text{ and } [\operatorname{Ir}(\operatorname{ppy})_2(\operatorname{bpy})]^+, \text{ respectively}). D_s, n, F$ and e are the static dielectric constant of the solvent (relative dielectric constant of CH<sub>3</sub>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).<sup>11</sup> 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.<sup>12</sup> 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 <sup>1</sup>H NMR spectra in CD<sub>3</sub>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<sub>3</sub>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 <sup>1</sup>H NMR in CD<sub>3</sub>CN (given in ppm) and LUMO distributions/energies of pyridiniums  $2a^+$ ,  $5^+$  and  $6^+$ .



Fig. 2 Cyclic voltammograms of  $2a \cdot OTf$  (blue),  $5 \cdot OTf$  (pink) and  $6 \cdot OTf$  (red) in deaerated CH<sub>3</sub>CN containing 0.1 M TBAPF<sub>6</sub>. 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)<sup>13</sup>). In contrast to fully reversible redox behavior of methyl viologen and resulting applications as a redox shuttle,<sup>3</sup> 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<sub>3</sub>CN (3.8 × 10<sup>-5</sup> M) was reduced upon addition of  $2a^+$  ((0.0–4.0) × 10<sup>-3</sup> M), and emission quantum yield ( $\Phi_{\text{em}}$ ) of  $[\text{Ru}(\text{bpy})_3]^{2^+}$  was decreased from 0.096 to



Fig. 3 Emission spectra of [Ru(bpy)\_3](PF\_6)\_2 (a,  $3.8\times10^{-5}$  M,  $\lambda_{ex}=500$  nm) and [Ir(ppy)\_2(bpy)]PF\_6 (b,  $3.8\times10^{-4}$  M,  $\lambda_{ex}=470$  nm) in the absence and presence of dinitropyridinium salt **2a**·OTf ((0.0–4.0)  $\times10^{-3}$  M: orange/green  $\rightarrow$  black) in deaerated CH\_3CN.

0.014 in the presence of  $2a^+$  (4.0  $\times$  10<sup>-3</sup> M). Emission from a cyclometalated iridium(III) complex [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup> in CH<sub>3</sub>CN  $(3.8 \times 10^{-4} \text{ M})$  was also quenched when  $2a^+$  coexisted in a solution ( $\Phi_{\rm em} = 0.085$  and 0.017 in the absence and presence  $(4.0 \times 10^{-3} \text{ M})$  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<sup>†</sup>). The plots exhibited good linear dependences, irrespective of the complex and pyridinium, as expressed by the Stern–Volmer equation:  $\Phi_{\rm em,0}/\Phi_{\rm em}$  $= 1 + k_q \tau_0 [Q^+]$  with  $\Phi_{em,0}$  and  $\Phi_{em}$  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,  $\tau_{0}$  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  $2a^+$  ( $k_q = 1.6 \times 10^9$  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 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<sub>3</sub>CN. Solid lines represent linear regressions with the intercept fixed at **1**.

 $\label{eq:table_$ 

		$[Ru(bpy)_3]^{2+}$		[Ir(ppy) <sub>2</sub> (bpy)] <sup>+</sup>	
$\mathbf{Q}^+$	$E_{1/2}/\mathrm{V}$	$-\Delta G/eV$	$k_{\rm q}/10^9~{ m M}^{-1}~{ m s}^{-1}$	$-\Delta G/eV$	$k_{\rm q}/10^9~{ m M}^{-1}~{ m s}^{-1}$
2a <sup>+</sup> 5 <sup>+</sup> 6 <sup>+</sup>	$-0.061 \\ -0.41 \\ -0.80$	+0.72 +0.37 +0.016	1.6 0.99 0.048	$^{+0.43}_{+0.084}_{-0.30}$	3.2 1.0 <0.01

was more efficient than those by 5<sup>+</sup> and 6<sup>+</sup> ( $k_q \le 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), 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 electronaccepting 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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