Syntheses, structural characterization and photophysical properties of 4-(2-pyridyl)-1,2,3-triazole rhenium(I) complexes[†]

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Novel chelators, i.e., 4-(2-pyridyl)-1,2,3-triazole derivatives, were synthesized by means of Cu(I)-catalyzed 1,3-dipolar cycloaddition and used to prepare luminescent Re(I) complexes [ReCl(CO)₃(Bn-pyta)], [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glc-pyta)] (Bn-pyta = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole, AcGlc-pyta = 2-(4-(2-pyridyl)-1,2,3-triazol-1-yl)ethyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside, Glc-pyta = 2-(4-(2-pyridyl)-1,2,3-triazol-1-yl)ethyl β-D-glucopyranoside). X-Ray crystallography of Bn-pyta and Glc-pyta indicated an azocompound-like structure while the 1,2,4-triazole isomer has an azine character. [ReCl(CO)₃(Bn-pyta)] crystallized in the monoclinic system with space group $P2_1/n$. Bn-pyta ligand coordinates with the nitrogen atoms of the 2-pyridyl group and the 3-position of 1,2,3-triazole ring, which is a very similar coordinating fashion to that of the 2,2'-bipyridine derivative. The glucoconjugated Re(I) complexes [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glc-pyta)] hardly crystallized, and were analyzed by applying extended X-ray absorption fine structure (EXAFS) analysis. The EXAFS analyses suggested that the glucoconjugation at the 1-position of the 1,2,3-triazole makes no influence to the coordinating fashion of 4-(2-pyridyl)-1,2,3-triazole. [ReCl(CO)₃(Bn-pyta)] showed a blue-shifted maximum absorption (333 nm, 3.97×10^3 M⁻¹ cm⁻¹) compared with [ReCl(CO)₃(bpy)] (371 nm, 3.35×10^3 M⁻¹ cm⁻¹) $10^3 \text{ M}^{-1} \text{ cm}^{-1}$). These absorptions were clearly assigned to be the mixed metal-ligand-to-ligand charge transfer (MLLCT) on the basis of time-dependent density functional theory calculation. The luminescence spectrum of [ReCl(CO)₃(Bn-pyta)] also showed this blue-shifted feature when compared with that of [ReCl(CO)₃(bpy)]. The luminescence lifetime of [ReCl(CO)₃(Bn-pyta)] was determined to be 8.90 μ s in 2-methyltetrahydrofuran at 77 K, which is longer than that of [ReCl(CO)₃(bpy)] (3.17 μ s). The blue-shifted electronic absorption and elongated luminescence lifetime of [ReCl(CO)₃(Bn-pyta)] suggested that 4-(2-pyridyl)-1,2,3-triazole functions as an electron-rich bidentate chelator.

Introduction

The development of non-radioactive biological labels is a recent important research topic, and has attracted a great deal of attention in fields including photochemistry, medicinal chemistry

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and molecular biology.¹⁻⁴ Organic fluorophores and luminescent lanthanide chelates were the first to be developed,⁵ but the use of these reagents has faced limitations relating to photodegradation rates, pH dependence, fluorescence lifetimes, Stokes shifts and design of new chelators. In an effort to overcome these limitations, luminescent transition metal complexes such as rhenium(I), ruthenium(II) and iridium(III) polypyridines have been developed, and α,α' -diimines such as 2,2'-bipyridine (bpy) have extensively been used as chelators.⁶⁻¹⁴ These complexes show intense and longlived photoluminescence in the visible region with the emission energy affected by chelators.¹⁵ Thus, the synthesis of new versatile chelating ligands is essential for the development of tailor-made luminescent metal labels.

The photophysical and photochemical properties of luminescent metal complexes can be modulated by controlling the electronic structure of α, α' -diimine ligands, which act as electron acceptors from a metal center. Introduction of electron-donating or electron-withdrawing groups to the α, α' -diimine ligands effectively adjusts the LUMO level of the complexes. In systematic studies on the photophysics of rhenium(I), osmium(II) and rhodium(III) complexes with polypyridyl ligands,¹⁶⁻¹⁸ it was found that electronic

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absorption and luminescence spectra of rhenium(I) complexes $[ReCl(CO)_3(4,4'-X-bpy)]$ are highly dependent on the nature of the 4,4'-substituents (X) of 2,2'-bipyridine.¹⁶ The blue-shifts of absorption and emission maxima by electron-donating groups such as amino groups are explained by the "energy-gap law".¹⁹⁻²² Fivemembered heterocyclic ligands such as imidazole, pyrazole and triazole have the greater tunability of the π -electronic structure and the synthetic versatility of luminescent metal complexes. Multiple coordination sites, however, may enable these azole ligands to form complicated multinuclear complexes with or without the electronic interaction between metal ions. To eliminate this complexity, ligands with an additional coordination site (such as a 2-pyridyl group) have been developed. Thus, imidazole, pyrazole and 1,2,4triazole with a 2-pyridyl group have been used as ligands for these luminescent complexes.²³⁻³⁹ Compared with the rich coordination chemistry of 1,2,4-triazole derivatives, 1,2,3-triazole derivatives have been little-studied except in antitumor dinuclear platinum(II) complexes,⁴⁰⁻⁴² dinuclear ruthenium(II) complexes,^{43,44} and spin-

crossover iron(II) complexes.45-47 The aim of this study is to develop a convenient synthesis of 4-(2-pyridyl)-1,2,3-triazole (pyta) derivatives as new α,α' -diiminelike ligands for luminescent metal complexes. The regioselective cycloaddition of azides and terminal alkynes, now well-known as "click chemistry", is a convenient method of synthesis of 1,2,3-triazole derivatives,48 and was first applied to install the coordination site on biomolecules for complexation to rhenium and technetium.⁴⁹ This methodology is now rapidly growing in the field of coordination chemistry, and was recently applied to the synthesis of palladium(II) and platinum(II) complexes,50 and iron(II), ruthenium(II) and europium(III) complexes.⁵¹ We here report "click chemistry" syntheses of 1-benzyl-4-(2-pyridyl)-1,2,3triazole (Bn-pyta), 2-(4-(2-pyridyl)-1,2,3-triazol-1-yl)ethyl 2,3,4,6tetra-O-acetyl-β-D-glucopyranoside (AcGlc-pyta) and 2-(4-(2pyridyl)-1,2,3-triazol-1-yl)ethyl β-D-glucopyranoside (Glc-pyta) and the structures and photophysical properties of rhenium(I) complexes having these ligands.

Experimental

General information and materials

All reagents were commercial products and used without further purification. 2-Azidoethyl 2,3,4,5-tetra-*O*-acetyl-β-Dglucopyranoside was prepared according to the literature.^{52 1}H and ¹³C NMR spectra were recorded using a JEOL AL-400 instrument. Electronic absorption spectra were recorded on JASCO V-670 or JASCO V-570 spectrophotometers. Elemental analyses were carried out using a Perkin-Elmer PE2400 Series II CHNS/O Analyzer (Nara Institute of Science and Technology). IR spectra were recorded on a Shimadzu FT-IR 8700 as KBr disks. Steadystate luminescence spectra were recorded on a JASCO FP-6600 spectrofluorometer. Electron-spray ionization time-of-flight (ESI-TOF) mass spectra were recorded on a JEOL JMS-T100LC instrument.

1-Benzyl-4-(2-pyridyl)-1,2,3-triazole (Bn-pyta). Benzyl azide (0.508 g) and 2-ethynylpyridine (0.419 g) were dissolved in a mixture of THF (40 mL) and water (40 mL). To the solution was added 1 M sodium ascorbate (aq) (0.8 mL) and 7.5 wt% CuSO₄ (aq) (1.3 mL). The mixture was stirred at 50 °C overnight.

After the mixture had cooled down, THF was taken off under reduced pressure. The resulting precipitate of the Cu complex was decomposed by addition of small portions of aqueous ammonia. The organics were extracted with CHCl₃, and washed with water, sat. NaHCO₃ (aq) and brine. After drying over Na₂SO₄, the solvent was taken off under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate) to give a white solid (0.720 g). Yield 80%. ¹H NMR (400 MHz, CDCl₃): δ /ppm = 8.53 (ddd, ${}^{3}J$ = 4.9 Hz, ${}^{4}J$ = 1.8 Hz, ${}^{5}J$ = 1.0 Hz, 1H, 6-pyH), 8.17 (dt, ${}^{3}J = 7.9$ Hz, ${}^{4}J = 1.1$ Hz, 1H, 3pyH), 8.04 (s, 1H, 5-triazoleH), 7.76 (dt, ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1.8$ Hz, 1H, 4-pyH), 7.40–7.31 (m, 5H, PhH), 7.20 (ddd, ${}^{3}J = 7.5$ and 4.9 Hz, ${}^{4}J = 1.2$ Hz, 1H, 5-pyH), 5.58 (s, 2H, -CH₂-). ${}^{13}C$ NMR $(100 \text{ MHz}, \text{CDCl}_3): \delta/\text{ppm} = 150.05 (C), 149.15 (6-pyC), 148.56$ (C), 136.75 (4-pyC), 134.17 (C), 129.05 (PhC), 128.73 (PhC), 128.19 (PhC), 122.74 (5-pyC), 121.78 (5-triazoleC), 120.12 (3pyC), 54.45 (-CH₂-). Anal. calcd. for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.92; H, 4.98; N, 23.95. IR (KBr): $\nu/cm^{-1} =$ 1605, 1597, 1421, 1225, 1045, 787, 727. UV-vis (CH₃CN): λ/nm $(\varepsilon \times 10^{-3}/M^{-1} \text{ cm}^{-1}) = 280 (8.53), 241 (15.3).$

2-(4-(2-Pyridyl)-1,2,3-triazol-1-yl)ethyl 2,3,4,6-tetra-O-acetylβ-D-glucopyranoside (AcGlc-pyta). 2-Azidoethyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (1.87 g) and 2-ethynylpyridine (0.499 g) were dissolved in the mixture of THF (50 mL) and water (50 mL). To the solution was added 1 M sodium ascorbate (aq) (0.9 mL) and 7.5 wt% CuSO₄(aq) (1.5 mL). The mixture was stirred at 50-60 °C for 2 days in the dark. After concentration under reduced pressure, the products were extracted with ethyl acetate. After drying over Na₂SO₄, the solvent was taken off under reduced pressure. The crude product was purified by silica gel column chromatography followed by recrystallization from ethyl acetate-hexane to give colorless needle-like crystals (1.71 g). Yield 73%. ¹H NMR (400 MHz, CDCl₃): δ /ppm = 8.57 (ddd, ³J = 4.9 Hz, ${}^{4}J = 1.8$ Hz, ${}^{5}J = 0.93$ Hz, 1H, 6-pyH), 8.17 (s, 1H, 5triazole*H*), 8.14 (ddd, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.2$ Hz, ${}^{5}J = 0.93$ Hz, 1H, 3-pyH), 7.76 (dt, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.8$ Hz, 1H, 4-pyH), 7.22 (ddd, ${}^{3}J = 4.9$ and 7.7 Hz, ${}^{4}J = 1.2$ Hz, 1H, 5-pyH), 5.16 $(t, {}^{3}J = 9.4 \text{ Hz}, 1\text{H}, 3\text{-Glc}H), 5.07 (t, {}^{3}J = 9.8 \text{ Hz}, 1\text{H}, 4\text{-Glc}H),$ 5.02 (dd, ${}^{3}J = 9.6$ Hz, ${}^{3}J = 8.0$ Hz, 1H, 2-GlcH), 4.69 (ddd, ${}^{2}J =$ 14.5 Hz, ${}^{3}J = 3.0$ Hz, ${}^{3}J = 2.0$ Hz, 1H, -O-CH₂-CHH-N-), 4.57 $(ddd, {}^{2}J = 14.5 \text{ Hz}, {}^{3}J = 9.0 \text{ Hz}, {}^{3}J = 3.0 \text{ Hz}, 1\text{H}, -\text{O-CH}_{2}\text{-CH}H$ N-), 4.49 (d, ${}^{3}J = 7.9$ Hz, 1H, 1-GlcH), 4.30 (ddd, ${}^{2}J = 10.5$ Hz, ${}^{3}J = 3.0$ Hz, ${}^{3}J = 2.0$ Hz, 1H, -O-CHH-CH₂-N-), 4.24 (dd, ${}^{2}J =$ $12.4 \text{ Hz}, {}^{3}J = 4.7 \text{ Hz}, 1\text{H}, 6\text{-Glc}H\text{H}), 4.13 (dd, {}^{2}J = 12.3 \text{ Hz}, {}^{3}J =$ 2.3 Hz, 1H, 6-GlcH*H*), 3.96 (ddd, ${}^{2}J = 10.5$ Hz, ${}^{3}J = 9.0$ Hz, ${}^{3}J = 3.0$ Hz, 1H, -O-CHH-CH₂-N-), 3.68 (ddd, ${}^{3}J = 7.0$ Hz, ${}^{3}J =$ 4.6 Hz, ${}^{3}J = 2.3$ Hz, 5-GlcH), 2.08 (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 1.98 (s, 3H, CH₃), 1.90 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): *δ*/ppm = 170.41 (*C*=O), 169.93 (*C*=O), 169.25 (*C*=O), 169.15 (C=O), 149.95 (C), 149.24 (6-pyCH), 148.20 (C), 136.66 (4-pyCH), 123.16 (5-triazoleCH), 122.71 (5-pyCH), 119.97 (3pyCH), 100.45 (1-GlcC), 72.52 (3-GlcC), 71.95 (5-GlcC), 70.80 (2-GlcC), 68.13 (4-GlcC), 67.78 (-O-CH₂-CH₂-N-), 61.68 (6-GlcC), 50.20 (-O-CH₂-CH₂-N-), 20.85 (CH₃), 20.70 (CH₃), 20.52 (CH₃). ESI-TOF HRMS: m/z for $C_{23}H_{28}O_{10}N_4Na$ ([M + Na]⁺) calcd. 543.17031, found 543.17126 (error 0.95 mmu, 1.75 ppm). Anal. calcd. for C23H28O10N4: C, 53.07; H, 5.42; N, 10.76. Found: C, 52.99; H, 5.39; N, 10.74. IR (KBr): $\nu/cm^{-1} = 1753 (\nu_{C=0})$. UV-vis (CH₃CN): $\lambda/nm (\varepsilon \times 10^{-3}/M^{-1} cm^{-1}) = 279.5 (7.44), 242.0 (13.2).$

2-(4-(2-Pyridyl)-1,2,3-triazol-1-yl)ethyl β-D-glucopyranoside (Glc-pyta). AcGlc-pyta (298 mg) was dissolved in a mixture of EtOH and water (1 : 1 v/v) (14 mL). To the solution was added 1.7 g of DOWEX 550OA OH- anion exchange resins. The mixture was stirred at 60 °C for 2 days. After removal of the resin by filtration, the filtrate was evaporated to afford Glc-pyta as a white powder (140 mg). Yield 69%. ¹H NMR (400 MHz, DMSO-d₆, 40 °C): δ /ppm = 8.61 (s, 1H, 5-triazole*H*), 8.58 (ddd, ${}^{3}J = 4.9$ Hz, ${}^{4}J = 1.7$ Hz, ${}^{5}J = 0.98$ Hz, 1H, 6-pyH), 8.01 (d, ${}^{3}J = 8.1$ Hz, 1H, 3-py*H*), 7.87 (dt, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.9$ Hz, 1H, 4-py*H*), 7.32 (ddd, ${}^{3}J = 4.8$ and 7.4 Hz, ${}^{4}J = 1.2$ Hz, 1H, 5-py*H*), $4.98 (d, {}^{3}J = 4.9 Hz, 1H, OH), 4.84 (d, {}^{3}J = 4.6 Hz, 1H, OH), 4.83$ $(d, {}^{3}J = 5.1 \text{ Hz}, 1\text{H}, OH), 4.65 (t, {}^{3}J = 5.2 \text{ Hz}, 2\text{H}, -CH_{2}-), 4.45$ $(t, {}^{3}J = 6.0 \text{ Hz}, 1\text{H}, 6\text{-GlcO}H), 4.26 (d, {}^{3}J = 7.8 \text{ Hz}, 1\text{H}, 1\text{-Glc}H),$ 4.17-4.11 (m, 1H, -CHH-), 4.02-3.96 (m, 1H, -CHH-), 3.71-3.66 (m, 1H, 6-GlcHH), 3.47–3.41 (m, 1H, 6-GlcHH), 3.18–3.11 (m, 2H, GlcH), 3.07–2.95 (m, 2H, GlcH). ¹³C NMR (100 MHz, DMSO-d₆, 40 °C): δ /ppm = 149.75 (*C*), 149.15 (6-py*C*), 146.70 (C), 136.76 (4-pyC), 123.60 (5-triazoleC), 122.50 (5-pyC), 119.14 (3-pyC), 102.75 (1-GlcC), 76.81 (GlcC), 76.47 (GlcC), 73.18 (GlcC), 69.94 (GlcC), 67.02 (CH₂), 60.99 (6-GlcC), 49.83 (CH₂). ESI-TOF HRMS: m/z for C₁₅H₂₀O₆N₄Na ([M + Na]⁺) calcd. 375.12805, found 375.12910 (error 1.05 mmu, 2.80 ppm). Anal. calcd. for C₁₅H₂₀O₆N₄·0.5H₂O: C, 49.86; H, 5.86; N, 15.50. Found: C, 49.43; H, 5.81; N, 15.60. IR (KBr): $\nu/cm^{-1} = 3400$ (v_{0-H}) . UV-vis (CH₃OH): $\lambda/nm (\varepsilon \times 10^{-3}/M^{-1} \text{ cm}^{-1}) = 280 (7.69),$ 240 (11.8).

[ReCl(CO)₃(Bn-pyta)]. The ligand Bn-pyta (101 mg) and [ReCl(CO)₅] (139 mg) were dissolved in MeOH (42 mL) and stirred for 24 h at 60 °C. After standing at room temperature, yellow fine needle-like crystals were collected by filtration. Yield 0.110 g (53%). ¹H NMR (400 MHz, CD₃CN): δ /ppm = 8.93 (ddd, ³J = 5.6 Hz, ${}^{4}J = 1.5$ Hz, ${}^{5}J = 0.91$ Hz, 1H, 6-pyH), 8.55 (s, 1H, 5triazole*H*), 8.10 (dt, ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1.5$ Hz, 1H, 4-py*H*), 7.98 (ddd, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.4$ Hz, ${}^{5}J = 0.88$ Hz, 1H, 3-pyH), 7.49 $(ddd, {}^{3}J = 7.6 \text{ and } 5.6 \text{ Hz}, {}^{4}J = 1.4 \text{ Hz}, 1\text{H}, 5\text{-py}H), 7.47\text{--}7.42 \text{ (m,}$ 5H, PhH), 5.73 (s, 2H, -CH₂-). ¹³C NMR (100 MHz, CD₃CN): $\delta/\text{ppm} = 153.64$ (6-pyC), 149.74 (C), 149.53 (C), 140.90 (4pyC), 134.36 (ipso-PhC), 129.92 (PhCH), 129.89 (PhCH), 129.44 (PhCH), 126.85 (5-pyC), 125.66 (5-triazoleC), 123.30 (3-pyC), 56.33 (-CH₂-). ESI-TOF HRMS: m/z for C₁₇H₁₂O₃N₄ClReNa ([M + Na]⁺) calcd. 565.00531, found 565.00312 (error -2.19 mmu, -3.88 ppm). Anal. calcd. for C₁₇H₁₂O₃N₄ClRe: C, 37.67; H, 2.23; N, 10.34. Found: C, 37.45; H, 1.94; N, 10.40. IR (KBr): $\nu/cm^{-1} =$ 2027 (v_{sym,C=0}), 1909 (v_{asym,C=0}), 1880 (v_{asym,C=0}). UV-vis (CH₃CN): λ/nm ($\varepsilon \times 10^{-3}/\text{M}^{-1}$ cm⁻¹) = 333 (3.97). FL (CH₃CN, λ_{ex} = 333 nm): λ /nm = 538.

[ReCl(CO)₃(AcGlc-pyta)]. AcGlc-pyta (160 mg), [ReCl(CO)₅] (109 mg) and MeOH (30 mL) were placed in a 100 mL flask, and stirred at 62 °C for 2 days. The resulting mixture was concentrated and cooled to 4 °C to afford a diastereomeric mixture of [ReCl(CO)₃(AcGlc-pyta)] as a pale yellow powder (160 mg). Yield 64%. ESI-TOF HRMS: m/z for C₂₆H₂₈O₁₃N₄Re ([M – Cl]⁺) calcd. 791.12104, found 791.11663 (error –4.41 mmu, –5.57 ppm). Anal. calcd. for C₂₆H₂₈O₁₃N₄ClRe: C, 37.80; H, 3.42; N,

6.78. Found: C, 37.53; H, 3.23; N, 6.84. IR (KBr): $\nu/cm^{-1} = 2027$, 1926, 1900, 1875, 1747, 1371, 1234, 1045, 781. UV-vis (CH₃CN): λ/nm ($\varepsilon \times 10^{-3}/M^{-1}$ cm⁻¹) = 332 (3.97). FL (CH₃CN, $\lambda_{ex} = 280$ nm): $\lambda/nm = 530$.

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[ReCl(CO)₃(Glc-pyta)]. Glc-pyta (83 mg), [ReCl(CO)₅] (94 mg) and MeOH (15 mL) were placed in a 100 mL flask and stirred at 60 °C for 2 days. The resulting mixture was concentrated and cooled to 4 °C. The precipitate was collected by filtration and washed with hexane to give a pale yellow powder (117 mg). Yield 76%. ESI-TOF HRMS: m/z for C₁₈H₂₀O₉N₄Re ([M – Cl]⁺) calcd. 623.07878, found 623.07755 (error –1.23 mmu, –1.97 ppm). Anal. calcd. for C₁₈H₂₀O₉N₄CIRe: C, 32.85; H, 3.06; N, 8.51. Found: C, 32.63; H, 3.01; N, 8.32. IR (KBr): $\nu/cm^{-1} =$ 3443 (ν_{0-H}), 2023 ($\nu_{sym,C=0}$), 1933 ($\nu_{asym,C=0}$), 1898 ($\nu_{asym,C=0}$). UV-vis (CH₃CN): λ/nm ($\varepsilon \times 10^{-3}/M^{-1}$ cm⁻¹) = 407 (0.918), 331 (3.87). FL (CH₃CN, $\lambda_{ex} =$ 331 nm): $\lambda/nm =$ 538.

Photophysical measurements

Time-resolved fluorescence measurements were performed for the 2-methyltetrahydrofuran solution of [ReCl(CO)₃(bpy)] and [ReCl(CO)₃(Bn-pyta)] at 77 K. A quartz test-tube (6 mm diameter) with sample solutions $(OD_{355} = 0.075 \text{ for } [ReCl(CO)_3(bpy)]$ and $OD_{355} = 0.182$ for [ReCl(CO)₃(Bn-pyta)]) was placed in a coldfinger filled with liquid nitrogen. The sample solutions (glassy solids at 77 K) were irradiated with the third harmonics (355 nm, 10 ns pulse duration, 10 mW, 10 Hz) of a Nd:YAG laser (Continuum, Surelite) without focusing. The luminescence signal was detected at right angles to the excitation laser beam, with a silicon PIN photo-diode (Hamamatsu, S7911) after passing through a sharp cut filter (HOYA, Y49). The temporal dependence of the luminescence intensity after photoexcitation was determined by detecting the output electric signal from the photo-diode with a digital oscilloscope (Sony Tektronix, TDS380P). Timedependent fluorescence profiles obtained by the exposure of 256 excitation laser pulses were averaged. The time-resolution of the measurement system was determined to be as short as 10 ns. Inspection of the absorption spectra before and after the time-resolved luminescence measurements confirmed that no degradation of the sample solutions was induced by the 355 nm laser irradiation.

Emission quantum yield (Φ) was determined by a relative method using aqueous Ru(bpy)₃²⁺ solution ($\Phi_{std} = 0.042$) as a standard.⁵³

X-Ray structural determination

Single-crystal X-ray diffraction data were recorded on Rigaku Mercury CCD and AFC/Mercury CCD diffractometers using graphite-monochromated Mo K α radiation. All data sets were corrected for Lorentzian polarization effects and for absorption. All structures were solved by the direct method (SIR92⁵⁴ or SIR97⁵⁵). Hydrogen atoms were placed into calculated positions, and refined with isotropic thermal parameters riding on those of the parent atoms. Refinement of the non-hydrogen atoms was carried out with the full-matrix least-squares technique (SHELXL-97⁵⁶). Crystal and refinement data are summarized in Table 1.†

	Bn-pyta	Glc-pyta	[ReCl(CO) ₃ (Bn-pyta)]
Formula	$C_{14}H_{12}N_4$	$C_{15}H_{20}N_4O_6$	$C_{17}H_{12}N_4O_3ClRe$
FW	236.28	352.35	541.96
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Fdd2	$P2_1$	$P2_1/n$
a/Å	28.4093(11)	11.560(4)	6.6557(5)
b/Å	29.0074(15)	5.4449(17)	20.5809(15)
c/Å	5.7657(2)	13.267(5)	13.0676(11)
β/°	90	100.247(4)	98.876(4)
V/Å ³	4751.4(3)	821.8(5)	1768.6(2)
Ζ	16	2	4
<i>F</i> (000)	1984	370	1032
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.321	1.424	2.035
Wavelength	Μο Κα	Μο Κα	Μο Κα
μ/mm^{-1}	0.0831	0.111	7.047
T/K	173	173	193(2)
θ limits/°	3.15-27.47	3.1-27.5	4.19-27.48
Min/max h, k, l	-36/36, -37/36, -7/7	-14/15, -6/7, -17/15	-8/5, -19/26, -15/16
Collected refins	11 614	6404	14 028
Unique reflns	1503	2063	4011
Refins with $I > 2\sigma(I)$	1388	1765	3716
Absorption correction	Numerical	Numerical	Multi-scan
GOF	1.028	1.004	1.007
$R\left[F^2 > 2\sigma(F^2)\right]$	0.0294	0.0380	0.0452
$R_{ m int}$	0.021	0.025	0.0336
wR (all data)	0.0353	0.0506	0.0774
Max, min $\Delta \rho / e \text{ Å}^{-3}$	0.57, -0.25	0.20, -0.21	0.77, -0.82
CCDC No.	633046	669575	633047

 Table 1
 Summary of crystal data information and collection/refinement parameters for Bn-pyta, Glc-pyta and [ReCl(CO)₃(Bn-pyta)]

XAS Data acquisition and analysis

The X-ray absorption spectra were recorded at the beam line 9C of the Photon Factory of the High Energy Acceleration Research Organization (KEK-PF; Tsukuba, Japan). The ring current was 300–450 mA, and the storage ring was operated with an electron energy of 2.5 GeV. The experiments at the Re L_{III} edge (10 531 eV) were carried out at room temperature in the transmission mode. The spectra were collected at room temperature with a Si(111) double-crystal monochromator, and 30% harmonic rejection was achieved by detuning the two crystal from parallel alignment. The samples were finely ground with boron nitrate (BN), and pressed to afford a pellet.

The EXAFS oscillations $\chi(k)$ were extracted from the X-ray spectra using the automated background subtraction algorithm (AUTOBK) developed by Newville *et al.*⁵⁷ The k^3 -weighted EXAFS oscillations, $k^3\chi(k)$, are theoretically given by following equation:

$$k^{3}\chi(k) = k^{3}S_{0}^{2}\sum\left\{\frac{N_{i}}{kr_{i}}F_{i}(k)\exp\left(-2k^{2}\sigma_{i}^{2}\right)\sin\left(2kr_{i}+\Phi_{i}(k)\right)\right\}$$
(1)

where S_0^2 , r_i , N_i , $F_i(k)$, $\Phi_i(k)$ and σ_i represent the amplitude reduction factor, the half-path-length, the degeneracy, the backscattering amplitude, the phase shift, and the Debye–Waller factor of the *i*th path, respectively, and *k* is the photoelectron wave vector defined as $k = [(2m/h^2)(E - E_0 + \Delta E_i)]^{1/2}$ with E_0 being the threshold energy and ΔE_i the energy shift of the *i*th path. Theoretical amplitude $F_i(k)$ and phase shift $\Phi_i(k)$ functions for the single and multiple scattering pathways were calculated by means of the FEFF 8.2 program.⁵⁸ The S_0^2 value was optimized in the range from 0.8 to 1. The ΔE_i value for each path was optimized in the range from -10 to 10 eV. The fits were performed on the inverse Fourier transform space for the region between 1.2 to 3.5 Å using the IFEFFIT program suite.⁵⁹

Computational methodology

Geometry optimization of [ReCl(CO)₃(bpy)] and [ReCl(CO)₃(Mepyta)] was performed using the PBE1PBE functional and the 6-31(G) basis set for C, H, N, O and Cl atoms, and the Stuttgart/Dresden pseudo-core potential (SDD) for Re atoms, implemented in the Gaussian03 program package.⁶⁰ The stationary point was established by the analysis of the harmonic vibrational frequencies. The electronic structure and transition energies were recalculated using the conductor-like polarizable continuum model (CPCM) and Dunning's correlation-consistent basis function, with the cc-pvdz basis set for C, H, N, O and Cl atoms instead of the 6-31(G) basis set.

Results and discussion

Synthesis and characterization

1,2,3-Triazole has two possible coordination sites, *viz*. the 2and 3-nitrogen atoms, but introduction of a 2-pyridyl group at the 4-position results in the preferred bidentate sites at the 3triazole nitrogen and the 2-pyridyl nitrogen. By applying the copper(1)-catalyzed 1,3-dipolar cycloaddition (a well-known example of "click chemistry"), the 4-(2-pyridyl)-1,2,3-triazole (pyta) derivatives were readily synthesized from azide derivatives and 2ethynylpyridine (Scheme 1). Thus, the reaction of benzyl azide with equimolar 2-ethynylpyridine in the mixture of THF and water in the presence of CuSO₄ and sodium ascorbate produced



Scheme 1 Synthesis of 4-(2-pyridyl)-1,2,3-triazole ligands and their rhenium(1) complexes. *Reagents and conditions*: (a) CuSO₄, 1 M sodium ascorbate, THF–H₂O (1 : 1 v/v), 50–60 °C, 16 h; (b) DOWEX 550OA OH⁻ anion exchange resins, EtOH–H₂O (1 : 1 v/v), 60 °C, 2 days; (c) [ReCl(CO)₅], MeOH, 60 °C, 24 h.

colorless crystals of 1-benzyl-4-(2-pyridyl)-1,2,3-trizole (Bn-pyta) after overnight stirring at 50 °C in 80% yield. The reaction is highly selective to give the 4-(2-pyridyl) isomer, although 4- and 5-(2-pyridyl) isomers are possible.⁴⁸ Fig. 1 shows the crystal structure of Bn-pyta. Selected bond lengths and angles are listed in Table 2. The angle between least-square planes of triazole and pyridine rings is determined to be 15.46°, which is larger than that of typical 3-(2-pyridyl)-1,2,4-triazoles such as 4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole (9.77°).⁶¹



Fig. 1 ORTEP drawings of Bn-pyta (a) and Glc-pyta (b) with thermal ellipsoids shown at 50% probability.

A significant difference between the 1,2,3-triazole and 1,2,4-triazole rings was found in the bond distances as shown in Fig. 2; the N(2)-N(3) bond distance of the 1,2,3-triazole ring (1.318(2) Å)

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Table 2Selected bond lengths (Å) and angles (°) of Bn-pyta and Glc-pyta

	Bn-pyta	Glc-pyta		
N(2)–N(3)	1.318(2)	1.322(3)		
N(3) - N(4)	1.353(2)	1.352(2)		
N(4) - C(7)	1.3442(19)	1.337(3)		
C(7) - C(6)	1.374(2)	1.367(3)		
C(6) - N(2)	1.365(2)	1.366(3)		
C(5) - C(6)	1.473(2)	1.466(4)		
C(6) - N(2) - N(3)	108.65(13)	108.9(2)		
N(2) - N(3) - N(4)	107.10(13)	106.6(2)		
N(3) - N(4) - C(7)	111.02(12)	111.2(2)		
N(4) - C(7) - C(6)	104.71(14)	105.3(2)		
C(7)–C(6)–N(2)	108.53(13)	108.1(2)		



Fig. 2 Schematic representation of crystal structure of 1,2,3-triazole and 1,2,4-triazole rings. Bond lengths are those of Bn-pyta and 4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole⁶¹ as typical examples of 1,2,3- and 1,2,4-triazole rings.

is shorter than the adjacent N(2)–C(6) and N(3)–N(4) bonds, while the corresponding N(2)–N(3) bond distance of 1,2,4-triazole (1.395(3) Å) is longer than those of adjacent two bonds. This structural feature suggests that 1,2,3-triazole has an azo character while 1,2,4-triazole has an azine character.

The rhenium(1) complex, [ReCl(CO)₃(Bn-pyta)], was prepared by the reaction of [ReCl(CO)₅] with Bn-pyta in methanol overnight at 60 °C. Yellow needle-like crystals were obtained in 53% yield and characterized by elemental analysis, ESI-MS (detection of $[M - Cl]^+$ ion peak identified by its characteristic isotope-pattern), ¹H and ¹³C NMR (large shifts by coordination to Re(1)), IR (three C=O peaks, indicating three facially coordinated carbonyl groups; $v_{C=O} = 2025 \text{ cm}^{-1} (v_{sym})$, 1915 and 1890 cm⁻¹ (v_{asym})), and electronic absorption spectroscopies. Fig. 3 shows the ORTEP drawing of [ReCl(CO)₃(Bn-pyta)].

The coordinating fashion of Bn-pyta to the Re(I) center is very similar to that of the 2,2'-bipyridine derivative.⁶² The selected bond distances and bond angles are listed in Table 3. The bond distance of Re–N(triazole) is 2.127(5) Å, which is shorter than that of Re–N(pyridine) (2.197(4) Å). A similar distortion is known in the Re(I) complexes of azole ligands having a 2-pyridyl group such as 2-(2-pyridyl)benzimidazole,³³ 2-(2-pyridyl)benzothiazole,⁶³ 2-(2-pyridyl)benzoxazole³³ and a 3-(2pyridyl)-1,2,4-triazole derivative.³² Interestingly, the bond distance of Re–N(triazole) is the shortest in the Re(CO)₃ complexes of pyridine–azole conjugates, probably due to the strong electrondonating property of the 1,2,3-triazole ring. The bite angle N–Re– N keeps constant at *ca.* 74.5° in these complexes.



Fig. 3 ORTEP drawing of [ReCl(CO)₃(Bn-pyta)] with thermal ellipsoids shown at 50% probability.

Table 3Selected bond lengths (Å) and angles (°) of $[ReCl(CO)_3(Bn-pyta)]$ (X-ray crystallography) and $[ReCl(CO)_3(Me-pyta)]$ (DFT calculation)

	[ReCl(CO) ₃ (Bn-pyta)] ^a	[ReCl(CO) ₃ (Me-pyta)] ^b
Re-Cl	2.4713(18)	2.4845
Re-N(1)	2.196(5)	2.2203
Re-N(2)	2.127(5)	2.1698
Re-C(15)	1.974(8)	1.9187
Re-C(16)	1.922(7)	1.9264
Re-C(17)	1.916(7)	1.9314
N(1)– Re – $N(2)$	74.5(2)	74.12
Cl-Re-C(15)	174.9(2)	175.66
N(1) - Re - C(17)	170.5(2)	170.40
N(2) - Re - C(16)	170.6(2)	170.07
C(16) - Re - C(17)	91.6(3)	90.45
" Determined by X-	-ray crystallography. ^b Deteri	mined by DFT calculation.

In order to validate the feasibility of this methodology for syntheses of the pyta-ligating moiety, we synthesized glycoconjugated pyta ligands and their Re(I) complexes. 2-Azidoethyl 2,3,4,6tetra-O-acetyl- β -D-glucopyranoside (AcGlc-N₃) was prepared by the method reported previously.52 The copper(I)-catalyzed 1,3-dipolar cycloaddition of AcGlc-N₃ with 2-ethynylpyridine afforded 2-(4-(2-pyridyl)-1,2,3-triazol-1-yl)ethyl 2,3,4,6-tetra-Oacetyl-β-D-glucopyranoside (AcGlc-pyta) without formation of its isomer. Saponification of AcGlc-pyta using DOWEX 550A OHanion exchange resins afforded the deprotected ligand, 2-(4-(2pyridyl)-1,2,3-triazol-1-yl)ethyl β-D-glucopyranoside (Glc-pyta). These ligands were characterized by elemental analysis, ESI-MS, and ¹H, ¹³C NMR and electronic absorption spectroscopies. Glcpyta crystallized in the monoclinic system, space group $P2_1$, from a mixture of ethanol and hexane. The crystal structure of Glc-pyta is shown in Fig. 1 and selected bond lengths and angles are listed in Table 2. The least-square planes of the triazole and pyridine rings are twisted relative to each other with a dihedral angle of 10.94° to form the (S)-configuration in the crystal due to the chirality of sugar unit. No significant structural differences in the pyta moieties was found between Bn-pyta and Glc-pyta. The Re(I) complexes of these ligands were prepared under similar conditions to Bn-pyta and characterized by elemental analysis, ESI-MS,

and ¹H and ¹³C NMR spectroscopies. ¹H and ¹³C NMR spectra indicated that the product is a mixture of two diastereomers due to the chirality of sugar moieties and the asymmetric octahedral Re(I) complex. The diastereomeric ratio is close to unity, indicating no stereoselectivity in the reaction. Since these glycoconjugated complexes hardly crystallized, the coordination geometries were examined by extended X-ray absorption fine structure (EXAFS) analysis at the Re L_{III} edge (Fig. 4). The resulting EXAFS oscillations $(k^3\chi(k))$ of [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glcpyta)] resembled that of [ReCl(CO)₃(Bn-pyta)], as shown in the insets of Fig. 4. The Fourier transform of $k^3\chi(k)$ shows three peaks at 1.6, 2.2 and 2.6 Å (before phase-shift correction). The EXAFS oscillations were fitted with the contributions from 4 single scattering paths between Re and neighboring N, C, Cl and O atoms and 2 multiple scattering paths for the Re-C≡O linear triatomic system (Fig. 5). The fitting results are listed in Table 4. The resulting structural parameters, e.g., half-path-lengths r_i , are quite close to those derived from the crystal structure of [ReCl(CO)₃(Bn-pyta)], indicating the similar coordination structures of [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glc-pyta)].



Fig. 4 Fourier transform of k^3 -weighted EXAFS oscillation (before phase-shift correction) $(k^3\chi(k))$ of [ReCl(CO)₃(Bn-pyta)] (a), [ReCl(CO)₃(AcGlc-pyta)] (b) and [ReCl(CO)₃(Glc-pyta)] (c) in BN pellets at the Re L_{III} edge. The insets are the corresponding Fourier-filtered $k^3\chi(k)$. Broken line represents observed data and solid line is the best-fit with standard EXAFS equation.

Photophysical properties

Fig. 6 shows the electronic absorption and luminescence spectra of [ReCl(CO)₃(Bn-pyta)] together with [ReCl(CO)₃(bpy)] in acetonitrile at 25 °C. [ReCl(CO)₃(Bn-pyta)] showed a blue-shifted electronic absorption at 333 nm ($\varepsilon = 3.97 \times$



Fig. 5 Important single and multiple scattering paths.

 10^3 M⁻¹ cm⁻¹) compared with [ReCl(CO)₃(bpy)] (371 nm, $\varepsilon = 3.35 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). A density functional theory (DFT) calculation was performed for [ReCl(CO)₃(Me-pyta)] (Me-pyta is 1-methyl-4-(2-pyridyl)-1,2,3-triazole as a reduced model for the ligand Bn-pyta) and [ReCl(CO)₃(bpy)] to analyze these electronic transitions. Equilibrium geometries of [ReCl(CO)₃(Mepyta)] and [ReCl(CO)₃(bpy)] were obtained by using the PBE1PBE functional and Stuttgart/Dresden pseudo-core potential (SDD) for the Re atom and the 6-31(G) basis set for other atoms, and confirmed by normal coordination analysis. The selected bond lengths and bond angles are listed in Table 3. The DFT calculation of [ReCl(CO)₃(Me-pyta)] reproduced well the coordination structure of [ReCl(CO)₃(Bn-pyta)]. The electronic transitions of $[ReCl(CO)_3(Me-pyta)]$ and $[ReCl(CO)_3(bpy)]$ were calculated by time-dependent formalism of DFT calculation according to the Vlček and Záliš method^{14,64,65} using the PBE1PBE functional and Dunning's correlation-consistent basis function, the cc-pvdz basis set for C, H, N, O and Cl atoms and SDD for the Re atom using the conductor-like polarizable continuum model (CPCM). The significant oscillator strength f was found at 340.4 nm (3.6424 eV, f = 0.0867) and 380.7 nm (3.2564 eV, f = 0.0819)for [ReCl(CO)₃(Me-pyta)] and [ReCl(CO)₃(bpy)], respectively. The



Fig. 6 Electronic absorption and normalized luminescence spectra (inset) of $[\text{ReCl}(\text{CO})_3(\text{bpy})]$ (a), $[\text{ReCl}(\text{CO})_3(\text{Bn-pyta})]$ (b) and $[\text{ReCl}(\text{CO})_3(\text{Glc-pyta})]$ (c) in acetonitrile. Bars in the electronic absorption spectra represent the oscillator strength (*f*, right axis) using TD-DFT calculation (PBE1PBE/SDD + cc-pvdz) of $[\text{ReCl}(\text{CO})_3(\text{bpy})]$ and $[\text{ReCl}(\text{CO})_3(\text{Me-pyta})]$.

calculation reproduced the experiments well, giving slightly larger λ_{max} values than the observed values for [ReCl(CO)₃(Bn-pyta)] and [ReCl(CO)₃(bpy)]. Fig. 7 shows the energy diagrams with HOMO-1 and LUMO orbitals of [ReCl(CO)₃(Me-pyta)] and [ReCl(CO)₃(bpy)] in acetonitrile.

The HOMO-1s of [ReCl(CO)₃(Me-pyta)] and [ReCl(CO)₃(bpy)] predominantly localize at the Re(I) and Cl atoms, which form a π -antibonding orbital. On the other hand, the LUMOs are essentially the π^* orbital of pyta and bpy ligands. Hence the electronic transition at the lowest energy region is clearly assigned to the mixed metal–ligand-to-ligand charge transfer (MLLCT) in both complexes. The same energy level of HOMO-1 in both

Table 4 Least-square fitting results for EXAFS data of [ReCl(CO)₃(Bn-pyta)], [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glc-pyta)]^e

Path ^b			Ligand							
			Bn-pyta		AcGlc-pyta		Glc-pyta			
	n_{leg}^{c}	N^d	r ^e /Å	$\sigma^f/ m \AA^2$	r ^e /Å	$\sigma^{f}/\text{\AA}^{2}$	r ^e /Å	$\sigma^f/\text{\AA}^2$		
1	2	3	1.90(6)	0.003	1.90(6)	0.004	1.90(9)	0.003		
2	2	1	2.2(10)	0.002	2.2(12)	0.001	2.2(11)	0.001		
3	2	2	2.5(3)	0.004	2.4(2)	0.003	2.5(4)	0.005		
4	2	3	3.08(8)	0.001	3.08(8)	0.002	3.08(9)	0.001		
5	3	5	3.08(8)	0.003	3.08(8)	0.003	3.08(9)	0.003		
6	4	3	3.08(8)	0.013	3.08(8)	0.014	3.08(9)	0.015		
R^{g}			0.015		0.014		0.015			

^{*a*} The structural model shown in Fig. 5 is used to fit Fourier-filtered $k_{\chi}^{3}\chi(k)$ data (range 1.2 < r < 3.5 Å). ^{*b*} Path number defined in Fig. 5. ^{*c*} Number of legs. ^{*d*} Degeneracy. ^{*e*} Half-path-length (interatomic distance for single scattering). ^{*f*} Debye–Waller factor. ^{*g*} *R*-factor, defined as $\Sigma[\chi(k)_{obs} - \chi(k)_{model}]^{2}/\Sigma[\chi(k)_{obs}]^{2}$.



Fig. 7 Energy diagram (au) and HOMO-1 and LUMO orbitals of [ReCl(CO)₃(bpy)] (left) and [ReCl(CO)₃(Me-pyta)] (right).

 $\label{eq:table_transform} \begin{array}{ll} \textbf{Table 5} & \text{Emission maxima, quantum yield and luminescence lifetime of} \\ [ReCl(CO)_3(bpy)] \text{ and } [ReCl(CO)_3(Bn-pyta)] \end{array}$

	λ_{\max}^{a}/nm	Φ^a	$\tau^b/\mu s$	
[ReCl(CO) ₃ (bpy)]	633	0.0027	3.17	
[ReCl(CO) ₃ (Bn-pyta)]	538	0.0033	8.90	
	1 (200 K hD		.1 1	

^{<i>a</i>} Determined	in	acetonitrile	at	298	К.	^a Determined	in	2-methyltetra-
hydrofuran at	77	К.						

complexes and the significantly higher energy level of LUMO in $[ReCl(CO)_3(Me-pyta)]$ than $[ReCl(CO)_3(bpy)]$ semiquantitatively explain the blue-shift of the MLLCT band of the former. According to the "energy-gap law",^{16,17,65} this blue-shift in the ligand pyta suppresses a radiationless deactivation to afford the long-lived excited state. The glycoconjugated Re(I) complexes $[ReCl(CO)_3(AcGlc-pyta)]$ and $[ReCl(CO)_3(Glc-pyta)]$ also show the blue-shifted MLLCT band at 332 and 331 nm, respectively. This explains the following luminescence properties.

[ReCl(CO)₃(Bn-pyta)] exhibited the blue-shifted luminescence spectrum compared with 633 nm of [ReCl(CO)₃(bpy)] (insets of Fig. 6). Table 5 lists the maximum emission wavelength (λ_{\max}) and emission quantum yield (Φ) in acetonitrile and the luminescence lifetime (τ) in 2-methyltetrahydrofuran (vide infra) of [ReCl(CO)₃(bpy)] and [ReCl(CO)₃(Bn-pyta)]. Fig. 8 shows the luminescence decay curves of [ReCl(CO)₃(Bn-pyta)] and [ReCl(CO)₃(bpy)] in 2-methyltetrahydrofuran at 77 K. The luminescence lifetime of [ReCl(CO)₃(Bn-pyta)] (8.90 µs) is almost three-times longer than that of $[ReCl(CO)_3(bpy)]$ (3.17 µs) and comparable to [ReCl(CO)₃(4,4'-diamino-2,2'-bipyridine)] (ca. 11 µs).¹⁶ The Φ value of [ReCl(CO)₃(Bn-pyta)] also greater than that of $[ReCl(CO)_3(bpy)]$ even at ambient temperature in acetonitrile. These results also indicate that the ligand Bn-pyta can function as an electron-rich bipyridine-like ligand, affording the long-lived luminescence with the higher quantum yield. The glycoconjugated Re(I) complexes [ReCl(CO)₃(AcGlc-pyta)] and [ReCl(CO)₃(Glc-pyta)] exhibited similar photophysical properties to that of [ReCl(CO)₃(Bn-pyta)], showing FL λ_{max} at 532 nm for the AcGlc-pyta complex and at 538 nm for the Glc-pyta complex, respectively. The long-lived luminescence properties of Re(I) complexes with the ligand pyta could be useful for time-gated imaging, especially in biological labeling systems.



Fig. 8 Luminescence decay curve of $[ReCl(CO)_3(bpy)]$ (a) and $[ReCl(CO)_3(Bn-pyta)]$ (b) in 2-methyltetrahydrofuran at 77 K. The dotted line and the solid line represent observed data and the best-fit with a single exponential function, respectively.

Conclusions

We have developed novel azole ligands with a 2-pyridyl group affording an additional coordination site, namely 4-(2-pyridyl)-1,2,3-triazole (pyta) ligands. The pyta ligands are readily and easily prepared by means of copper(I)-catalyzed 1,3-dipolar cycloaddition of commercially available 2-ethynylpyridine and azide compounds. The reaction proceeds under relatively mild conditions and affords the ligands selectively in fairly good yields. X-Ray crystallography clearly indicates that the 1,2,3-triazole has an azo-like character while its isomer, 1,2,4-triazole, has an azine nature. The coordinating ability of pyta was established on the ReCl(CO)₃ core. The blue-shift in electronic absorption and luminescence spectra of the resulting rhenium(I) complex clearly indicated that pyta acts like a bipyridine mimic with strongly electron-donating substituents. The photophysical and photochemical properties of pyta were theoretically clarified by DFT calculations.

Enhanced luminescence intensity and lifetime could be highly advantageous in the application of pyta metal complexes as luminescence probes in time-gated imaging. The ready formation of the sugar-attached pyta complexes in aqueous conditions indicates that the present approach leads to a powerful method to install the bipyridine-like ligands and their photofunctional metal complexes into biomolecules, *e.g.* saccharides, proteins and nucleic acids.

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