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Synthesis of Homoleptic and Heteroleptic Ruthenium Complexes Appended with Glucosyl Ligand by the Click-to-Chelate Approach[1]

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Abstract—Homoleptic and heteroleptic complexes of $Ru(TAGP\text{-}tapy)_3Cl_2$ {TAGP-tapy is 2-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl]-pyridine} bearing a clustered glucose-derived ligand and $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ (bpy is 2,2'-bipyridine) have been synthesized by the chelating reaction of $RuCl_3 \cdot 3H_2O$ with TAGP-tapy and *cis*-$Ru(bpy)_2Cl_2$ with TAGP-tapy, respectively. The bidentate 1,2,3-triazole-linked glucose-derived ligand TAGP-tapy was prepared by copper-catalyzed coupling (click reaction) of 2-ethynylpyridine with acetyl protected glucosyl azide, 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (TAGP-N_3). TAGP-N_3 was prepared by nucleophilic substitution reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (TAGP-Br) with NaN_3. These ruthenium complexes were purified by column chromatography or HPLC. Structures of the intermediates and ruthenium complexes were confirmed by HPLC, ^1H and ^{13}C NMR, FT-IR, and ESI-MS spectroscopies. UV-Vis and fluorescence spectroscopic methods were used to study optical properties of the ligand TAGP-tapy and ruthenium complexes. TAGP-tapy exhibited interesting solvent-polarity dependent fluorescence properties and a significant red-shift in emissions. Both complexes demonstrated distinctive fluorescence emission band in the visible region.

Keywords: homoleptic ruthenium complex, heteroleptic ruthenium complex, glucosyl ligand, click-to-chelate, carbohydrate-protein interactions

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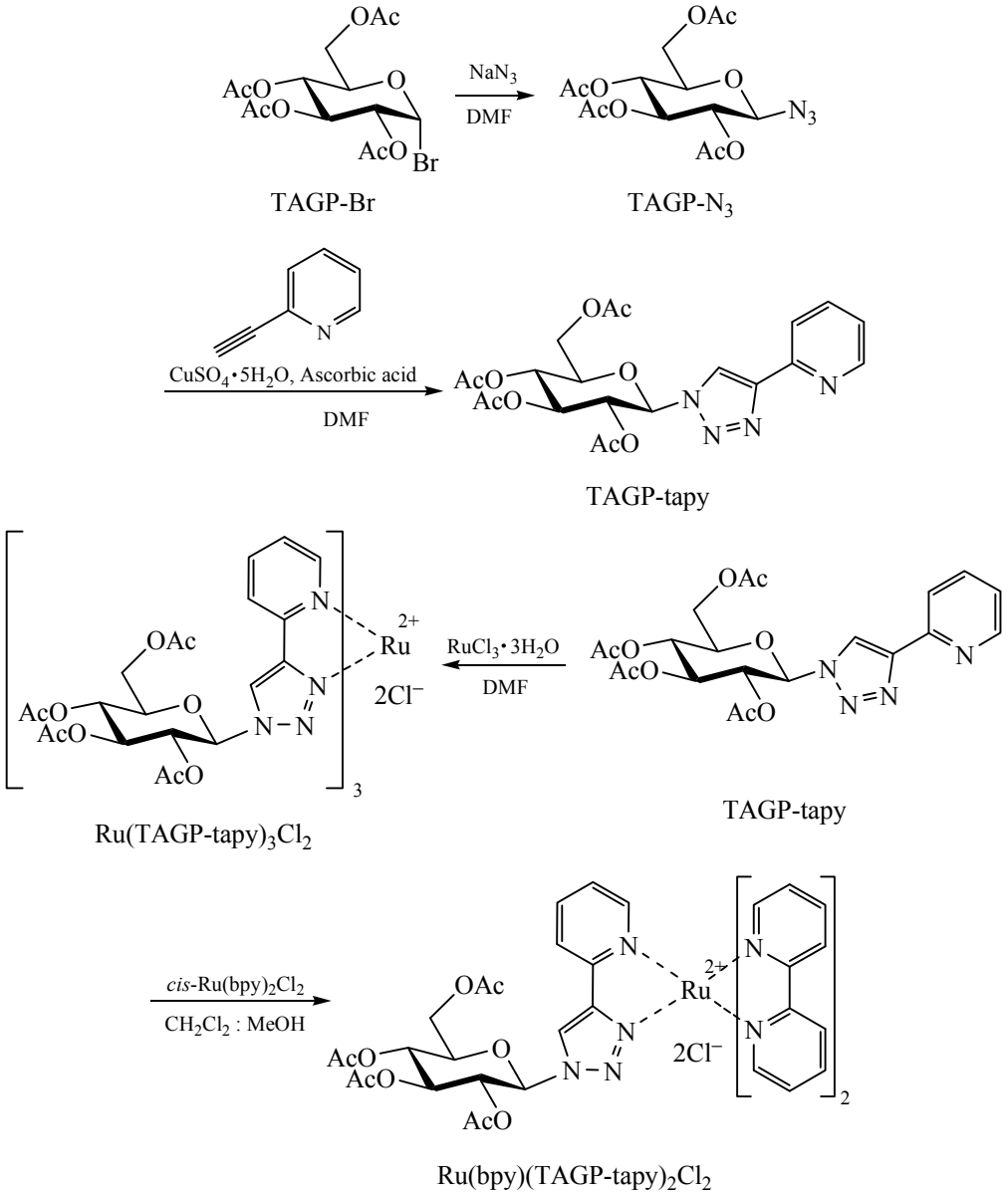
INTRODUCTION

Carbohydrate-protein interactions mediate many important physiological processes, such as cell growth, interactions with bacteria and viruses, and functioning of immune system, that are important for drug development and clinical diagnostics [1, 2]. Since proteins responsible for cellular recognition processes are found in aggregates that present multiple binding sites for mono-valent carbohydrate interaction, this natural multivalency enhances the binding affinity of mono-valent carbohydrate-protein interaction, which is known as cluster glycoside effect [3]. Dendritic polymers and organic compounds modified with carbohydrates at their branches by the click reaction were reported recently [4, 5]. Chemical labeling of non-ultraviolet or non-fluorescent carbohydrates with the fluorescent tag is an essential step that makes the intracellular microscopic insight possible [6]. Therefore, there has been a growing interest in developing carbohydrate-functionalized fluorescent markers over recent years. A carbohydrate clustered around the metal center would enhance the binding constant of generally weak interaction among carbohydrates and proteins. A metalloglycocluster is an especially attractive carbohydrate probe, since the metal center determines characteristic photochemical and electrochemical properties that can be utilized as an indicator. Based on the above, this study targeted synthesis of the fluorescent-labeled carbohydrate as a probe molecule.

Many efforts have already been directed towards design and synthesis of various sugar containing structures based on the metal-ligand non-covalent interactions. A big number of sugars ruthenium complexes with various topologies, such as linear, star and dendritic, have been synthesized [7]. In general, bipyridine, phenanthroline and diketone derivatives are used as ligands chelating with ruthenium ion to form certain structures [8–13]. The copper catalyzed click reaction of azides with alkynes containing amino groups, such as 2-ethynylprydine, has been developed

[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of TAGP-tapy, $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$, and $Ru(TAGP\text{-}tapy)_3Cl_2$.



as one of the promising methods for preparing bidentate amine ligands consisting of the 1*H*-1,2,3-triazole (tapy) group. Synthesis of metal complexes using a multidentate chelating ligand with 1*H*-1,2,3-triazole ring is called click-to-chelate. Earlier we have reported a one-pot synthesis of 3- to 12-arm star branched polymer Ru(II) complexes and stepwise chelating synthesis of copolymers by the click-to-chelate approach [14–17]. In the current study we designed homoleptic and heteroleptic ruthenium complexes, $Ru(TAGP\text{-}tapy)_3Cl_2$ and $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$, appended with different glucosyl ligands as potential carbohydrate probes (Scheme 1).

$TAGP\text{-}N_3$ was synthesized by nucleophilic substation of TAGP-Br with NaN_3. The following synthesis of the ligand TAGP-tapy involved the click process of $TAGP\text{-}N_3$ with 2-ethynylpyridine. Then the homoleptic and heteroleptic ruthenium complexes were designed. Arms of the ruthenium complexes were held together by a luminescent Ru(II) core, appended with glucosyl ligand by the click-to-chelate approach. Two types of ruthenium complexes containing different cores and ligands were synthesized aiming systematic study of effects of the core linkage and their composition influence on the carbohydrate-protein binding. In general, preparation of the homoleptic and heteroleptic

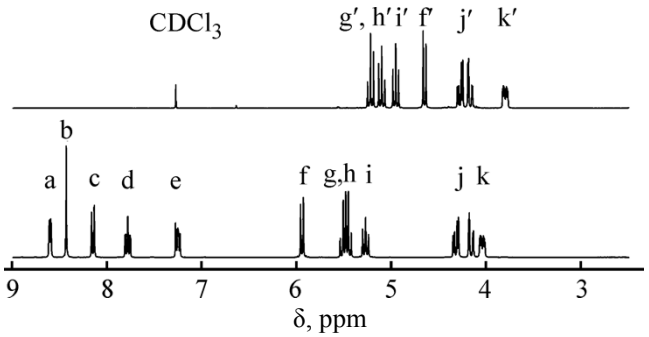


Fig. 1. ^{1}H NMR spectra of TAGP-N_3 and TAGP-tapy in $CDCl_3$.

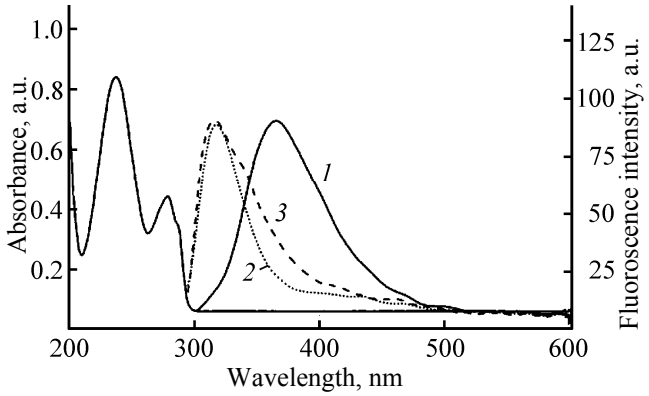


Fig. 2. UV-Vis absorption and fluorescence spectra of TAGP-tapy: (*1*) THF, (*2*) DMF–H_2O = 3 : 5, and (*3*) MeCN–H_2O = 3 : 7. The emission spectrum was obtained after excitation at 280 nm for TAGP-tapy, λ_{ex} = 280 nm.

ruthenium complexes can be implemented via two strategies (Scheme 1):

(1) One pot complexation of $Ru(TAGP\text{-}tapy)_3]Cl_2$ using $Ru(III)Cl_3 \cdot 3H_2O$ with ligand TAGP-tapy.

(2) One pot complexation of $Ru(bpy)_2$(TAGP-tapy) Cl_2 using *cis*-$Ru(bpy)_2Cl_2$ with ligand TAGP-tapy.

The structures and properties of the synthesized intermediates and non-covalent ruthenium complexes were studied by means of FT-IR, ^{1}H and ^{13}C NMR, ESI-MS, UV-Vis, and fluorescence spectroscopies. The complexes synthesized in this study are expected to provide more species of the sugar fluorescent markers as probe molecules for investigating carbohydrate-protein interactions.

RESULTS AND DISCUSSION

Synthesis of ligand TAGP-tapy. Acetyl protected TAGP-Br was treated with sodium azide in dry DMF to give TAGP-N_3. The following cycloaddition reaction of TAGP-N_3 with an excess of 2-ethynylpyridine was catalyzed by Cu(II) (Scheme 1). Upon conversion of azide into the triazole substituted adduct TAGP-tapy, the solvent was evaporated. TAGP-tapy was obtained as the sole product with nearly quantitative yield, although it was contaminated by copper ion. The latter was removed by washing with ethyl acetate and ammonia solution containing a small amount of EDTA [20].

In the FT-IR spectrum introduction of the azido group was recorded by presence of the characteristic stretching band at ca 2100 cm^{-1}. Bands of the azido group completely disappeared upon completion of the click reaction with 2-ethynylpyridine. In the ^{1}H NMR spectrum of TAGP-N_3 (Fig. 1), the signals of neighboring the azido group proton (f') and methyne protons on the pyraniod ring (g'–i', k') residue were recorded at 3.82 ppm and in the range of 4.59–5.31 ppm, respectively. The click reaction was also verified by ^{1}H NMR measurements. In the ^{1}H NMR spectrum of TAGP-tapy (Fig. 1) the signals of protons of the triazole cycle were observed at ca 8.43 ppm. In ESI-MS spectrum of TAGP-tapy the main peak at 476.91 (*m/z*) was in good agreement with the formula ($C_{21}H_{25}N_4O_9$, 477.16). According to the spectral data, TAGP-N_3 could be synthesized by the substitution reaction, and TAGP-tapy could be quantitatively synthesized via the click reaction.

By coincidence, we detected fluorescence for the solution of triazoyl-substituted TAGP in THF. Photophysical study of TAGP-tapy demonstrated two absorption bands with the maximum at ca 280 nm in the UV-Vis spectrum (Fig. 2) and a fluorescence emission maximum at 317 nm when excited at 280 nm. These results indicated that the fluorescence properties were exclusively originated from the conjugated triazole–pridine system. TAGP-tapy also displayed positive solvatofluorochromism, the fluorescence efficiency was increased with the increase of solvent-polarity (Fig. 2). A red-shift of about 50 nm was observed for the emission of TAGP-tapy from 317 nm in THF to 366 nm in a mixture of acetonitrile–water. Such effect can lead to detection of triazole-pyridine conjugated biologically active compounds by the fluorescence method.

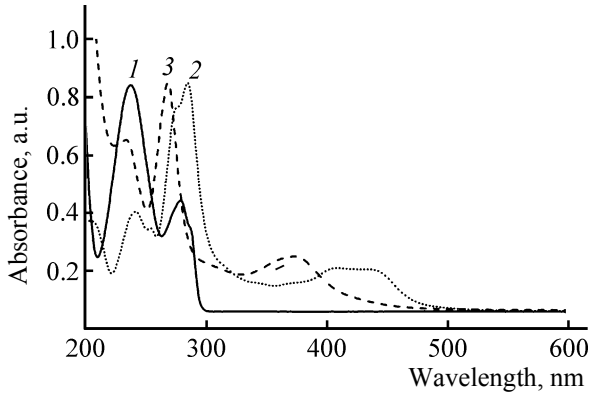


Fig. 3. UV-Vis absorption spectra of (*1*) TAGP-tapy, (*2*) $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$, and (*3*) $Ru(TAGP\text{-}tapy)_3Cl_2$ in MeCN.

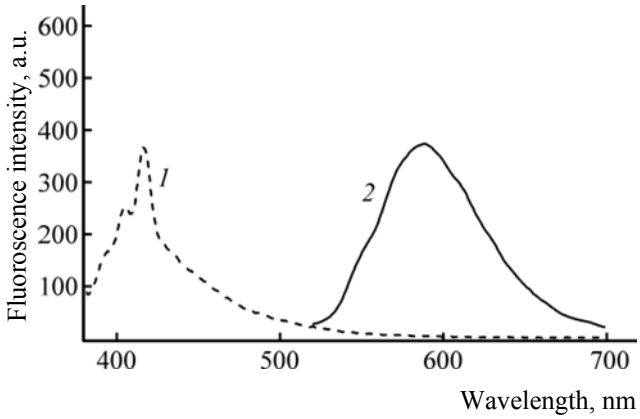


Fig. 4. Fluorescence spectra of (*1*) $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ and (*2*) $Ru(TAGP\text{-}tapy)_3Cl_2$ in MeOH (λ_{ex} = 370 nm).

Synthesis of homoleptic and heteroleptic ruthenium complexes. As presented in Scheme 1, the glucosyl possessing bidentate amine ligand TAGP-tapy reacted with the precursor *cis*-$Ru(bpy)_2Cl_2$ in CH_2Cl_2 : MeOH (1 : 1) under reflux to produce a stable heteroleptic complex $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$. *cis*-$Ru(bpy)_2Cl_2$ gave a stable complex with the ligand with the ratio of 1 : 1. $Ru(TAGP\text{-}tapy)_3Cl_2$ was synthesized in one step by the reaction of the ligand TAGP-tapy with $RuCl_3 \cdot 3H_2O$. The method is suitable for the synthesis of homoleptic ruthenium complexes. Notably, $RuCl_3$ trihydrate led to formation of homoleptic ruthenium complexes more efficiently than anhydrous $RuCl_3$, because of poor solubility of the latter in most of solvents. Both one-pot methods are very simple, rapid and efficient for preparing heteroleptic and homoleptic ruthenium complexes. Ruthenium complexes were purified by column chromatography on silica with MeCN : H_2O : KNO_3 (100 : 7.5 : 0.5) as an eluent. Presence of some traces recorded by HPLC suggested formation of $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$.

The measured molecular-ion peaks appeared at 444.65 (calculated 444.10) for $Ru(bpy)_2(TAGP\text{-}tapy)^{2+}$ and 764.50 (calculated 765.185) for $Ru(TAGP\text{-}tapy)_3^{2+}$. Additionally, ESI-MS spectra of the complexes indicated that the tapy moiety acted as a bipyridine-like chelator. ^1H NMR spectrum of $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ was complicated because of the overlap of two ligands bands and a mixture of the *fac*- and *mer*-isomers.

UV-Vis and fluorescence spectroscopies were used to assess the optical properties of $Ru(TAGP\text{-}tapy)_3]Cl_2$ and $Ru(bpy)_2(TAGP\text{-}tapy)]Cl_2$. Absorption spectra of the complexes were similar to those of PSO-substituted ligands and ruthenium complexes previously reported [17]. As a typical control spectrum, TAGP-tapy exhibited the maximum absorbance at 280 nm due to the electronic π–π* transition of the tapy moiety, and a 285 nm band as a weak shoulder because of a π–π* transition of one py ligand. Upon TAGP-tapy chelating with $RuCl_3 \cdot 3H_2O$ and formation of $Ru(TAGP\text{-}tapy)_3]Cl_2$, the above maximum absorbance had a blue shift to 267 nm, and the 285 nm absorption band was totally absent in the spectrum due to lack of bpy ligand. A new absorbance peak appeared at ca 371 nm due to the metal-to-ligand charge transfer (MLCT) effect caused by Ru(II)/tapy complex core. The characteristic maximum absorption band for $Ru(TAGP\text{-}tapy)_3Cl_2$ was shifted to shorter wavelength than that of $Ru(bpy)_3^{2+}$ complex (450 nm in acetonitrile) because of the poor electro-accepting property of triazole ring. The MLCT effect, on the other hand, resulted in the slightly yellow color of the aq. $Ru(TAGP\text{-}tapy)_3]Cl_2$ solution. Ru(II) Complexes of TAGP-tapy gave UV-Vis spectra similar to those of $[Ru(Bn\text{-}tapy)_3](PF_6)_2$, suggesting a similar coordination on Ru(II) ions. The maximum absorbance of $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ (Fig. 3) presented a red shift to 283 nm compared with TAGP-tapy, and a weak shoulder was observed due to the presence of one tapy moiety. The broad and relatively intense band at ca 430 nm was assigned to a metal-to-ligand charge-transfer (MLCT) effect caused by the Ru(II)–(tapy and bpy) complex core. The higher-energy shoulder observed was assigned to the second MLCT transition. Spectroscopic and photophysical studies demonstrate that inherently favorable properties of the parent complexes were not substantially altered by the ligand substitutions.

Room-temperature fluorescence emission spectra of the complexes recorded in MeOH (Fig. 4) demonstrated

maximum excitation wavelength at 450 nm for $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ and 370 nm for $Ru(TAGP\text{-}tapy)_3Cl_2$. Electronic emission spectra of the complexes exhibited strong bands at 590 nm for $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ and at 417 nm for $Ru(TAGP\text{-}tapy)_3Cl_2$. Fluorescence properties studies of $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ and $Ru(TAGP\text{-}tapy)_3Cl_2$ indicated their potential in imaging proteins within living cells.

EXPERIMENTAL

All chemicals and reagents were of analytical grade or of the highest purity available and used without further purification. Ultrapure water was used throughout the experiments. Most of reagents and solvents were purchased from Aladdin Reagent (Shanghai, China). TLC analyses were performed on silica gel plates and column chromatography was carried out on silica gel (200–300 mesh), purchased form Qingdao Haiyang Chemicals. A semi-preparative column (Dikma Tech. Inc., Luster C18, 10 mm, 21.2×250 mm) was used to purify ruthenium complexes. Purity of ruthenium complexes (>98%) and the intermediates (>95%) were determined by TLC (Qingdao silica gel plates of GF254, 0.25 mm layer thickness) and HPLC analysis (Waters, C18 column, 4.6×150 mm). UV-Vis absorption spectra were recorded on a SHIMADZU UV-2550 spectrophotometer. Fluorescence was recorded on a HITACHIF-2500 fluorescence spectrometer with the excitation and emission slit widths at 5.0 nm. FT-IR spectra were recorded on a Thermo Nicolet IS5, Thermo Fisher Scientific, USA). ^1H and ^{13}C NMR spectra were measured on a Varian INOVA-300 MHz spectrometer with TMS as the internal standard. ESI/MS spectra were measured on a ZQ 2000 (Waters, US) and solariX FT-ICR mass spectrometer (Bruker Daltonik) with an ESI/MALDI dual ion source and 9.4 T superconductive magnet.

Synthesis of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (TAGP-N_3). TAGP-N_3 was prepared according to the literature procedure [18]. To a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (411.2 mg, 1 mmol, 1.0 eq.) in DMF (10 mL), sodium azide (78.0 mg, 1.2 mmol, 1.2 eq.) was added and the reaction mixture was stirred for 4 h. Then it was diluted with water (50 mL) and extracted with EtOAc (3×100 mL). The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography (SiO_2, EtOAc–petroleum ether 1 : 2, R_f = 0.45). TAGP-tapy was obtained as a white solid, Yield 89.0%. IR spectrum, ν, cm^{-1}: 2120, 1748, 1372, 1245, 1209, 1064, 906. ^1H NMR spectrum, δ, ppm: 5.23 t (1H), 5.11 t (1H), 4.98 t (1H), 4.65 d (1H), 4.32–4.12 m (2H), 3.84–3.76 m (1H), 2.11–2.01 s.s.s.s (12H). ^{13}C NMR spectrum, δ, ppm: 170.58, 170.10, 179.25, 169.18, 87.91, 74.02, 72.61, 70.72, 67.90, 61.75, 20.65, 20.54, 20.51, 20.50.

Synthesis of 2-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl]-pyridine (TAGP-tapy). TAGP-tapy was prepared according to a literature procedure [19]. A mixture of TAGP-N_3 (186.7 mg, 0.5 mmol) with 2-ethynylpyridine (61.9 mg, 0.6 mmol), Cu(II) sulfate pentahydrate (25.0 mg, 0.1 mmol) and ascorbic acid (35.2 mg, 0.2 mmol) in DMF (15 mL) were stirred at room temperature under TLC monitoring (eluent: petroleum ether–ethyl acetate = 1 : 1, R_f = 0.4). The solvent was removed under reduced pressure, the residue was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with a bit of EDTA in aqua ammonia (20 mL), dried above Na_2SO_4, filtered, and concentrated. Flash chromatography with PE/EtOAc as an eluent, gave TAGP-tapy as white solid, 86.0%. IR spectrum, ν, cm^{-1}: 2120, 1608, 1461, 1425, 1372, 1215, 1114, 1028. ^1H NMR spectrum, δ, ppm: 8.61 d (1H), 8.44 s (1H), 8.16 d (1H), 7.85–7.76 m (1H), 7.30–7.22 m (1H), 5.98–5.92 d (1H), 5.55–5.46 m (2H), 5.27 t (1H), 4.37–4.28 m (1H), 4.20–4.13 m (1H), 4.09–4.01 m (1H), 2.10–1.90 s.s.s.s (12H). ^{13}C NMR, spectrum, δ, ppm: 170.45, 169.86, 169.26, 168.81, 149.55, 149.50, 148.91, 136.96, 123.18, 120.65, 120.41, 85.84, 75.13, 72.68, 70.52, 67.67, 61.52, 20.66, 20.53, 20.51, 20.18.

Preparation of $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$. TAGP-tapy (95.3 mg, 0.2 mmol, 1 eq.) and *cis*-bis-(2,2'-bipyridine)dichlororuthenium(II) dihydrate (*cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$) (104.1 mg, 0.2 mmol, 1 eq.) were suspended in CH_2Cl_2 : MeOH (1 : 1) and the suspension was degassed by bubbling with nitrogen for 15 min. The reaction mixture was heated at 100°C for 8 h before being filtered through a hirsch funnel. The solvent was removed under reduced pressure and the residue was purified by the silica gel column chromatography eluting with MeCN : H_2O : KNO_3 (sat.) (100 : 7.5 : 0.5). The fraction containing $Ru(bpy)_2(TAGP\text{-}tapy)Cl_2$ was collected and the solvent was evaporated. The resulting solid was dissolved in CH_3CN to remove the excess of KNO_3 by filtration to give the compound as red solid, yield 40.0%. ^1H NMR

spectrum, δ, ppm: 9.45 d (1H), 8.75–7.38 m (20H), 6.14 d.d (1H), 5.51–5.18 m (3H), 4.35–4.15 m (3H), 2.08–1.48 s.s.s.s (12H). ^{13}C NMR spectrum, δ, ppm: 170.81, 170.79, 169.87, 169.75, 157.80, 157.55, 157.46, 157.39, 157.37, 151.81, 151.60, 151.41, 150.39, 148.25, 138.30, 138.03, 137.99, 137.90, 137.67, 127.65, 127.57, 126.92, 126.79, 125.30, 125.25, 124.17, 124.10, 124.00, 123.61, 123.03, 122.93, 86.29, 74.90, 72.09, 70.98, 67.47, 61.40, 19.26, 19.15, 19.08, 18.80.

Preparation of Ru(TAGP-tapy)$_3$Cl$_2$. Ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$) (18.3 mg, 0.07 mmol), TAGP-tapy (100.1 mg, 0.21 mmol) and *N,N*-dimethylformamide (DMF; 10 mL) were placed in a 50-mL flask. The mixture was degassed by bubbling with nitrogen for 15 min and heated at 160°C for 3 h. The mixture solution containing the target product was collected by filtration and concentrated under reduced pressure. The resulting orange solid was purified by silica gel column chromatography eluting with MeCN : H_2O : KNO_3 (sat.) (100 : 7.5 : 0.5). The fractions containing the Ru(TAGP-tapy)$_3$Cl$_2$ was collected, and the solvent was evaporated. The resulting solid was dissolved in CH_3CN to remove the excess KNO_3 by filtration to give the compound as a brown solid. Yield: 32.0 mg, 0.02 mmol, 28.55%. ^{1}H NMR spectrum, δ, ppm: 9.60–9.38 m (3H), 8.44–7.36 m (12H), 6.31–6.08 m (3H), 5.64–5.17 m (9H), 4.51–4.07 m (9H), 2.19–1.87 m (36H). ^{13}C NMR spectrum, δ, ppm: 170.70, 169.90, 169.71, 169.46, 169.22, 168.84, 167.95, 152.77, 152.00, 151.05, 150.67, 148.88, 148.14, 138.28, 132.19, 131.02, 128.46, 126.21, 125.72, 125.52, 125.12, 124.56, 124.15, 123.09, 122.60, 122.29, 86.31, 85.87, 75.17, 74.75, 72.49, 72.04, 71.23, 70.82, 70.54, 70.15, 67.73, 67.40, 61.33, 38.78, 33.99, 30.22, 28.73, 23.55, 22.61, 19.24, 18.72, 12.98, 10.00.

CONCLUSIONS

In this study the complexes Ru(TAGP-tapy)$_3$Cl$_2$ and Ru(bpy)$_2$(TAGP-tapy)Cl$_2$ were synthesized. The glucosyl ligand TAGP-tapy was prepared by click reaction, which exhibited interesting fluorescence properties (solvatofluorochromism). A fluorescence red-shift was observed from 320 nm in THF to 366 nm in a mixture of acetonitrile/water. Adopted TAGP-tapy as a ligand, Ru(TAGP-tapy)$_3$Cl$_2$ and Ru(bpy)$_2$(TAGP-tapy)Cl$_2$ were prepared by its chelating with $RuCl_3 \cdot 3H_2O$ and *cis*-Ru(bpy)$_2$Cl$_2$, respectively. The click-to-chelate approach can offer an excellent tool for the preparation of the homoleptic and heteroleptic ruthenium complexes appended with glucosyl ligand. Following this synthetic approach, different sugar-functionalized derivatives may be prepared and applied to various carbohydrate-protein binding studies.

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