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Synthesis and photophysical properties of fluorescent 2,1,3-benzothiadiazole-triazole-linked glycoconjugates: selective chemosensors for Ni(II)

Angélica V. Moro *, Patrícia C. Ferreira, Pedro Migowski, Fabiano S. Rodembusch, Jairton Dupont, Diogo S. Lüdtke *

Instituto de Química, Universidade Federal do Rio Grande do Sul, UFRGS, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, RS, Brazil

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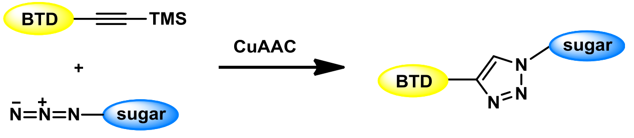
ABSTRACT

The synthesis of new fluorescent 2,1,3-benzothiadiazole-triazole-linked glycoconjugates is described by a straightforward synthetic route, using a copper(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC). UV–visible (UV–vis) and steady-state fluorescence in solution were applied in order to characterize its photophysical behavior. The dyes present absorption in the violet region with fluorescence emission in the cyan-green region, which can be related to the methoxy derivatives due to an intramolecular charge transfer (ICT) in the excited state. The studied derivatives present potential optical application since combine large extinction coefficient for absorption, large Stokes shift and high fluorescence emission. Additionally, these dyes exhibit binding selectivity to Ni^{+2} among a series of cations in CH_3CN solution.

1. Introduction

Benzothiadiazolyl derived molecules are widely investigated nowadays due to their well-known photophysical properties such as high extinction coefficient, intense fluorescence, and large Stokes shift.[1] These features make them useful in a variety of applications such as optical materials and chemosensors.[2] Fluorescent 2,1,3-benzothiadiazole (BTD) derivatives have been described as useful dyes with a number of applications in metal,[3] protein,[4] and DNA[5] detection, as live cell-imaging probes[6] and dyes for real-time PCR.[7]

On the other hand, carbohydrates are naturally available molecules, which constitute the largest part of biomass produced by living organisms and therefore are abundant and inexpensive. In addition, carbohydrates present low toxicity and are polyfunctional molecules with varied scaffolds. These attractive features can be used for the design of functional molecules with available sites for metal coordination. In particular, glycoconjugation would be a promising approach for the synthesis of chiral fluorescent molecules with many potential applications as chemosensors.[8] One method of choice for an efficient glycoconjugation is the copper(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition reaction (CuAAC),[9,10] which is the best known example of the click chemistry concept.[11] Sugar-derived triazoles have been the subject of intense research in recent years, mainly due to the reluctance of the triazole linker to undergo hydrolysis, oxidation, and reduction in the biological environment. In addition, its ability to participate in hydrogen-bonding and dipole interactions has attracted the attention of synthetic carbohydrate chemists, medicinal chemists as well as materials chemists.[12] The click chemistry approach for fluorescent labeling of biomolecules has been applied for proteins functionalized with an alkyne or azide group[13] as well as for amino acids.[14] In connection with our recent interest on the use of carbohydrates as a chiral pool for the synthesis of chiral molecules,[15] we hypothesized if it would be possible to efficiently introduce a fluorescent group within the sugar framework. A straightforward approach to this aim would be the CuAAC between sugar azides and a fluorescent BTD derivative bearing an alkyne moiety (Scheme 1). The resulting molecules would possess several coordinating atoms and might be used as fluorescent probes for the detection of metals in solution, since many sites would be available for metal coordination.



Scheme 1. General approach for the synthesis of BTD-triazole-glycoconjugates.

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* Corresponding authors. Tel./fax: +55 51 3308 7201; e-mail addresses: angelventurini@gmail.com (A.V. Moro), dsludtke@iq.ufrgs.br (D.S. Lüdtke).

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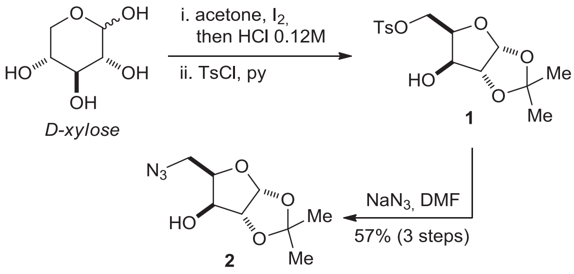
Herein we report our results on the synthesis of BTD-triazole-linked glycoconjugates through a Cu(I)-catalyzed alkyne–azide cycloaddition, their photophysical properties, and their application as fluorescent probes for the selective detection of nickel(II).

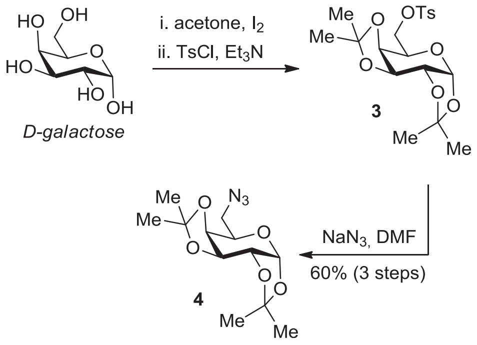
2. Results and discussion

Initially, we prepared the sugar azides **2** and **4** in an efficient sequence, starting from D-xylose and D-galactose as the starting sugars. First, D-xylose was treated with acetone in the presence of catalytic amounts of iodine,[16] followed by partial deprotection to afford the corresponding diol. Selective reaction of the primary hydroxyl group with TsCl in pyridine resulted in the tosylate **1**, which was subjected to reaction with NaN_3 to afford the desired azide **2**[17] in 57% overall yield over three steps (Scheme 2).



Scheme 2. Synthesis of azide **2**.

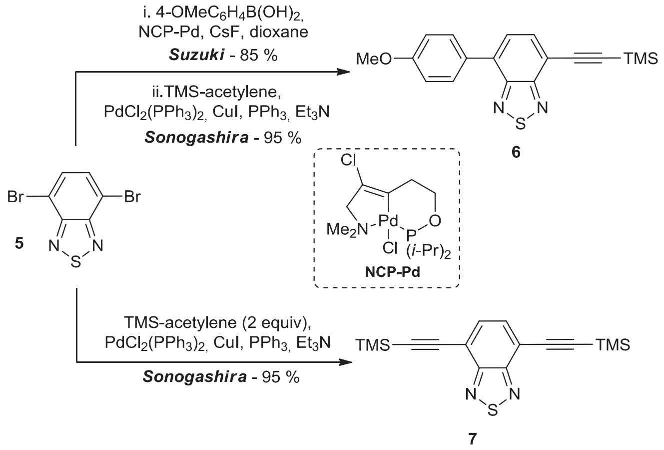
Following the same strategy, D-galactose was submitted to protection of the hydroxyl groups as the corresponding acetonides, followed by tosylation of the free primary alcohol to afford tosylate **3**. A clean substitution reaction with sodium azide delivered the corresponding azide **4**[18] in 60% yield over the three-step sequence (Scheme 3).



Scheme 3. Synthesis of azide **4**.

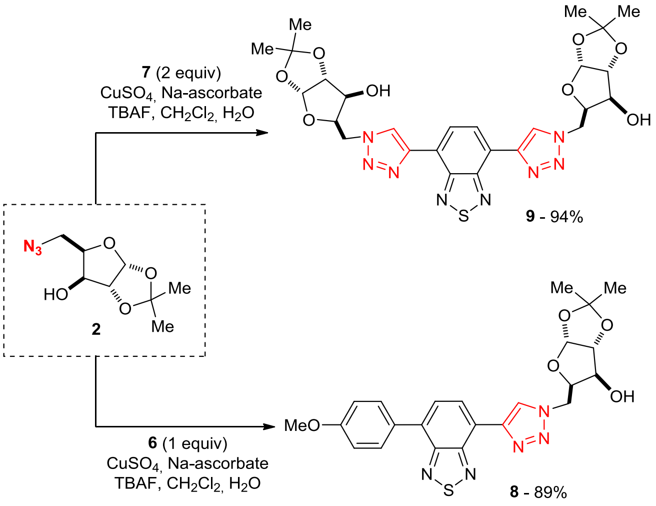
It is worth to note that the sequences delineated above are very efficient and have been carried out in gram-scale, allowing the fast synthesis of significant amounts of azides **2** and **4**. Next, BTD dibromide **5** was converted to the TMS-protected alkynes **6** and **7**, by palladium-catalyzed reactions (Scheme 4). When **5** was subjected to Suzuki coupling with 4-methoxyphenylboronic acid, in the presence of catalytic amounts of the non-symmetrical NCP pincer palladacycle (NCP–Pd),[19] the arylated product was formed in 85% yield. Subsequently, a Sonogashira reaction with TMS–acetylene, catalyzed by $PdCl_2(PPh_3)_2$ afforded the unsymmetrical alkyne **6**. On the other hand, a direct double Sonogashira reaction using 2 equiv of TMS–acetylene resulted in the symmetrical alkyne **7** in 95% yield (Scheme 4).

Importantly, attempts to obtain alkynes **6** and **7** in their deprotected forms were unsuccessful, due to the fast decomposition of the resulting terminal alkynes. Indeed, even the protected alkynes **6** and **7** have limited stability and should be prepared and immediately used in the CuAAC reaction.



Scheme 4. Synthesis of alkynes **6** and **7**.

With the required starting materials in hands, the cycloaddition reactions were performed. Gratifyingly, reaction of sugar azide **2** with BTD–alkynes **6** and **7**, under copper catalysis, in the presence of sodium ascorbate and TBAF, smoothly resulted in the BTD-triazole-glycoconjugates **8** and **9** in excellent yields (89 and 94%, respectively) (Scheme 5).

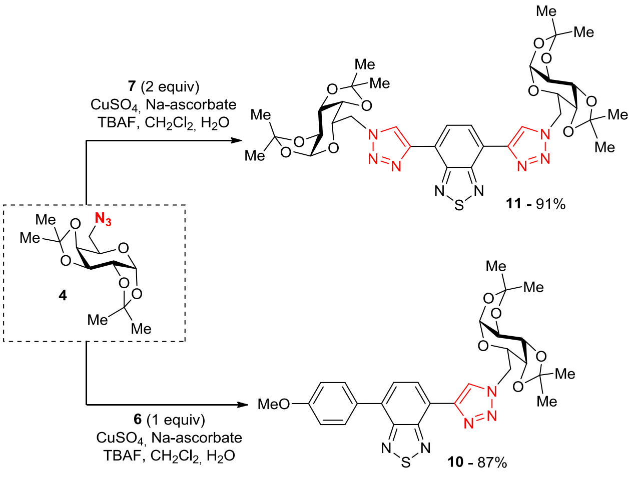


Scheme 5. CuAAC with azide **2**.

Similarly, reaction of BTD–alkynes **6** and **7** with the galactose-derived azide **4** afforded both the unsymmetrical and symmetrical the 1,2,3-triazolyl glycoconjugates **10** and **11** very efficiently and the products were isolated in 87 and 91% yields, respectively (Scheme 6).

With an efficient synthesis of the BTD-triazole-glycoconjugates established, their photophysical properties were examined. The absorption and emission spectra of the dyes **8**–**11** in 1,4-dioxane are shown in Fig. 1.

The dyes **8**–**11** present absorption bands at the same region, indicating that the additional triazolyl moiety does not play a fundamental role on the electronic conjugation in the ground state of the dyes. The lowest energy absorption bands are in agreement with $\pi\rightarrow\pi^*$ transitions due to their large molar extinction coefficient values (ε_{max}). The relevant data are summarized in Table 1.



Scheme 6. CuAAC with azide **4**.

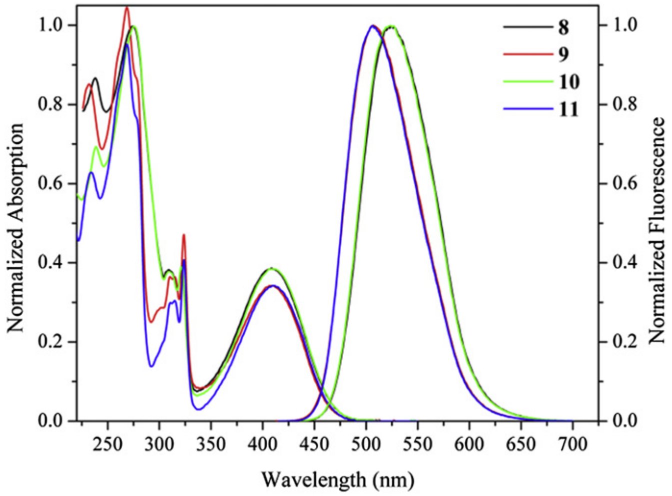


Fig. 1. Normalized absorbance and fluorescence emission of dyes **8**–**11** in 1,4-dioxane.

Table 1
UV–vis data of the dyes **8**–**11**, where λ_{abs} is the absorption in nanometers and ε is the molar extinction coefficient in $\times 10^4$ M^{-1} cm^{-1}

Dye	Solvent	λ_{abs} (λ)
8	Ethanol	404(0.88), 320(0.84), 308(0.81), 273(2.20)
	Acetonitrile	404(0.93), 320(0.81), 308(0.77), 273(2.22)
	1,4-Dioxane	410(1.06), 321(1.08), 309(1.06), 273 (2.74)
9	Ethanol	396(0.87), 322(1.01), 308(0.78), 266(2.14)
	Acetonitrile	402(0.95), 322(1.07), 308(0.78), 267(2.45)
	1,4-Dioxane	411(1.02), 324(1.41), 310(1.08), 268(3.06)
10	Ethanol	398(1.09), 321(1.20), 308(0.88), 267(2.60)
	Acetonitrile	403(1.15), 321(1.21), 308(0.84), 267(2.88)
	1,4-Dioxane	412(1.29), 324(1.56), 315(1.15), 310(1.13)
11	Ethanol	404(1.04), 320(1.02), 309(1.02), 275(2.63)
	Acetonitrile	404(1.01), 320(0.88), 309(0.83), 273(2.47)
	1,4-Dioxane	411(1.21), 322(1.23), 309(1.19), 275(3.14)

Table 2
Fluorescence and excitation data of the dyes **8**–**11**, where λ_{exc} is the excitation maximum in nanometers, λ_{em} is the fluorescence emission maximum in nanometers, ϕ_{fl} is the fluorescence quantum yield, and $\Delta\lambda_{ST}$ is the Stokes shift in nanometers (cm^{-1})

Dye	Solvent	λ_{exc}	λ_{em}	$\Delta\lambda_{ST}$[a]	ϕ_{fl}
8	Ethanol	415	547	143(6470.9)	0.126
	Acetonitrile	415	541	137(6268.2)	0.286
	1,4-Dioxane	424	523	113(5269.8)	0.289
9	Ethanol	409	508	112(5567.5)	0.436
	Acetonitrile	414	509	107(5229.3)	0.502
	1,4-Dioxane	421	508	97(4645.9)	0.406
10	Ethanol	417	544	146(6743.3)	0.489
	Acetonitrile	416	542	139(6363.7)	0.561
	1,4-Dioxane	423	524	112(5187.9)	0.447
11	Ethanol	411	508	104(5067.4)	0.137
	Acetonitrile	415	509	105(5106.1)	0.288
	1,4-Dioxane	423	508	97(4645.9)	0.342

[a] The Stokes shift was obtained from the difference of the emission and absorption maximum ($\Delta\lambda_{ST}=\lambda_{em}-\lambda_{abs}$).

It is worth mentioning that the same photophysical behavior could be observed in acetonitrile and ethanol (see Supplementary data).

The normalized fluorescence emission spectra of these dyes were obtained using the absorption maxima as the excitation wavelengths. The relevant data are summarized in Table 2. The derivatives **8** and **10** present red shifted emission bands (~537 nm) in despite of the dyes **9** and **11** (~508 nm). These results allowed to observe that the π-conjugation has a significant effect on the photophysical properties of these compounds, indicating that this structural change is fundamental for the fluorescence itself. Evidences of intramolecular charge transfer (ICT) in the excited state could be observed to the derivatives **8** and **10**, where a redshift takes place increasing the solvent polarity, since the species with charge separation (ICT state) may become the lowest energy state.[20] Additionally, the solvatochromic effect between the dyes **8** and **10** from **9** and **11**, can also be rationalized concerning the dyes structure, where it was already observed that as the symmetry of the compound increases (compounds **9** and **11** possess a more symmetric structure than **8** and **10**) the excited state lowers, and consequently there is less stabilization by the solvent dipoles.[20b] In this way, as already observed in the literature, a very efficient intramolecular charge transfer takes place in the excited state between the terminal methoxy group and the benzothiadiazole nucleus.[1]

From this analysis, although the acetonitrile presents higher dielectric constant than ethanol, the observed emission maxima in this protic polar solvent is due to the ability to present specific interactions (hydrogen bonds) with these dyes.[21] Large Stokes shifts could be calculated for all studied dyes (~4600–6700 cm^{-1}). Concerning the absence of a solvatochromic effect in derivatives **9** and **11**, as well as the large Stokes shift for all dyes, the obtained values cannot be related only to a charge transfer in the excited state.[1] The excitation spectra of the dyes **8**–**11** in different solvents were recorded at different λ_{em} in the range of 300–520 nm and are presented in Fig. 2. In each case, the fluorescence excitation spectra resemble each other and also with the absorption spectra in the respective solvent. The same small solvatochromic effect could be observed. This suggests that there is only one species for the dyes **8**–**11** in the S_0 state, although a better structuration could be observed in the excitation spectra.

To get insight into the binding properties of the dyes **8**–**11** toward metal ions (Zn^{+2}, Cd^{+2}, Co^{+2}, Mg^{+2}, Ni^{+2}, and Ag^{+}), it was investigated the fluorescence profile of the dyes upon addition of 20 equiv of selected cations to the acetonitrile solution (Fig. 3). As can be observed, the fluorescence emission was not affected by Zn^{+2}, Cd^{+2}, Ag^{+}, and Mg^{+2}, slightly quenched by Co^{+2} and significantly quenched by Ni^{+2}, as already observed in similar structures.[22] It is worth mentioning that the same photophysical behavior could be observed to the dyes **8**, **10**, and **11** (see Supplementary data). Dyes **9**–**11** presented the higher decrease of

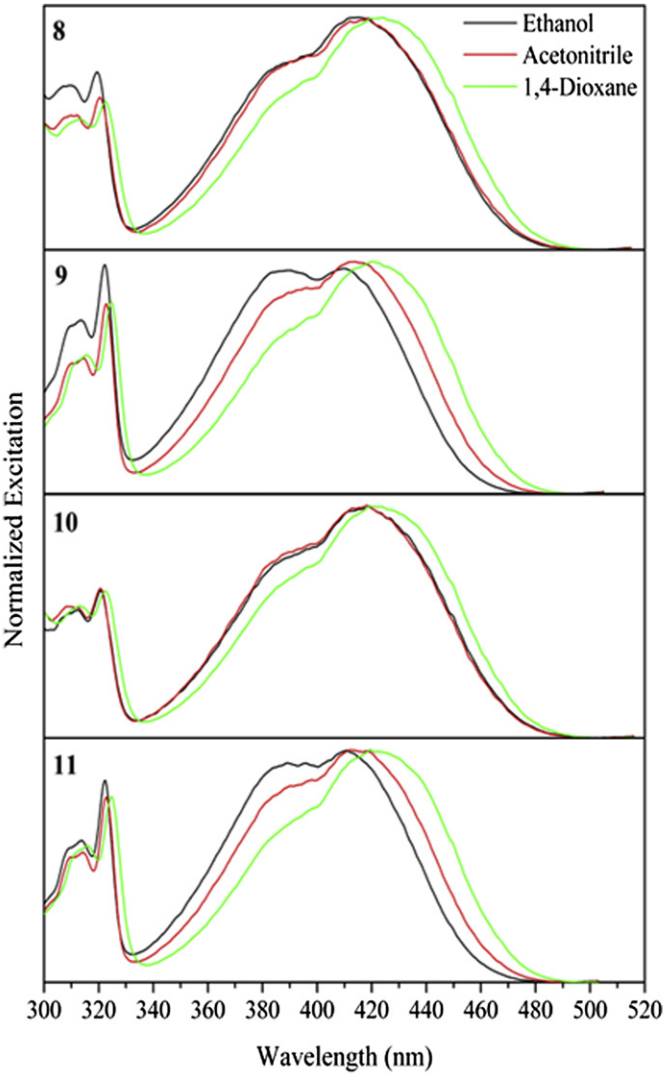


Fig. 2. Normalized excitation spectra of dyes **8**–**11** in 1,4-dioxane.

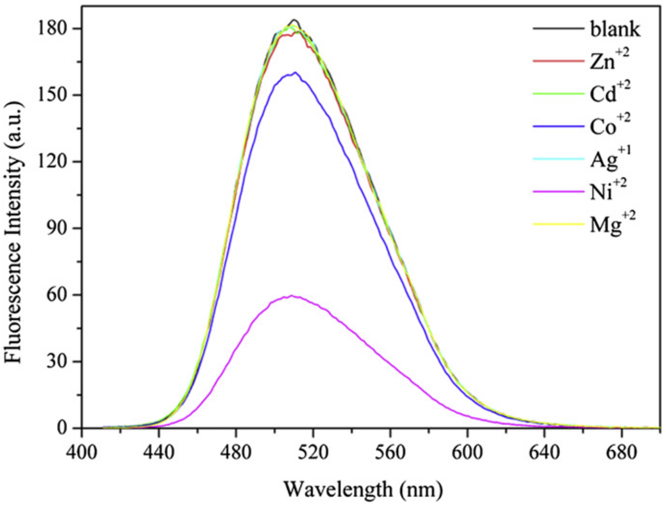


Fig. 3. Fluorescence spectra of dye **9** upon addition of various NO_3^- salt (20 equiv) in MeCN (λ_{ex}=405 nm).

fluorescence emission upon addition of the Ni^{+2}, with the dye **9** presenting the higher one.

Due to the better fluorescence response upon addition of the metal, dye **9** was selected for detailed fluorescence assessments. In acetonitrile solution, the addition of Ni^{+2} (from 0.06 to 5.75 equiv) decreased gradually and finally reached its quenching plateau at ~6 equiv (Fig. 4). Regarding the results presented in the literature, although the dye **9** does not present fluorescence response in the higher range of metal concentration, the dye seems clearly be more sensitive.[22] On the other hand, the results in ethanol indicates that the dye **9** is less sensitive, probably due to the solvent ability to present hydrogen bond with the binding sites in the structure, although an higher linear relation could be obtained (2.38×10^{-6} to 5.48×10^{-5} M). The additional fluorescence emission curves in ethanol are presented in Supplementary data.

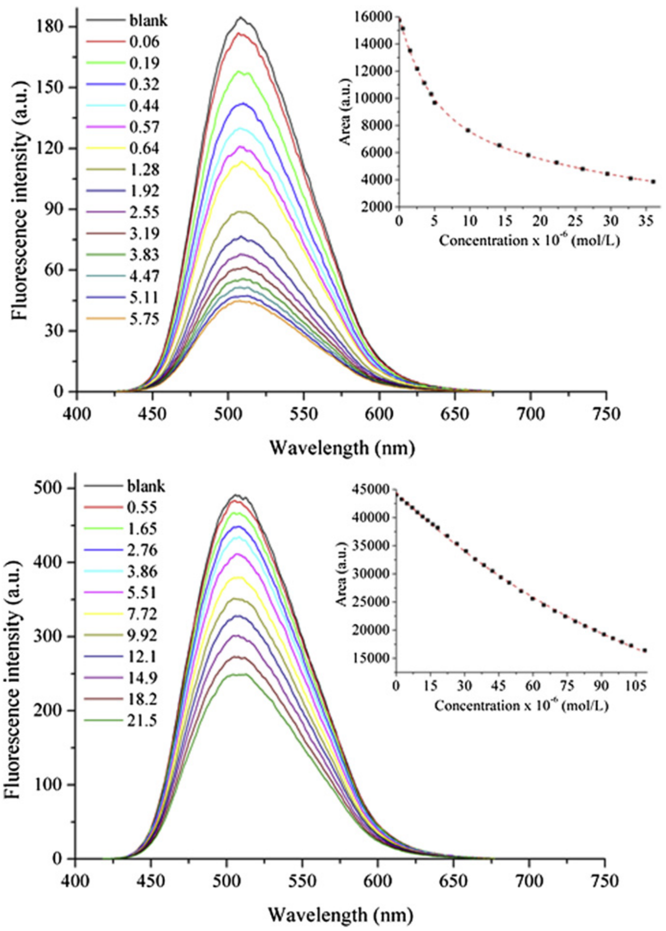


Fig. 4. Fluorescence spectra of dye **9** (8.14×10^{-6} M) upon addition of Ni^{+2} ion in acetonitrile (top) and ethanol (bottom) (λ_{ex}=405 nm).

In both solvents, the fluorescence intensity is progressively quenched with increasing concentration of Ni^{+2} (Fig. 4), as clearly observed by the decrease of fluorescence intensity as a function of the metal (inset), which can probably be related to a photoinduced electron transfer (PET) or charge transfer (CT) mechanism.[22,23]

3. Conclusions

In summary, the synthesis of four new fluorescent triazolyl glycoconjugates was accomplished through a copper(I)-catalyzed azide–alkyne cycloaddition between a sugar-derived azide and a BTD–alkyne. The synthesis is straightforward and delivers the compounds in a short and efficient synthetic sequence. In addition, photophysical studies revealed that the glycoconjugates **8**–**11** present absorption in the violet region with fluorescent emission in the cyan-green region. The large extinction coefficient for absorption, large Stokes shift, and high fluorescence emission make this molecules promising for optical applications. In addition, it was shown that dyes **8**–**11** can be used as chemosensors exhibiting strong selective binding to Ni^{+2} in acetonitrile solution.

4. Experimental

4.1. General procedures

^1H and ^{13}C NMR spectra were recorded at 400 or 300 MHz and 100 or 75 MHz, respectively, with tetramethylsilane as internal standard. High-resolution mass spectra were recorded on a Bruker Daltonics Micro-TOF instrument in ESI-mode. Column chromatography was performed using Merck Silica Gel (230–400 mesh) following the methods described by Still.[24] Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or ethanolic solution of phosphomolybdic acid. Sugar azides were prepared according to literature procedures.[17,18] Yields refer to chromatographically and spectroscopically homogeneous materials with purity of >95%, as judged by ^1H NMR spectroscopy. Spectroscopic-grade solvents (Merck) were used for fluorescence and UV–visible (UV–vis) measurements. UV–vis absorption spectra were performed on a Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence spectra were measured with a Shimadzu spectrofluorometer model RF-5301PC. Spectrum correction was performed to enable measuring a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or detector using Rhodamine B as a standard (quantum counter). All experiments were performed at room temperature at a concentration of $\sim 10^{-5}$ M. The quantum yields of fluorescence (ϕ_{fl}) were obtained at 25 °C in spectroscopic-grade solvents using the optical dilute method—absorbance lower than 0.05 related to a dye concentration of 10^{-6} mol/L. To the quantum yields of fluorescence calculation the refractive indices of solvents were taking into account. Quinine sulfate (Riedel) in 0.1 N H_2SO_4 at an excitation wavelength of 390 nm ($\phi_{fl}=0.51$) was used as quantum yield standard.[25] Stock solutions of the dyes **8**–**11** (10^{-6} M) and the metal nitrates (10^{-4} M) were prepared in acetonitrile and ethanol. For all chemosensor studies the excitation wavelength was set at 405 nm.

4.2. General procedure for the Suzuki reaction[5]

A solution of CsF (1.7 mmol, 250 mg), 4-methoxyphenylboronic acid (1.7 mmol, 250 mg), NCP–Pd (1 mol %), and BTD dibromide **5** (1.7 mmol, 500 mg) in dioxane in a Schlenk tube was stirred at 130 °C for 24 h. After this time the reaction mixture was cooled and the solvent removed under reduced pressure. The crude product was purified by flash chromatography to afford the product in 85% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.90 (d, J=7.7 Hz, 1H), 7.86 (d, J=8.8 Hz, 2H), 7.52 (d, J=7.7 Hz, 1H), 7.06 (d, J=8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.1, 153.9, 153.2, 133.6, 132.3, 130.4, 129.0, 127.4, 114.2, 112.2, 55.4.

4.3. General procedure for the Sonogashira reaction

To a solution of appropriate BTD bromide (0.5 mmol) in triethylamine (1.5 mL) in a Schlenk tube, $PdCl_2(PPh_3)_2$ (2 mg) triphenylphosphine (13 mg), copper iodide (13 mg), and trimethylsilylacetylene (0.7 or 1.4 mmol, depending on the BTD bromide used) were sequentially added. The reaction mixture was stirred under argon atmosphere at 90 °C for 4 h. After this time, the solvent was evaporated and the crude product was filtered in a column of silica, concentrated under reduced pressure, and immediately used in the next step.

4.4. General procedure for the CuAAC reaction

To a solution of alkynyl BTD **6** (0.5 mmol) and the azido sugar (0.5 mmol), in dichloromethane (5 mL) and water (5 mL), $CuSO_4\cdot 5H_2O$ (13 mg, 0.05 mmol), sodium ascorbate (10 mg, 0.05 mmol) were added. Next, TBAF 1 M in THF (1 mL, 1 mmol) was dropwise added. The reaction mixture was stirred at room temperature for 24 h and washed with an EDTA solution 0.1 M (10 mL) and then extracted with ethyl acetate (3×10 mL). The organic layer was washed with a saturated aqueous solution of NaCl, dried under $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Note: when the reaction was performed with bis-alkynyl BTD **7** *2 equiv of all reagents were used.*

4.5. Compound 8

Yield=89%. Purified by flash chromatography eluting with hexane/ethyl acetate (40:60). $[\alpha]_D^{20}$ −50 (c 1.0, AcOEt). ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.85 (s, 1H), 8.54 (d, J=7.5 Hz, 1H), 7.93 (d, J=8.8 Hz, 2H), 7.76 (d, J=7.5 Hz, 1H), 7.07 (d, J=8.8 Hz, 2H), 6.05 (d, J=3.6 Hz, 1H), 4.93 (dd, J=13.9, 7.9 Hz, 1H), 4.73 (dd, J=13.9, 6.0 Hz, 1H), 4.65 (d, J=3.6 Hz, 1H), 4.61 (ddd, J=7.9, 6.0, 2.7 Hz, 1H), 4.32 (d, J=2.7 Hz, 1H), 3.89 (s, 3H), 3.73 (br s, 1H), 1.47 (s, 3H), 1.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.9, 153.8, 152.4, 143.4, 133.4, 130.4, 129.6, 127.3, 125.9, 125.2, 121.2, 114.1, 112.1, 105.2, 85.2, 79.2, 74.6, 55.4, 48.4, 26.8, 26.1. IR (KBr, cm^{-1}): 3464, 2992, 2926, 2841, 1614, 1512, 1479, 1249, 1007, 821, 750, 514. HRMS (ESI) calcd for $C_{23}H_{23}N_5O_5S$+H: 482.1498, found: 482.1508.

4.6. Compound 9

Yield=94%. Purified by flash chromatography eluting with ethyl acetate/methanol (95:05). $[\alpha]_D^{20}$ −36 (c 1.0, DMSO). ^1H NMR (DMSO-d_6, 300 MHz) δ: 9.02 (s, 2H), 8.55 (s, 2H), 5.94 (d, J=3.6 Hz, 2H), 5.73 (d, J=4.8 Hz, 2H), 4.82 (dd, J=14.0, 3.9 Hz, 2H), 4.70 (dd, J=14.0, 8.4 Hz, 2H), 4.64–4.48 (m, 4H), 4.17–4.15 (m, 2H), 1.35 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 151.5, 141.8, 125.3, 125.2, 122.2, 110.8, 104.6, 85.1, 79.3, 73.7, 49.3, 26.6, 26.0. IR (KBr, cm^{-1}): 3440, 3147, 2994, 2922, 2889, 1219, 1090, 1011, 809. HRMS (ESI) calcd for $C_{26}H_{30}N_8O_8S$+H: 615.1986, found: 615.1985.

4.7. Compound 10

Yield=87%. Purified by flash chromatography eluting with hexane/ethyl acetate (70:30). $[\alpha]_D^{20}$ −47 (c 1.0, AcOEt). ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.89 (s, 1H), 8.60 (d, J=7.4 Hz, 1H), 7.94 (d, J=8.8 Hz, 2H), 7.78 (d, J=7.4 Hz, 1H), 7.08 (d, J=8.8 Hz, 2H), 5.50 (d, J=4.9 Hz, 1H), 4.74 (dd, J=14.2, 4.4 Hz, 1H), 4.67 (dd, J=7.9, 2.5 Hz, 1H), 4.63 (dd, J=14.2, 8.2 Hz, 1H), 4.39–4.34 (m, 2H), 4.27 (dd, J=7.9, 1.9 Hz, 1H), 3.90 (s, 3H), 1.55 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 160.9, 155.0, 153.7, 144.1, 134.1, 131.5, 130.9, 128.5, 126.9, 126.2, 123.0, 115.1, 110.9, 110.1, 97.3, 72.2, 71.8, 71.4, 68.2, 56.4, 51.7, 27.1, 25.9, 25.5. IR (KBr, cm^{-1}): 2983, 2936, 1724, 1379, 1248, 1208, 1069, 998, 828, 510. HRMS (ESI) calcd for $C_{27}H_{29}N_5O_6S$+H: 552.1917, found: 552.1899.

4.8. Compound 11

Yield=91%. Purified by flash chromatography eluting with hexane/ethyl acetate (70:30). $[\alpha]_D^{20}$ −94 (c 1.0, AcOEt). ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.88 (s, 2H), 8.64 (s, 2H), 5.55 (d, J=4.8 Hz, 2H), 4.74 (dd, J=14.1, 4.3 Hz, 2H), 4.64 (dd, J=7.9, 2.5 Hz, 2H), 4.62 (dd,

J=14.1, 7.9 Hz, 2H), 4.38–4.34 (m, 4H), 4.28 (dd, J=7.9, 1.9 Hz, 2H), 1.55 (s, 6H), 1.45 (s, 6H), 1.39 (s, 6H), 1.29 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 152.3, 142.8, 125.9, 125.3, 122.7, 109.9, 109.1, 96.2, 71.1, 70.8, 70.4, 67.2, 50.6, 26.0, 24.9, 24.4. IR (KBr, cm^{-1}): 2986, 2924, 2003, 1456, 1369, 1256, 1203, 1064, 995, 512. HRMS (ESI) calcd for $C_{34}H_{42}N_8O_{10}S{+}H$: 755.2823, found: 755.2839.

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Supplementary data

Copies of NMR spectra for new compounds and additional photophysical information. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.043.

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