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Benzothiadiazoyl-triazoyl cyclodextrin: a selective fluoroionophore for Ni(II)

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ABSTRACT

A new multichromophoric cyclodextrin substituted with benzothiadiazoyl-triazole moiety has been synthesized by a one-pot click reaction between azido-cyclodextrin and TMS-ethynyl benzothiadiazole in the presence of TBAF. This fluorescent chemosensor exhibits a high selectivity to Ni^{2+} among a series of cations in CH_3CN solution. The association constant for the 1:1 complex was determined to be 2.88×10^7 M^{-1}.

1. Introduction

In recent years, considerable efforts have been devoted to the design and synthesis of molecular sensors for the analytical detection of environmentally and biologically relevant metal ions.[1] Nickel is an essential element to plants and many other biota and able to form complex with amino acids, peptides, phosphates, nucleotides, and nucleic acids.[2] It is implicated in various enzyme activities such as ureases, hydrogenases, superoxide dismutases, acireductone dioxygenases, acetyl-coenzyme A synthases, carbon monoxide dehydrogenases, and methyl-coenzyme M reductases,[2] and frequently used in catalytic processes. However, as an industrial pollutant, nickel is a toxic element that can cause lung injury, allergy, and carcinogenesis. Selective monitoring of Ni^{2+} in industrial, environmental, and food samples is, therefore, needed. Up to date, most of Ni^{2+}-selective sensors are based on potentiometric methods.[3] Several Ni^{2+}-sensitive fluorescent sensors have been reported but there are serious interferences from other transition metal ions like Cu^{2+}, Pb^{2+}, Zn^{2+}, and Fe^{2+}.[4] As a continuing program on the design and synthesis of sugar-derived macrocycles possessing complexing properties,[5] we are particularly interested in the functionalization of cyclodextrins.[6] Using click chemistry,[7] we have prepared 2-pyridyl-triazole substituted β-cyclodextrins as Zn^{2+}-sensitive fluorescent chelating agents, where pyridyl-triazole was designed for ion coordination. The coordination properties of 1,2,3-triazoles encouraged us to explore other triazole-heterocycle conjugates as potential fluoroionophores.[8] Recently, benzothiadiazole derivatives have been used in the development of organic light-emitting materials and devices, thanks to their high fluorescence efficiency.[9] Furthermore, thiadiazole has been used as metal binding site.[10] We then decided to functionalize the β-cyclodextrin with benzothiadiazoyl-triazole to investigate their potential as novel fluorescent sensors.

2. Results and discussion

We have first realized the synthesis of benzothiadiazoyl-triazole appended methyl glucopyranoside **4** (as the model compound) and β-cyclodextrin **6** (Scheme 1). Sonogashira coupling of 4-bromo-2,1,3-benzothiadiazole **1** with trimethylsilylethyne afforded TMS-ethynyl benzothiadiazole **2**. We found that this TMS protected alkyne derivative can be directly used for the Huisgen 1,3-dipolar cycloaddition with methyl 6-azido-6-deoxy-2,3,4-tri-*O*-acetyl-α-D-glucopyranoside **3** or acetyl protected per-(6-azido)-β-CD **5**[6] in the presence of a $CuSO_4$/ascorbate mixture and TBAF for in situ deprotection of TMS group (Scheme 1). It is to be noted that direct use of silylated alkyne as the Huisgen cycloaddition partner in the presence of TBAF has never been reported before. Synthesis of triazole derivative by direct use of TMS-alkyne has been recently reported with the one-pot Ag(I)-mediated deprotection.[11] In situ desilylation of TMS-alkyne under basic conditions has been described with the formation of bis-triazole as the major compound.[12]

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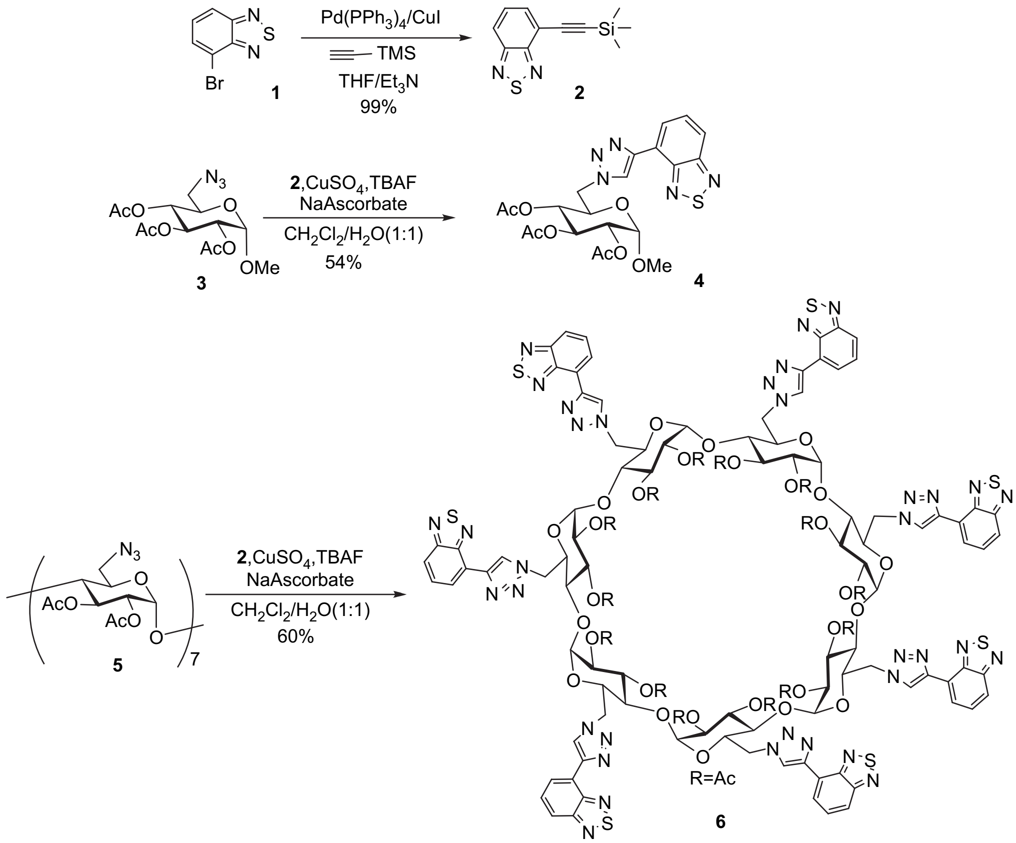

Scheme 1. Synthesis of benzothiadiazoyl-triazoyl sugar derivatives.

Compounds **4** and **6** can be easily purified by chromatography and characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.

Figure 1 shows the UV–vis absorption and fluorescence spectra of TMS-ethynyl benzothiadiazole **2** and benzothiadiazoyl-triazoyl sugar derivatives **4** and **6**. The absorbance shifts to the red 10 nm for **4** and 15 nm for **6**, consistent with enhanced conjugation in the benzothiadiazole-triazole. The emission maximum shifted also from 427 nm (for **2**) to 463 and 468 nm for **4** and **6**, respectively, when excited at 355 nm. The fluorescence quantum yield (Φ_F) for **2**, **4**, and **6** was determined to be 0.215, 0.484, and 0.242 with reference to quinine sulfate in 0.5 N H_2SO_4 solution, with a molar extinction coefficient of 4644 and 32,458 mol^{-1} L cm^{-1} for the ligands **4** and **6**.

To get insight into the binding properties of benzothiadiazoyl-triazoyl CD toward metal ions, we first investigated fluorescence changes upon addition of 50 equiv of selected cations to the MeCN solution of **6**. As presented in Figure 2, the fluorescence emission was not affected by Ca^{2+}, Mn^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Pb^{2+}, slightly quenched by Fe^{2+} and Zn^{2+}, strongly quenched by Co^{2+}, Cu^{2+}, and Hg^{2+}, and totally quenched by Ni^{2+}. The selectivity toward Ni^{2+} was further ascertained by the competition experiment by adding 50 equiv of Ni^{2+} ion to the competing metal ion-ligand mixtures, where the emission was quenched as in the presence of Ni^{2+} alone (Fig. 2). We have further compared the fluorescence emission in the presence of 1 equiv of Co^{2+}, Cu^{2+}, Hg^{2+}, and Ni^{2+} and showed that the selectivity followed the order $Ni^{2+}>Cu^{2+}>Co^{2+}>Hg^{2+}$ (Fig. 3).

We then decided to realize the titration experiment by both absorption and fluorescence measurements with Ni^{2+} in acetonitrile solution. Increase of Ni^{2+} concentration caused an increase in the absorbance around 325 and 410 nm as well as a decrease in the range of 337–372 nm for the CD-**6**, with two isosbestic points at 337 and 372 nm (Fig. 4). This was attributed to the formation of a CD-**6**–Ni^{2+} complex.[13] The fluorescence intensity is progressively quenched with increasing concentration of Ni^{2+} (Fig. 5). The inset

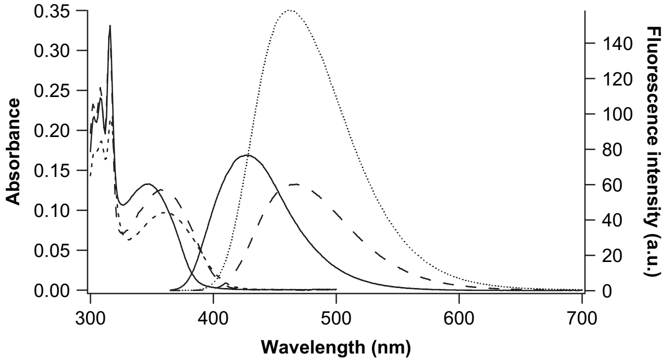

Figure 1. UV–vis and fluorescence spectra of compounds **2** (—, 4.99×10^{-3} M), **4** (···, 2.67×10^{-5} M), and **6** (- -, 3.77×10^{-6} M) in MeCN. λ_{em}=355 nm.

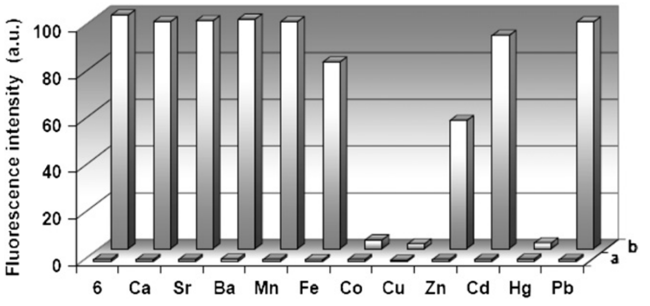

Figure 2. The fluorescence intensity change profiles of **6** (c=3.77×10^{-6} M) in MeCN with selected cations (1.89×10^{-4} M) in the presence (a) or absence (b) of Ni^{2+} (1.89×10^{-4} M). λ_{ex}=355 nm.

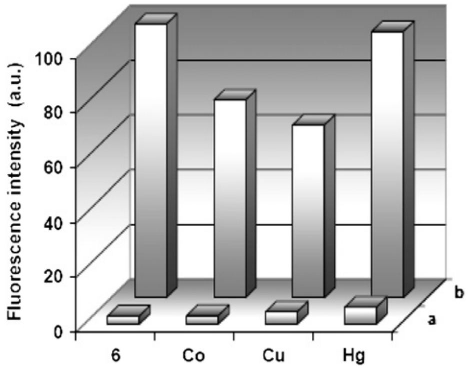

Figure 3. The fluorescence intensity change profiles of **6** (c=3.77×10^{-6} M) in MeCN with 1 equiv of selected cations in the presence (a) or absence (b) of Ni^{2+} (1 equiv). λ_{ex}=355 nm.

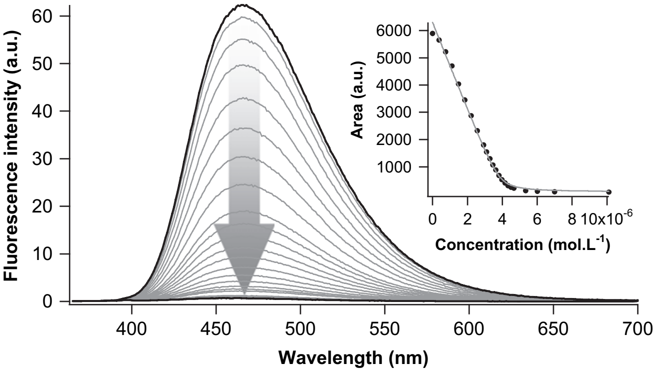

Figure 5. Fluorescence spectra obtained during the titration of **6** in MeCN (c=3.77×10^{-6} M) with $Ni(ClO_4)_2$ (from 0 to 2.5 equiv). λ_{ex}=355 nm. Inset: titration curve of the integrated fluorescence as a function of Ni^{2+} concentration.

of Figure 5 shows the decrease of fluorescence intensity as a function of Ni^{2+} concentration. The curve was well-fitted with a 1:1 complexation equation model and provided a high stability constant log $K(Ni^{2+}$:**6**)=7.46±0.53. To the best of our knowledge, CD-**6** represents the most sensitive Ni^{2+} ionophore. The remarkable fluorescence quenching induced by the paramagnetic Ni^{2+} cation can be ascribed by a photoinduced electron transfer (PET) or charge transfer (CT) mechanism.[1] As nickel salts have been widely used in catalytic systems, enantiomerically pure CD-**6** might also find applications in asymmetric systhesis.[14]

Concerning the model compound **4**, addition of 50 equiv of selected cations to the MeCN solution of **4** showed that the fluorescence emission was not affected by Mn^{2+}, Cd^{2+}, and Pb^{2+}, slightly quenched by Fe^{2+}, Co^{2+}, Zn^{2+}, and Hg^{2+}, strongly quenched by Cu^{2+} and Ni^{2+} (Fig. 6). Compound **4** has thus a worse binding affinity to Co^{2+} and Hg^{2+} compared to **6**. We have further compared the fluorescence emission in the presence of 15 equiv of Cu^{2+} and Ni^{2+} and showed that the selectivity followed the order $Ni^{2+}>Cu^{2+}>Co^{2+}>Hg^{2+}$ as in the case of the cyclodextrin **6**.

We have also performed the titration experiment with the model compound **4**. A similar fluorescence quenching was observed with increasing concentration of Ni^{2+} (Fig. 7). The curve was well-fitted with a 1:1 complexation equation model and provided a stability constant log K=4.48±0.03. Consequently, the monomer **4** binds much weakly the Ni^{2+} ion than the macrocycle cyclodextrin **6** because of loss of cooperativity.[6]

In summary, we have developed a highly selective and sensitive fluorescent chemosensor for Ni^{2+}. The multichromophoric cyclodextrin substituted with benzothiadiazoyl-triazole moiety has been prepared by a one-pot Huisgen [2+3] cycloaddition between azido-cyclodextrin and TMS-ethynyl benzothiadiazole. Metal complexation studies revealed that CD-**6** exhibits good binding affinity to Co^{2+}, Cu^{2+}, Hg^{2+}, and Ni^{2+} with the selectivity in the order $Ni^{2+}>Cu^{2+}>Co^{2+}>Hg^{2+}$. This work confirms that triazoles may be used as the metal binding sites in the design and synthesis of novel fluorescent chemosensors.[6,15]

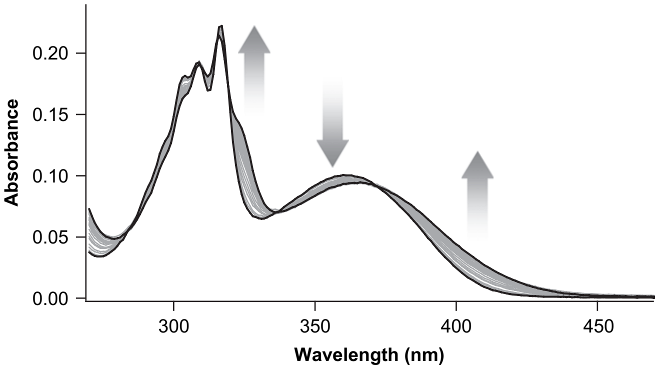

Figure 4. Absorption spectra obtained during the titration of **6** in MeCN (c=3.77×10^{-6} M) with $Ni(ClO_4)_2$ (from 0 to 2.5 equiv).

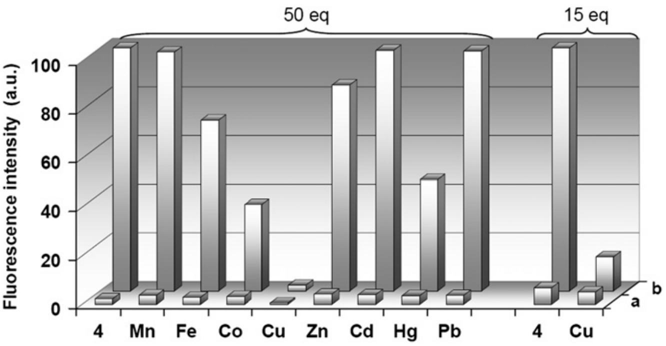

Figure 6. The fluorescence intensity change profiles of **4** (c=2.67×10^{-5} M) in MeCN with selected cations (50 or 15 equiv) in the presence (a) or absence (b) of Ni^{2+}. λ_{ex}=355 nm.

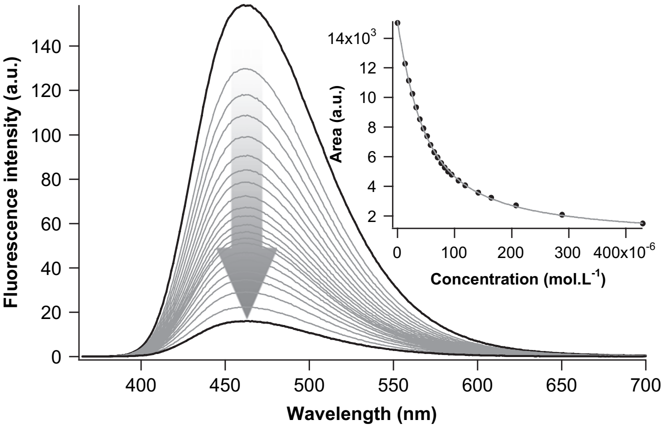

Figure 7. Fluorescence spectra obtained during the titration of **4** in MeCN (c=2.67×10^{-5} M) with $Ni(ClO_4)_2$ (from 0 to 16 equiv). λ_{ex}=355 nm. Inset: titration curve of the integrated fluorescence as a function of Ni^{2+} concentration.

3. Experimental section

3.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 or AM360 or Jeol ECS400 spectrometers in $CDCl_3$ solutions. Optical rotations were measured using a Perkin–Elmer 341 polarimeter and a 10-cm 1-mL cell. Column chromatography was performed on E. Merck Silica Gel 60 (230–400 mesh). Analytical thin-layer chromatography was performed on E. Merck aluminum percolated plates of Silica Gel $60F_{254}$ with detection by UV and by spraying with 6 N H_2SO_4 and heating about 2 min at 300 °C. High resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse de l'Université Pierre et Marie Curie-Paris 6. UV–vis absorption spectra were recorded on a Uvikon-940 KONTRON spectrophotometer. Corrected emission spectra were obtained on a Jobin-Yvon Spex Fluorolog 1681 spectrofluorometer. Stock solutions of **4** and **6** (3×10^{-4} M) were prepared in MeCN. Stock solutions of metal perchlorate salts were prepared in MeCN. For all fluorescence studies, the excitation wavelength was set at 355 nm. The evolution of the full fluorescence intensity from the ligands **4** and **6** as a function of Ni^{2+} concentration contains information on the stability constant of the complex through the following equation:

$$Y(C_\mathrm{M}) = Y_0 + \frac{Y_\mathrm{lim} - Y_0}{2} \times \left\{ 1 + \frac{C_\mathrm{M}}{C_\mathrm{L}} + \frac{1}{KC_\mathrm{L}} - \left[\left(1 + \frac{C_\mathrm{M}}{C_\mathrm{L}} + \frac{1}{KC_\mathrm{L}} \right)^2 - 4\frac{C_\mathrm{M}}{C_\mathrm{L}} \right]^{1/2} \right\}$$

where Y designate the fluorescence intensity of a C_L-concentrated solution of ligand as a function of the concentration C_M of added cation. Y_0 and Y_lim are the fluorescence intensity values for C_M=0 and for full complexation, respectively. K is the stability constant of the 1:1 complex. The fluorescence quantum yield (Φ_F) was determined by the standard method using 1.0×10^{-5} M quinine sulfate in 0.5 N H_2SO_4 solution as reference. The refractive index of the solvent was taken into account in the measurement.

3.2. Synthesis of 4-((trimethylsilyl)ethynyl)-2,1,3-benzothiadiazole 2

To a mixture of 4-bromo-2,1,3-benzothiadiazole (0.60 g, 2.8 mmol), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol), CuI (0.027 g, 0.14 mmol), THF (25 mL), and Et_3N (20 mL) was added trimethylsilylethyne (0.47 mL, 3.3 mmol) under argon at rt. The reactants were heated to reflux and kept at this temperature overnight. Removal of the solvent gave a residue that was purified by chromatography on silica gel using a mixture of petroleum ether and dichloromethane (7:1, v/v) to give **2** as a yellow solid (0.65 g, 99%). Mp 48 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 7.53 (dd, J=8.7, 6.8 Hz, 1H), 7.69 (d, J=6.8 Hz, 1H), 7.97 (d, J=8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.1, 100.1, 101.7, 117.0, 122.2, 129.2, 133.7, 154.6. HRMS m/z calcd for $C_{11}H_{12}N_2NaSSi$ $[M+Na]^+$: 255.0388, found: 255.0383.

3.3. Synthesis of methyl 2,3,4-tri-*O*-acetyl-6-benzothiadiazoyl-triazoyl-6-deoxy α-D-glucopyranoside 4

To a solution of azido-sugar **3** (10 mg, 0.044 mmol) and trimethylsilylethynyl benzodithiadiazole **2** (11.5 mg, 0.049 mmol) in CH_2Cl_2 (1 mL), were added, respectively, the copper sulfate (4 mg, 0.016 mmol), the sodium ascorbate (10 mg, 0.050 mmol), the tetrabutylammonium fluoride (28 mg, 0.089 mmol), and water (1 mL). The reaction was stirred at rt for 15 h (color changed from brown to purple). The crude was diluted in a mixture of 10 mL CH_2Cl_2/0.1 N EDTA solution (1:1). The water layer was extracted with CH_2Cl_2 (3×5 mL), the organic layers were combined, washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified on silica gel with ethyl acetate/petroleum ether (6:4) and gave 12 mg (54%) of a yellow solid. R_f 0.33 (EtOAc/petroleum ether, 3:7), mp 154 °C, $[\alpha]_D$ +6.8 (c 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.13 (s, 3H, Ac), 3.14 (s, 3H, OMe), 4.28 (ddd, 1H, J=2.2, 8.4, 10.3 Hz, H-5), 4.52 (dd, 1H, J=8.5, 14.3 Hz, H-6), 4.71 (dd, 1H, J=2.2, 14.3 Hz, H-6′), 4.87 (dd, 1H, J=3.5, 10.0 Hz, H-2), 4.93 (t, 1H, J=9.8 Hz, H-4), 4.97 (d, 1H, J=3.5 Hz, H-1), 5.51 (t, 1H, J=10.0 Hz, H-3), 7.72 (dd, 1H, J=7.0, 8.5 Hz, H–Ar), 7.98 (d, 1H, J=8.8 Hz, H–Ar), 8.55 (d, 1H, J=7.0 Hz, H–Ar), 8.87 (s, 1H, H–triazole). ^{13}C NMR (90 MHz, $CDCl_3$) δ 20.8, 20.9, 51.2, 55.7, 68.0, 69.9, 70.3, 70.9, 96.8, 121.0, 123.5, 125.7, 130.1, 143.4, 152.0, 155.5, 170.1. HRMS m/z calcd for $C_{21}H_{23}N_5NaO_8S$ $[M+Na]^+$: 528.1165, found: 528.1160.

3.4. Synthesis of 6-benzothiadiazoyl-triazoyl β-cyclodextrin 6

To a solution of azido-cyclodextrin **5** (62.9 mg, 0.033 mmol) and trimethylsilylethynyl benzothiadiazole **2** (55.6 mg, 0.239 mmol) in CH_2Cl_2 (5 mL), were added, respectively, the copper sulfate (8 mg, 0.032 mmol), the sodium ascorbate (5 mg, 0.025 mmol), the tetrabutylammonium fluoride (115.2 mg, 0.365 mmol), and water (5 mL). The reaction was stirred at rt for 3 h. The crude is diluted in a mixture of 10 mL CH_2Cl_2/0.1 N EDTA solution (1:1). The water layer was extracted with CH_2Cl_2 (3×5 mL), the organic layers are combined, washed with brine, dried over $MgSO_4$, and evaporated under vacuum. To remove the rest of copper complex, the residue was diluted in a mixture of CH_2Cl_2/KCN solution and stirred for 1 h. The organic layer was then dried over $MgSO_4$ and evaporated under vacuum. Purification over silica gel with CH_2Cl_2/EtOH (9:1) gave 60 mg (60%) of a yellow solid. R_f 0.78 (CH_2Cl_2/EtOH, 8:2), mp 213 °C (decomp.), $[\alpha]_D$ −0.22 (c 1.35, $CHCl_3$). ^1H NMR (360 MHz, $CDCl_3$) δ 2.01 (s, 21H, 7×Ac), 2.10 (s, 21H, 7×Ac), 3.76 (t, 7H, J=7.9 Hz, 7×H-4), 4.72 (m, 7H, 7×H-5), 4.85 (m, 14H, 7×H-2,6), 5.22 (d, 7H, J=14.0 Hz, 7×H-6′), 5.45 (t, 7H, J=8.3 Hz, 7×H-3), 5.55 (s, 7H, 7×H-1), 7.46 (m, 7H, 7×H–Ar), 7.70 (d, 7H, J=7.7 Hz, 7×H–Ar), 8.30 (d, 7H, J=6.5 Hz, 7×H–Ar), 8.82 (s, 7H, H–triazole). ^{13}C NMR (90 MHz, $CDCl_3$) δ 20.9, 50.7, 69.9, 70.2, 70.8, 77.4, 96.9, 120.8, 123.0, 125.4, 127.1, 129.7, 142.9, 151.7, 155.2, 169.6, 170.6. MS m/z calcd for $C_{126}H_{120}N_{35}O_{42}S_7$ $[M+H]^+$: 3019.64, found: 3019.62; calcd for $C_{126}H_{119}N_{35}NaO_{42}S_7$ $[M+Na]^+$: 3041.62, found: 3041.58; calcd for $C_{126}H_{119}N_{35}KO_{42}S_7$ $[M+K]^+$: 3057.60, found: 3057.55. HRMS m/z calcd for $C_{126}H_{119}N_{35}Na_2O_{42}S_7$ $[M+2Na]^{2+}$: 1532.3063, found: 1532.3057.

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