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Sugar-Functionalized Water-Soluble Cyclotriveratrylene Derivatives: Preparation and Interaction with Fullerene

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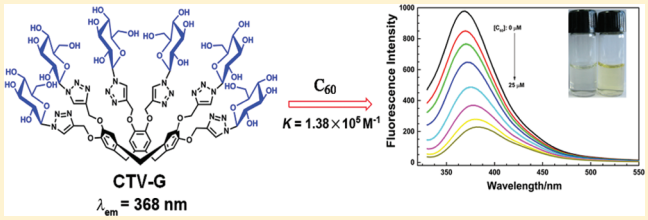
Supporting Information

ABSTRACT: Cyclotriveratrylene (CTV) has attracted much attention because of its good chemical stability, small cavity, stable conformation, and facile modification. In this article, two water-soluble CTV derivatives (**CTV-G** and **CTV-L**) functionalized by glucose and lactose residues were synthesized, respectively. Unexpectedly, sugar-bearing CTVs exhibit a distinct photoluminescence, which might be ascribed to the enhanced planar conformation of cyclotriveratrylene ring derived from the spatial effect of bulky branch groups. The interaction between the water-soluble CTV derivatives and C_{60} was investigated in organic solvent and aqueous solution, which was further characterized by fluorescence spectra, ultraviolet−visible spectra, and Raman spectra. **CTV-G** can associate with C_{60} to form supramolecular complex with 1:1 molar ratio (K_a = 1.38 × 10^5 M^{-1}, 298 K). As for **CTV-L**, a similar complex with a lower association constant (K_a = 5.09 × 10^4 M^{-1}, 298 K) can also be formed.



INTRODUCTION

Cyclotriveratrylene (CTV), discovered almost a century ago, has attracted much attention due to its good chemical stability, small cavity, stable conformation, and facile modification.[1−5] Considering its bowl-shape conformation with a molecular cavity, the application of CTV as a host molecule, especially as a fullerene host, has been widely reported in recent years.[6,7] CTV and its derivatives are well-known to bind fullerenes both in solution and in the solid state. Modification with appending functional groups can extend side-arms to the upper rim on the basic CTV platform, which expands the cavity effectively and enhances the binding ability to C_{60} in solution. Therefore, various cyclotriveratrylene derivatives with extended cavities have been developed through versatile functionalizations. The CTV-based receptor that has three 2-ureido-4-[1*H*]-pyrimidinone side-arms can form hydrogen-bonded self-assembled capsules binding fullerenes inside,[8,9] which was further applied to the isolation of C_{70} and C_{84} from mixtures of fullerenes. Attaching aromatic moieties of 2-[9-(1,3-dithiol-2-ylidene)-anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF) to the basic CTV platform can afford another host exTTF-CTV, which shows a very effective association with both C_{60} and C_{70}.[10] These derivatives form stable complexes with fullerenes in organic solvent and can be used to purify fullerenes efficiently from crude soot or fullerite mixtures.[11,12]

In the past decade, the applications of fullerenes have been gradually extended to many other research fields, such as pharmaceutical science and biological science.[13−15] For instance, fullerene derivatives were reported to be used in photodynamic therapy[16] or as inhibitors for the HIV-1 protease.[17] However, fullerene is almost insoluble in aqueous media, which, to some extent, hampers its biological application. Thus, it is necessary to exploit water-soluble macrocyclic host systems to improve the water-solubility of C_{60} by forming water-soluble supramolecular complexes. Cyclodextrin or calixarene derivatives are of particular interest. γ-CD has been used to dissolve C_{60} in water.[18] Two CTV derivatives containing peripheral triethyleneglycol chains also have an ability to form water-soluble supramolecular complexes with C_{60}, which makes them interesting candidates for biological applications.[19]

Sugar, as a multihydroxyl biological molecule, possesses good water-solubility and biocompatibility.[20] Introducing sugar to a CTV platform can not only provide CTV with a good solubility in water but also extend the cavity of CTV with appending sugar chains, which would furnish a novel water-soluble host for fullerene. In this article, two CTV-based glycoconjugates (**CTV-G** and **CTV-L**, Figure 1) were first designed and prepared smoothly through click reaction (Scheme 1). With an extended cavity based on the basic CTV platform, the two sugar-bearing CTVs show a good ability to form supramolecular complexes with C_{60} in both polar organic solvent and aqueous solution. Supramolecular interaction between CTV derivatives and C_{60} can be detected through fluorescence spectra and ultraviolet spectra. The two water-soluble hosts for C_{60} overcome the natural repulsion of fullerene for water and show a promising potential in biological applications.

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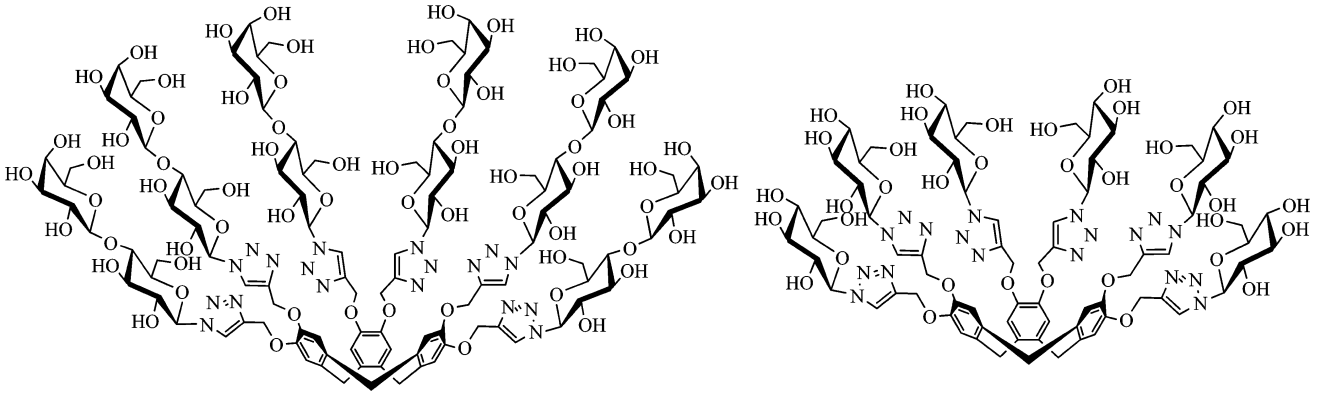
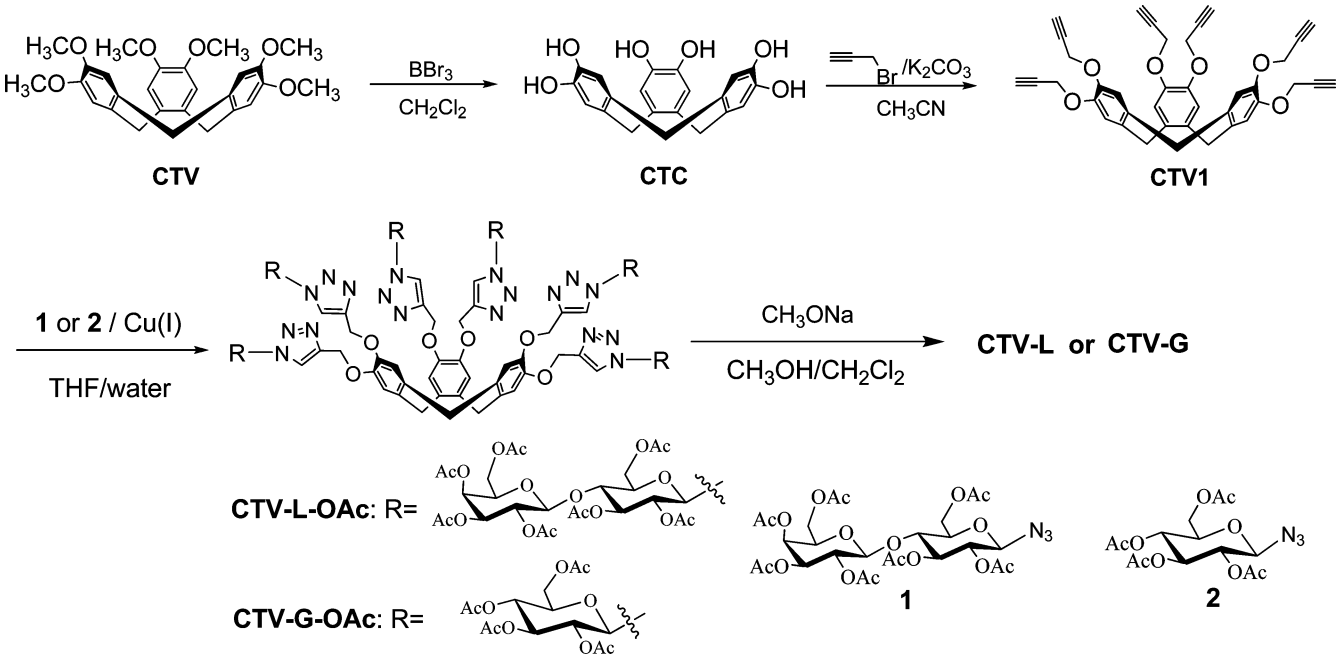


Figure 1. Chemical structures of **CTV-L** and **CTV-G**.

Scheme 1. Synthetic Routes to CTV-Based Glycoconjugates CTV-G and CTV-L



RESULTS AND DISCUSSION

Synthesis of Sugar-Bearing CTV Hosts: CTV-G and CTV-L. The synthetic routes to sugar-bearing CTV are outlined in Scheme 1. Using the known cyclotriveratrylene[21−23] as the starting material, cyclotricatechylene (**CTC**) can be obtained through a classic demethylation method in a good yield by treatment of CTV with BBr_3 in anhydrous dichloromethane. After exposure to propargyl bromide under basic condition, the six phenolic hydroxyl groups of **CTC** were propargylated to furnish **CTV1**, whose structure can be proved by signal peaks at 3284 and 2126 cm^{-1} in the IR spectrum (Figure S1, Supporting Information) and chemical shifts at 78.9 ppm and 76.1 ppm in the ^{13}C NMR spectrum (Supporting Information), respectively. Cu(I)-catalyzed azide/alkyne click ligation[24] between **CTV1** and azido-functionalized sugar derivatives (**1** or **2**) was chosen to introduce six sugar groups into the CTV platform, owing to the efficiently selective ligation and mild reaction condition based on the click reaction. Formation of the triazole ring is confirmed by the chemical shift nearly at 8.41 ppm in the ^1H NMR spectrum and the peaks nearly at 124.3 and 144.2 ppm on the ^{13}C NMR spectrum of the corresponding desired intermediates, **CTV-L-OAc** and **CTV-G-OAc** (Supporting Information). After entire removal of the acetyl group with MeONa/MeOH, **CTV-G** and **CTV-L** can be obtained quantitively (Scheme 1), which were further characterized by ^1H NMR, ^{13}C NMR, MS, and IR spectra (Figure S1, Supporting Information). **CTV-L-OAc** and **CTV-G-OAc**, as the protected sugar-bearing CTVs, are readily soluble in common solvents, such as methylene chloride, chloroform, and tetrahydrofuran but insoluble in methanol, ethanol, and water. The solubility of the resulting glycoconjugates, **CTV-G** and **CTV-L**, are different from their precursors, showing a good solubility in DMF, DMSO, toluene−DMSO (1:1, v/v), and water.

Optical Properties of Sugar-Bearing CTV. Both **CTV-G** and **CTV-L** exhibit an absorption maximum peak nearly at 290 nm in toluene−DMSO (1:1, v/v) solution or in water, respectively (Figure 2). Unexpectedly, **CTV-G** and **CTV-L** also display an emission maximum peak at 368 nm in toluene−DMSO (1:1, v/v) solution. In water medium, the emission

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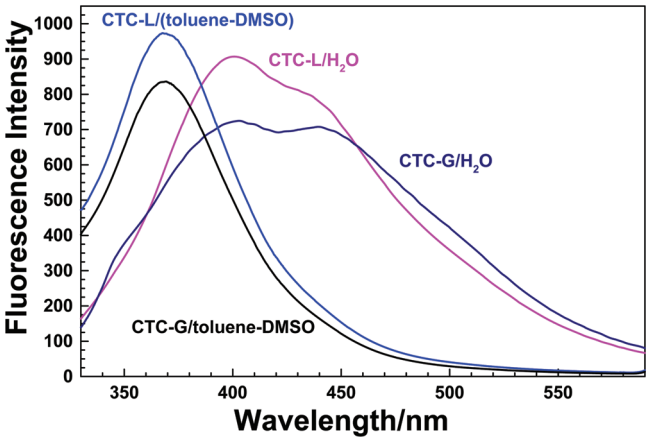

Figure 2. Fluorescence spectra of **CTV-L** and **CTV-G** in water and toluene–DMSO (1:1, v/v) (λ_{ex} = 310 nm).

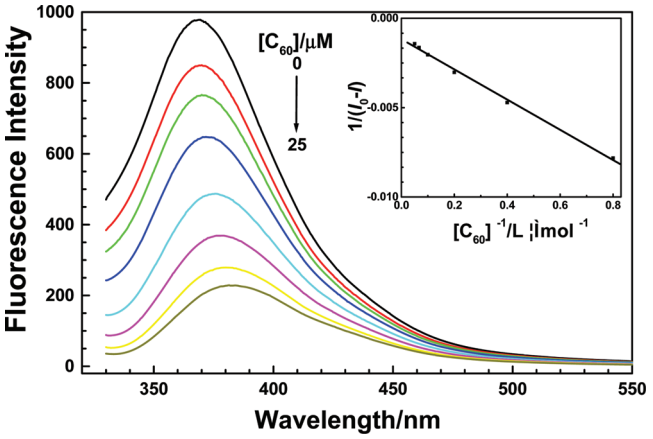

Figure 3. Fluorescence spectra of **CTV-G** (5.0×10^{-6} mol L^{-1}) in the absence and presence of various concentrations of C_{60} in the toluene–DMSO solution at room temperature (λ_{ex} = 310 nm). The concentrations of C_{60} ($\times 10^{-6}$ mol L^{-1}) are 0.0, 1.25, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0, respectively. The inset is the plot of $[C_{60}]^{-1}$ vs ΔI.

peak shifts to 400 nm with a vibronic shoulder peak at 440 nm. When the molecule is excited from the ground-state to the excited-state, the polarity of the excited molecule is higher than that of the ground one. Solvent with a higher polarity can produce a better stabilizing effect on the excited molecule, and then the energy for electron excitation becomes lower.[25] Therefore, the obvious bathochromic/red shift in photoluminscence spectra of sugar-bearing CTV in high polarity solvents was observed. The fluorescence in the region from 350 to 390 nm probably results from the formation of ground-state dimer because of the interactions between the benzene rings upon excitation[26] or excimeric emission caused by the interaction between the phenyl groups.[27] As for sugar-bearing CTV, besides the reasons aforementioned, the fluorescence might be ascribed to the enhanced planar conformation of the cyclotriveratrylene ring derived from the spatial effect of bulky branch chains. When excited at 310 nm, the fluorescence intensity of CTV is very low. For **CTC** and **CTV1**, their fluorescence intensities are even nearly zero under the same conditions (Figure S2, Supporting Information). After the incorporation of six sugar groups into CTV platform, the obtained sugar-bearing CTVs possess a distinct photoluminescence. Compared with **CTV-G**, the branched lactopyranosyl chains of **CTV-L** are bulkier and make the CTV skeleton more coplanar, and the fluorescence intensity is correspondingly higher (Figure 2), considering the greater enhanced planar conformation of cyclotriveratrylene ring.

Studies for Complexation between Sugar-Bearing CTV and Fullerene. CTV and its derivatives are well-known to bind fullerenes in solution and in the solid state. The binding of C_{60} in solution is enhanced through the use of extended-cavity CTV derivatives.[1] Optical spectroscopy assays have drawn much attention in the investigation of C_{60}–CTVs binding because they are highly sensitive, convenient, and cost-effective. Supramolecular interaction between sugar-bearing CTV and C_{60} was studied by spectrofluorometric titrations in toluene–DMSO (1:1, v/v) at 25 °C. Both sugar-bearing CTV and C_{60} are soluble in the cosolvent. Continuous changes were observed in the fluorescence spectra of sugar-bearing CTV upon successive additions of the fullerene to the host solution. Upon the addition of C_{60} solution (0–25 mM), the fluorescence intensity of **CTV-G** gradually decreased and was significantly quenched by 80% when the concentration of C_{60} is up to 25 mM (Figure 3). As mentioned above, the fluorescence of sugar-bearing CTV might be ascribed to the enhanced planar conformation of the cyclotriveratrylene ring derived from the spatial effect of bulky sugar moieties. The enhanced planar conformation of the cyclotriveratrylene ring makes the π-electron delocalization and excitation much easier. As for the ground-state C_{60}, it possesses remarkable electron-acceptor properties and is capable of accommodating as many as six electrons in solution.[28] When sugar-bearing CTV interacts with C_{60}, the photoinduced intermolecular electron transfer from sugar-bearing CTV donors to C_{60} takes place and leads to the fluorescence quenching of sugar-bearing CTV. Meanwhile, a 16 nm red-shift (from 370 to 386 nm) of its emission maximum was observed, which might be attributed to further enhanced planar conformation of the CTV part when binding with the C_{60} or the aggregation of sugar-bearing CTV complexes because of the increasing concentration of C_{60}. On the basis of the linear fitting of the plot of $[C_{60}]^{-1}$ vs ΔI, the complex formed by host and C_{60} was in 1:1 ratio, and the association constant K_a of host **CTV-G** with C_{60} in toluene–DMSO solution is 1.38×10^5 M^{-1} at 298 K (R^2 = 0.9966). Similar fluorescence quenching was also observed for **CTV-L** in the presence of different concentrations of C_{60} (Figure S3, Supporting Information), which indicates that the C_{60}–**CTV-L** complexation possesses a relatively smaller association constant estimated to be 5.09×10^4 M^{-1} (R^2 = 0.9997). Apparently, the **CTV-G** with shorter glucopyranosyl chains forms a slightly more stable complex with C_{60}, maybe because the resulting cavity is more suitable to accommodate the spherical C_{60} molecule. The bulkier lactopyranosyl chains result in a shallower cavity of the CTV due to the steric effect. The complexation between **CTV-G** and C_{60} can also be confirmed by ultraviolet–visible (UV–vis) absorption spectrum. As shown in Figure 4, C_{60} exhibits two absorption peaks nearly at 284 and 335 nm, respectively, in toluene–DMSO (1:1, v/v) solution. When the same amount of C_{60} was mixed with **CTV-G** (C_{60}/**CTV-G** = 1:2, molar ratio) under the same conditions, the absorption peak of C_{60} at 284 nm shifted to 293 nm; furthermore, the absorption intensity at 335 nm decreased about 30%. The absorption peak of C_{60} at 284 nm shifted to 288 nm when it was mixed with **CTV-L** (C_{60}/**CTV-L** = 1:2, molar ratio) under the same conditions (Figure S4, Supporting Information). The absorption intensity at 335 nm decreased

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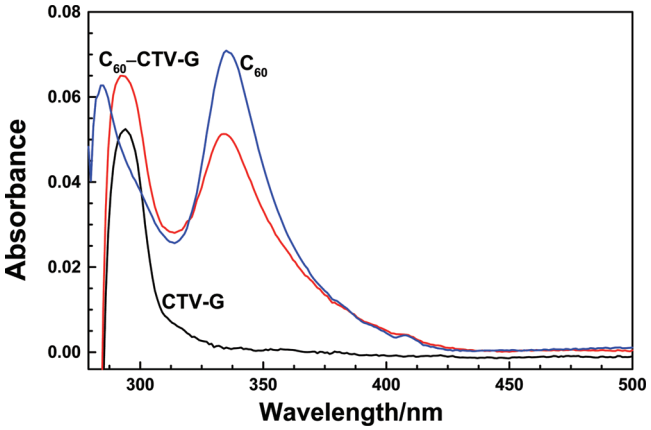

Figure 4. Absorption spectra of C_{60}–**CTV-G** (C_{60}: 2.5 μM; **CTV-G**: 5.0 μM), C_{60} (2.5 μM), and **CTV-G** (5.0 μM) in toluene–DMSO (1:1, v/v).

about 16%, which also shows the relatively weaker interaction in C_{60}–**CTV-L**. On the basis of these data, not only the complexation between sugar-bearing CTV and C_{60}, but also the energy transfer through the interaction can be proved apparently.

Fullerenes exhibit interesting biological activities both in vitro and in vivo due to their easy excitation by visible light and the special properties of the resulting excited-states.[19] However, the low solubility of fullerenes in aqueous media appears to be a major problem for their biological applications. Preparation of water-soluble supramolecular complexes between CTV-based host systems and fullerenes is a reliable strategy to overcome the natural repulsion of fullerenes for water. The host–guest interaction of sugar-bearing CTV hosts and C_{60} was investigated in aqueous solution. Figure 5 shows the UV–vis

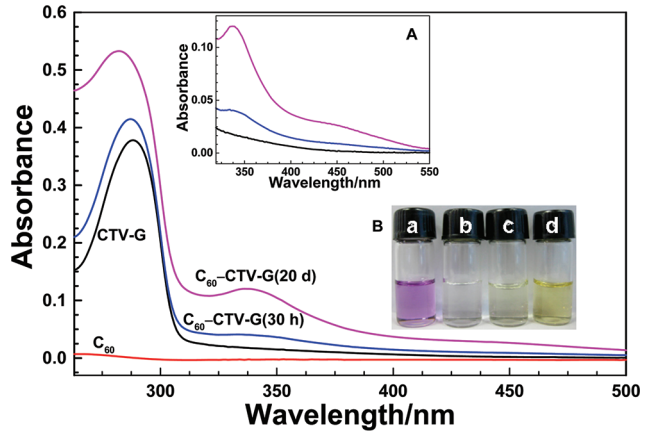

Figure 5. Absorption spectra of aqueous C_{60}–**CTV-G** and **CTV-G** solution, and C_{60} in water. The concentration of **CTV-G** is 5.0×10^{-5} M. Inset A is the amplificatory spectra in the region from 320 to 550 nm, and inset B shows the colors of C_{60} in various solvents: (a) C_{60} in toluene; (b) C_{60} in water after centrifugation; (c) **CTV-G** in water; and (d) C_{60}–**CTV-G** in water after centrifugation.

absorption spectra of C_{60}, **CTV-G**, and C_{60}–**CTV-G** complex, respectively, in aqueous solution after centrifugation. As expected, C_{60} has no absorption intensity because of its insolubility in aqueous solution. However, in the presence of **CTV-G**, a new absorption peak at 342 nm (characteristic signal peak of C_{60} in UV–vis region) was observed for C_{60}–**CTV-G** complex, which proves that **CTV-G** can bind C_{60} in aqueous solution to form a water-soluble complex. Similar results were also found for C_{60}–**CTV-L** ensemble. (Figure S5, Supporting Information) The interaction of sugar-bearing CTV hosts with C_{60} can be visually monitored by a color change of the corresponding solutions. For instance, the aqueous solution of **CTV-G** is almost colorless, but after addition of C_{60} and followed by centrifugation, the color of aqueous C_{60}–**CTV-G** solution gradually changes into yellow (Figure 5). These novel CTV hosts with peripheral sugar chains show their ability to form water-soluble supramolecular complexes with C_{60}. Sugar–triazole cluster structure based on the bowl-shape CTV can provide an internal cavity capable of encapsulating the hydrophobic C_{60} guest, thus preventing the aggregation in an aqueous solution due to the fullerene–fullerene interaction. Multiple hydroxyl groups from sugar moieties make the supramolecular complexes water-soluble. The hydrophobic triazole groups and six-membered ring skeleton of sugars can increase the hydrophobic and van der Waals interactions between the inner surface of sugar-bearing CTV hosts and C_{60}, which are useful to enhance the major driving forces for the formation of supramolecular complexes. Further study with Raman spectra shows the existence of C_{60} in C_{60}–**CTV-G** complex, in which the featured peak at 1470 cm^{-1} was assigned

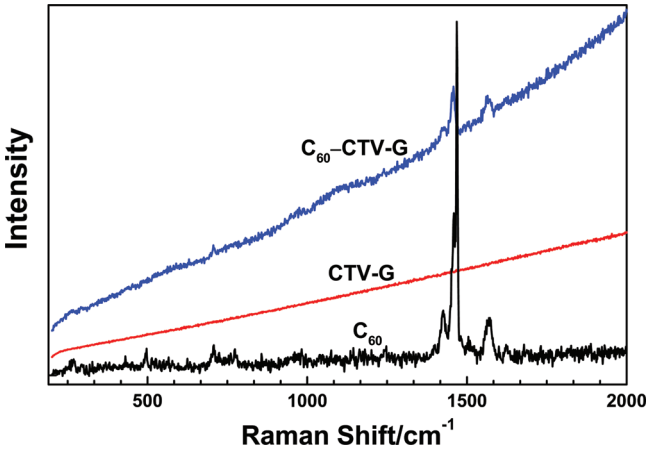

Figure 6. Raman spectra of C_{60}–**CTV-G**, **CTV-G**, and C_{60}.

to the totally symmetric pentagonal pinch mode of C_{60} (Figure 6).[29]

CONCLUSIONS

On the basis of macrocyclic host CTV, two water-soluble sugar-bearing CTV derivatives (**CTV-G** and **CTV-L**) modified with glucose and lactose were synthesized, respectively. Cu(I)-catalyzed azide/alkyne click ligation efficiently facilitated the preparation. Thanks to the enhanced planar conformation of functionalized cyclotriveratrylene ring, sugar-bearing CTVs exhibit distinct photoluminescence, which can be used to conveniently detect their interaction with C_{60} through spectrofluorometric titration. The supramolecular complexation between the water-soluble CTV derivatives and C_{60} was investigated in organic solvent and aqueous solution, respectively, which were confirmed by fluorescence, UV–vis, and Raman spectra. Both **CTV-G** and **CTV-L** can bind C_{60} to form a supramolecular complex with 1:1 molar ratio (for **CTV-G**, $K_a = 1.38 \times 10^5$ M^{-1}; for **CTV-L**, $K_a = 5.09 \times 10^4$ M^{-1}). The

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host−guest interaction between sugar-bearing CTV and C_{60} in aqueous solution will boost the potential biological applications of C_{60}.

EXPERIMENTAL SECTION

Materials and Characterization. All chemical reagents are commercially available and used as received unless otherwise stated. CTV was prepared from 1,2-dimethoxybenzene according to the reported method.[30−32] Azido-functionalized sugar derivatives (**1** or **2**) were prepared according to reported methods.[33,34] Ultrapure water (18.2 MΩ cm) was purified with a Millipore purification system (Milli-Q water).

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 M Hz NMR spectrometer. UV−vis spectra were measured using a UV−vis−NIR spectrophotometer and quartz cells with a 1 cm path length. The fluorescence spectra were measured in a conventional cell with a 1 cm path length at room temperature. Mass spectra were measured using a MALDI TOF-MS or liquid chromatography−mass spectrometry (LC−MS) with the ESI(+) technique. IR spectra were recorded in KBr pellets using a FTIR spectrometer. Raman spectra were recorded by dropping the sample solutions **CTV-G** or **CTV-L** onto a slide glass or silicon wafer after air drying. C_{60} was tested in powder form on a slide glass.

Synthesis of CTV1.[35] To a solution of **CTC** (0.366 g, 1 mmol) in 33 mL of acetonitrile were added potassium carbonate (1.656 g, 12.0 mmol) and propargyl bromide (6.0 mL, 6.0 mmol, 80% in toluene) under a nitrogen atmosphere at room temperature. The reaction mixture was refluxed overnight and then cooled down to room temperature. The suspension was then filtered and washed with acetonitrile. After the solvent of the filtrate was removed under reduced pressure, the desired product was obtained as a light brown solid. Further purification can be done by crystallization from the $CHCl_3$/EtOH mixture (298 mg, yield 50.1%, mp 153−155 °C): ^{1}H NMR ($CDCl_3$) δ (ppm) 7.04 (s, 6H, Ar−*H*), 4.72 (t, J = 2.8 Hz, 12H, Ar−O*CH*$_2$), 4.62 (d, J = 2.4 Hz, 3H, Ar−*CH*$_2$−Ar), 3.58 (d, J = 13.6 Hz, 3H, Ar−*CH*$_2$−Ar), 2.56 (t, J = 2.4 Hz, 6H, C≡C−*H*); ^{13}C NMR ($CDCl_3$) δ (ppm) 146.5, 133.3, 117.4, 78.9, 76.1, 57.4, 36.5, 31.0; IR ν (cm^{-1}) 3284 (vs), 2925 (w), 2125 (w), 1610 (w), 1506 (s), 1456 (w), 1260 (s), 1194 (m), 1140 (m), 1088 (m), 1023 (w), 661 (s). Anal. Calcd for $C_{39}H_{30}O_6$: C, 78.77; H, 5.09; O, 16.14. Found: C, 78.55; H, 5.20; O, 16.29.

Synthesis of CTV-L-OAc. To the solution of **CTV1** (100 mg, 0.168 mmol) and sugar derivative **1** (1.580 g, 2.39 mmol) in tetrahydrofuran−water cosolvent (50 mL, v/v = 2/1) were added sodium ascorbate (40 mg) and copper sulfate (30 mg). The heterogeneous mixture was stirred vigorously in a dark room at 50−60 °C until complete consumption of the reactants (on the basis of TLC analysis). After removal of tetrahydrofuran under a reduced pressure, the residue was dissolved in water (20 mL), and the product was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo. The crude product was purified by column chromatography using ethyl acetate/petroleum ether (5/1) as eluent to give the desired product (520 mg, 68%) as an off-white solid: ^{1}H NMR (DMSO-d_6) δ (ppm) 8.41 (d, J = 3.6 Hz, 6H), 7.26 (d, J = 5.6 Hz, 6H), 6.26 (d, J = 8.8 Hz, 6H), 5.51−5.43 (m, 12H), 5.25−5.12 (m, 30H), 4.89−4.81 (m, 12H), 4.37−4.33 (m, 3H), 4.27−4.20 (m, 12H), 4.05−4.00 (m, 24H), 3.45−3.42 (m, 3H), 2.11 (s, 18H), 2.01−1.98 (m, 90H), 1.90 (s, 18H); ^{13}C NMR (DMSO-d_6) δ (ppm) 170.5, 170.1, 169.9, 169.6, 146.9, 144.2, 144.0, 133.3, 132.1, 124.3, 117.0, 100.6, 84.2, 76.3, 75.0, 72.9, 70.9, 69.5, 67.6, 65.6, 62.7, 61.4, 58.0, 56.6, 55.3, 31.2, 20.9; MALDI-TOF-MS calcd. for $C_{195}H_{240}N_{18}O_{108}$, 4563.39 ($m/z$), found 4563.50. Anal. Calcd for $C_{195}H_{240}N_{18}O_{108}$: C, 51.32; H, 5.30; N, 5.52. Found: C, 51.51; H, 5.19; N, 5.65.

Synthesis of CTV-G-OAc. **CTV-G-OAc** was obtained as an off-white solid (544 mg, 71%) from sugar derivative **2** (0.753 g, 2.018 mmol) according to the same synthetic method for **CTV-L-OAc**: ^{1}H NMR (DMSO-d_6) δ (ppm) 8.55 (d, J = 6.0 Hz), 7.25 (d, J = 4.0 Hz, 6H), 6.35 (d, J = 9.2 Hz, 6H), 5.67−5.64 (m, 6H), 5.56−5.51 (m, 6H), 5.22−5.14 (m, 18H), 4.34 (t, J = 9.2 Hz, 6H), 4.26−4.20 (m, 3H), 4.14−4.02 (m, 12H), 3.52−3.49 (m, 3H), 2.07−1.49 (m, 72H); ^{13}C NMR (DMSO-d_6) δ (ppm) 170.5, 170.1, 169.9, 169.0, 146.9, 144.4, 144.2, 132.0, 124.1, 116.9, 87.1, 84.4, 72.7, 70.6, 68.0, 62.7, 62.5, 62.2, 56.6, 31.2, 20.9; IR ν (cm^{-1}) 2950 (w), 1758 (s), 1613 (w), 1507 (s), 1450 (w), 1372 (s), 1232 (s), 1102 (s), 1039 (s), 918 (m); MALDI-TOF-MS calcd. for $C_{123}H_{144}N_{18}O_{60}$, 2833.88 ($m/z$), found 2832.40. Anal. Calcd for $C_{123}H_{144}N_{18}O_{60}$: C, 52.12; H, 5.12; N, 8.89. Found: C, 52.35; H, 5.24; N, 8.75.

Synthesis of CTV-L. To a solution of **CTV-L-OAc** (150 mg, 0.023 mmol) in methanol−dichloromethane (2:1; 30 mL) was added a solution of sodium methoxide in methanol (1.0 M) until the pH value reached to 11. The reaction was stirred for 24 h at room temperature, and the obtained suspension was then filtered and washed with dichloromethane. A foamy product was obtained as a white solid after purification on a Biogel P_2 column (77 mg, 84%): ^{1}H NMR (DMSO-d_6) δ (ppm) 8.43 (s, 6H), 7.39 (s, 6H), 5.64 (d, J = 9.2 Hz, 6H), 5.15 (s, 12H), 4.25 (d, J = 6.4 Hz, 6H), 3.87 (t, J = 8.4 Hz, 6H), 3.76−3.33 (m, 114H); ^{13}C NMR (DMSO-d_6) δ (ppm) 146.2, 142.7, 132.4, 124.2, 115.5, 115.4, 103.8, 87.0, 79.7, 77.8, 75.5, 75.1, 73.2, 71.7, 70.5, 68.1, 60.4, 30.7; MALDI-TOF-MS calcd. for $C_{111}H_{156}N_{18}O_{66}$, 2797.94 ($m/z$), found 2820.88 (M + Na). Anal. Calcd for $C_{111}H_{156}N_{18}O_{66}$: C, 47.64; H, 5.62; N, 9.01. Found: C, 47.45; H, 5.70; N, 9.13.

Synthesis of CTV-G. **CTV-G** was obtained as a foamy solid (84 mg, 87%) from **CTV-G-OAc** (150 mg, 0.053 mmol) according to the same synthetic method for **CTV-L**: ^{1}H NMR (DMSO-d_6) δ (ppm) 8.37 (d, J = 6.4 Hz, 6H), 7.40 (s, 6H), 5.51 (d, J = 8.0 Hz, 6H), 5.15 (s, 12H), 3.98−3.92 (m, 32H), 3.44−3.40 (m, 12H), 3.22 (s, 6H); ^{13}C NMR (DMSO-d_6) δ (ppm) 146.8, 143.3, 133.0, 124.8, 116.0, 88.0, 80.5, 77.4, 72.5, 70.0, 61.2, 31.2; ESI-MS (positive ions) calcd. for $C_{75}H_{96}N_{18}O_{36}$, 1825.66 (m/z), found 1847.69 (M + Na^+). Anal. Calcd for $C_{75}H_{96}N_{18}O_{36}$: C, 49.34; H, 5.30; N, 13.81. Found: C, 49.50; H, 5.41; N, 13.93.

Studies of Sugar-Bearing CTV−C_{60} Interaction Based on Spectrofluorometric Titration. A solution of **CTV-G** or **CTV-L** was prepared in toluene−DMSO (1:1, v/v). Aliquots of C_{60} in the same solvent were added to the solution. The final concentration of **CTV-G** or **CTV-L** was 5×10^{-6} M. After each addition, the sample was allowed to equilibrate for 2 h prior to recording a spectrum. Additions of C_{60} were continued until no significant change in the fluorescence signal was observed. The excitation wavelength was 310 nm and the emission scan ranged from 330 to 550 nm.

Preparation of Sugar-Bearing CTV−C_{60} Complexes in Aqueous Solution. The aqueous solutions of sugar-bearing CTV−C_{60} complexes were prepared by stirring an aqueous solution of **CTV-G** or **CTV-L** (1.0×10^{-3} M) containing C_{60} solid (>99%) for 30 h. After centrifugation, clear aqueous solutions containing sugar-bearing CTV−C_{60} complex were obtained for further studies.

ASSOCIATED CONTENT

Supporting Information

FTIR spectra of **CTV1**, **CTV-G-OAc**, and **CTV-G**; fluorescence spectra of CTV, **CTC**, and **CTV1**; fluorescence spectra of **CTV-L** in the absence and presence of various concentrations of C_{60} in the toluene−DMSO solution; UV−vis spectra of C_{60}−**CTV-L** (2:1, molar ratio) in toluene−DMSO (1:1, v/v); UV−vis spectra of spectra of **CTV-L** complex with C_{60} in aqueous solution; Raman spectra of C_{60}−**CTV-L**, **CTV-L**, and C_{60}; and ^{1}H NMR, ^{13}C NMR, and mass spectra of key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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