CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.201804024

Link to VoR: http://dx.doi.org/10.1002/chem.201804024

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"Clicked" Porphyrin-Cucurbituril Conjugate: A Novel Multifunctional Supramolecular Assembly Based on tri-Glycosylated Porphyrin and Monopropargyloxycucurbit[7]uril

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.2018xxxxx.

Abstract

Herein, we report the design, synthesis and characterization of a novel multifunctional supramolecular assembly based on a photoactive glycosylated porphyrin and covalently attached mono-functionalized cucurbit[7]uril (CB7). To obtain the target supramolecular assembly, azido-functionalized tetraphenylporphyrin (TPP) was used as a building block. TPP was first glycosylated by copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction and then, a monopropargyloxy-functionalized-CB7 unit was conjugated to glycosylated TPP with a second CuAAC reaction. The host-guest chemistry of the assembly was investigated by ^{1}H-NMR experiments in order to find out the availability of the CB7 as a host. The imidazole-based guest which is known to have high affinity toward CB7 was observed to form inclusion complex with CB7. It was also demonstrated that this supramolecular assembly can serve as an efficient photosensitizer for the generation of singlet oxygen.

Keywords: Monopropargylcucurbit[7]uril, supramolecular assembly, tri-glycosylated porphyrin, photosensitizer, singlet oxygen.

Introduction

Multi-functional supramolecular materials combining various important functions and abilities in one platform can find a wide range of applications in the emerging technologies.[1] In this regard, porphyrin derivatives are highly appealing as a chromophore and a building block in the construction of photoactive multifunctional assemblies as they can exhibit photocatalytic, photodynamic and electroactive properties and allow the attachment of various functionalities to their large hydrophobic cores in order to bring together multi-functionalities.[2-7]

A number of different functional groups were attached to porphyrin core including hydrophilic oligoethylene glycols, dendrons, mono or polysaccharides in order to alter the solubility and photophysical properties and to make use of these compounds for various applications (e.g., photocatalysis, light harvesting, sensing, photodynamic therapies, etc.). [8-14]

There are also examples in the literature in which cucurbit[n]urils (CBs) are attached to the porphyrin core through non-covalent interactions,[15, 16] however, those works do not involve in the conjugation of functionalized CBs directly to porphyrin core in order to be able to utilize the CBs as receptors. CBs are highly versatile macrocycles possessing a hydrophobic cavity along with carbonyl decorated hydrophilic portals. Owing to these features they have an ability of binding to various guests with high affinity and selectively including dyes, drugs and peptides. Due to their distinctive features, they have been utilized in the construction of supramolecular assemblies.[17] Although post-surface functionalized CBs with reactive functional groups are very useful building blocks in the assembly of supramolecular structures, the examples are still rather limited. One of the reasons might be due to the difficulties associated with the functionalization of CB derivatives especially monofunctionalization.[18-23] To date, mainly two approaches have been employed for the synthesis of functionalized CB derivatives: (1) post-functionalization[19-22] and (2) using the functionalized precursors.[23, 24] Post functionalization seems to be more practical as it allows the modification of as-prepared

CB homologues in moderate yields. Kim *et al.* used these functionalized CB derivatives in the preparation of various nanostructured materials.[20, 17b, 17d] Isaacs and co-workers recently reported the synthesis and the application of monofunctionalized CB7 derivatives, which was synthesized from a functional group containing precursor.[23, 24]

Here, we report first time the conjugation of mono-propargyloxy-CB7 unit to a tri-mannosylated-TPP) core through copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. The rationale behind the design of this assembly as follows: TPP is selected as a core of the assembly because of its singlet oxygen ($^1O_2$) production ability that could be used as a photosensitizer for photodynamic therapies against cancer cells or bacteria inactivation as well as photocatalysis. Multi mannose groups were chosen because of their hydrophilic nature that may increase the solubility of the resulting assembly and for the multivalent interaction as the mannose units have ability to interact with mannose receptors on the bacterial surface that would be useful for the photodynamic antibacterial therapy. CB7 was chosen to be conjugated to this platform for several reasons. First due to its bulky nature, interactions between the porphyrin units are expected to be minimized and as a result, singlet oxygen efficiency will be enhanced. In the photodynamic cancer or antibacterial therapies, in order to increase the efficiency of the therapy, anticancer drugs or antibiotics, respectively, can be further encapsulated and carried by CB7 units. This assembly could also be used for photocatalysis and energy harvesting in which CB units could encapsulate respectively, an analyte and donor/acceptor molecules for an efficient photocatalytic and energy transfer processes. However, the current scope of this manuscript will be on the synthesis, full characterization, host-guest chemistry and singlet oxygen generation ability of the assembly. Other aforementioned applications will be explored in our future works.

Results and Discussion

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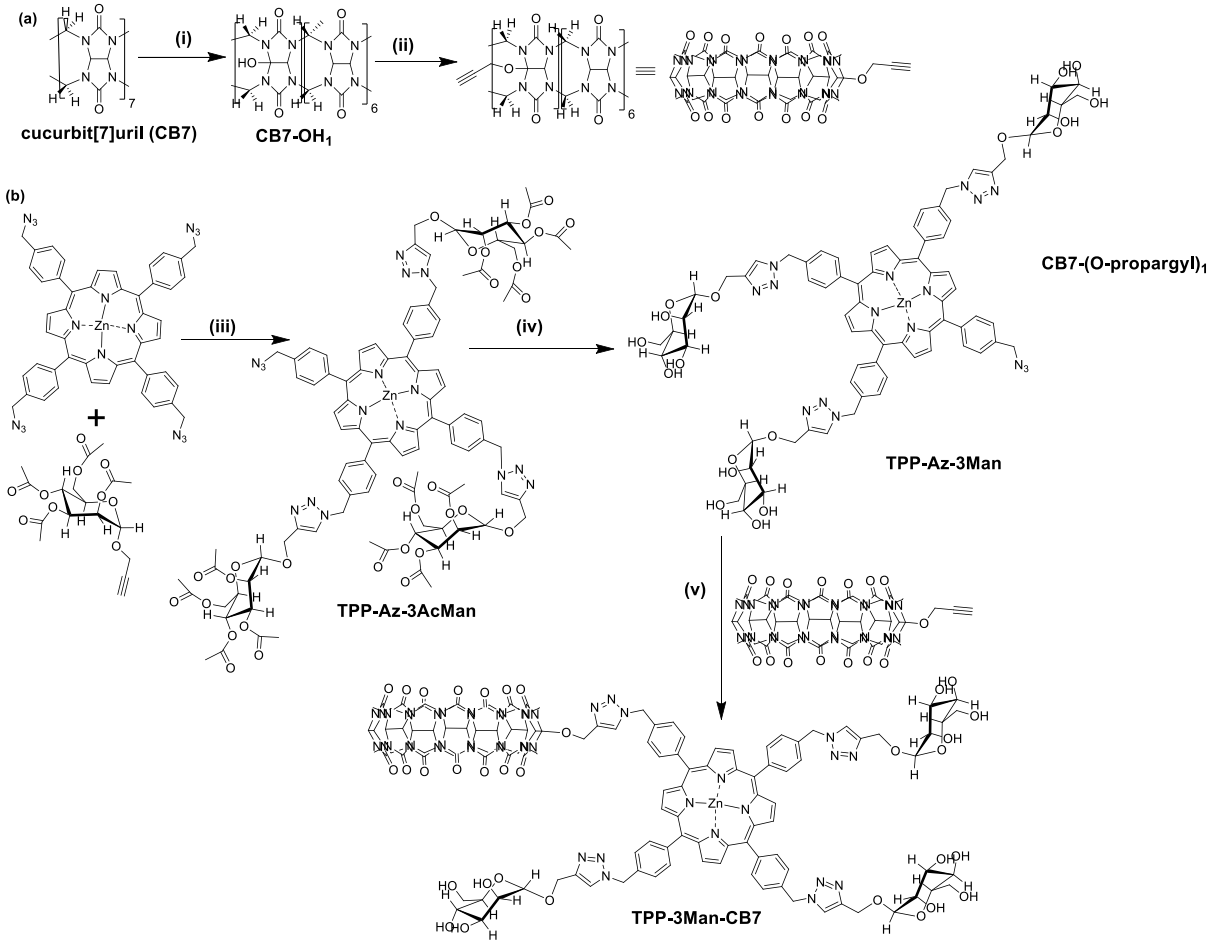
The synthetic route of our target assembly is shown in the reaction Scheme 1. First, CB7 was synthesized and characterized by ^{1}H NMR, ^{13}C NMR spectroscopies and ESI-MS (Figures S1-S4).[25] Then, monohydroxy-CB7 (CB7-OH_1) and mono-propargyloxy-cucurbit[7]uril (CB7-(O-propargyl)$_1$) were prepared as shown in Scheme 1a according to literature procedures.[19-21] The formation of CB7-OH_1 and CB7-(O-propargyl)$_1$ was confirmed by ^{1}H NMR, ^{13}C NMR spectroscopies, ESI-MS, FT-IR and thermal characterization was done with TGA (Figures S5-S13).



Scheme 1. a) Synthesis of mono-fucntionalized CB7: (i) $K_2S_2O_8$, H_2O, 85 °C; (ii) NaH, propargyl bromide, DMSO, 0°C-25 °C, N_2 (g), 48 h. **b)** (iii) Synthesis of the assembly: $CuSO_4.5H_2O$/Na-L-Ascorbate, THF/H_2O, 60 °C; 14h (iv) $NaOCH_3$, MeOH, 25 °C, 14 h; (v) $CuSO_4.5H_2O$/Na-L-Ascorbate, DMSO/H_2O, 48h.

After having mono- propargyloxylated CB7 at hand, we set out for the synthesis of the porphyrin derivatives. First, the synthesis of 5,10,15,20-tetrakis(*α*-bromo-*p*-tolyl)porphyrin (**TPP-Br**) was accomplished[26] followed by azidation to afford **TPP-N_3** in 93% yield. **TPP-Br** and **TPP-N_3** were characterized by ^{1}H NMR spectroscopy and ESI-MS (Figures S14-S18). Before proceeding with Cu-catalyzed azide-alkyne click reaction (CuAAC), the core of **TPP-N_3** was metallated with Zn so as to prevent inclusion of Cu that will decrease its catalytic effect. Metallation was successfully achieved by refluxing **TPP-N_3** with $Zn(OAc)_2$ in MeOH and characterized by ^{1}H and ^{13}C NMR spectroscopies, ESI-MS, FT-IR and TGA (Figures S19-S23). In ^{1}H NMR spectrum, the upfield shift from 4.88 ppm to 4.75 ppm and the disappearance of singlet at -2.78 ppm was the proof for the successful metallation. The TGA of the compound demonstrated two types of decomposition (Figure S23). The first decomposition starts at 233 °C which is due to the loss of azide groups from the compound. The second decomposition that starts around 517 °C is probably for the loss of benzene rings attached to the core.

Acetylated propargylated mannose (1-*α*-propargyloxy mannose) was synthesized using the literature procedure.[14b] and characterized by ^{1}H NMR and FT-IR spectroscopies (Figures S24, S25). The click (CuAAC) reaction between three equivalents of 1-α-propargyloxy mannose and one equivalent **Zn-TPP-N_3** yielded a mixture of analogues of 1, 2, 3 and 4-mannosyl-clicked porphyrins. These were successfully separated by column chromatography to afford **TPP-Az-3AcMan** (tri-clicked analogue) in 50% yield together with 4% of **TPP-3Az-1AcMan** (mono-clicked analogue), 16% of **TPP-2Az-2AcMan** (di-clicked analogue), and 20% of **TPP-4AcMan** (tetra-clicked analogue), successively. **TPP-Az-3AcMan** was selected for the further use due to solubility considerations and fully characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR spectroscopies and ESI-MS (Figures S26-S29). In the ^{1}H-NMR spectrum (Figure 1C), the characteristic singlet at 8.55 ppm for the hydrogen of triazole ring and the multiplet around 2.00 ppm for acetylic hydrogens are evident for the attachment of mannosyl units. The peak at 170.1

ppm coming from carbonyl carbon in ^{13}C NMR further confirms the presence of acetylated mannose groups attached to TPP (Figure S27). In the ESI-mass spectrum, the related signals are readily assigned to corresponding molecular ions as shown in Figure S28. Another important proof for the formation of **TPP-Az-3AcMan** was obtained from FT-IR spectrum which shows the partial reduction of azide stretching at 2095 cm^{-1} and the existence of C=O stretching peak at 1748 cm^{-1} as expected (Figure 2a). **TPP-Az-3AcMan**) dissolves well in DMSO, DMF and partially in methanol, THF, chloroform, acetone, acetonitrile but not well in ethanol and water.

Prior to setup the final synthetic step**,** acetyl groups on mannose of **TPP-Az-3AcMan**, were hydrolyzed via Zemplén deacetylation using sodium methoxide solution in methanol. [24] The product obtained after hydrolysis (**TPP-Az-3Man)** dissolves well in DMSO partially in methanol but it has a poor solubility in water. **TPP-Az-3Man** was characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR spectroscopies and ESI-MS and (Figures S30-S33). The disappearance of acetylic hydrogen peaks around 2.00 ppm in ^{1}H NMR spectrum (Figure 1B) and the C=O stretching peak at 1748 cm^{-1} in the FT-IR spectrum along with the emergence of a broad peak at 3350 cm^{-1} for hydroxyl groups confirm the success of the deacetylation reaction (Figure 2b). The ESI-mass spectrum clearly shows the molecular ions of the product and there was no trace from acetylated form (Figure S32).

In the final step, TPP-CB7 conjugate (**TPP-3Man-CB7**) was synthesized by a second CuAAC reaction between **TPP-Az-3Man** and excess CB7-(O-propargyl)$_1$ in DMSO/H_2O mixture (4:1). The product was isolated after purification using sephadex G-25 column (MeOH/water, 1:1, v/v) in 91% yield. The solubility properties of **TPP-3Man-CB7** were investigated and summarized as follows: in DMSO, 10 mg/mL; in H_2O, 0.2 mg/mL and in H_2O:DMSO mixture (4:1, v/v), 2 mg/mL. It also dissolves in acidic water (e.g. 0.1M HCl (aq) solution). Poor solubility in neat water, probably due to extensive H-bonding between the

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mannosyl-OH groups but the presence of even small amount of DMSO weakens the interactions and solubilizes the assembly in water. **TPP-3Man-CB7** was fully characterized by ^{1}H and ^{13}C NMR, FT-IR spectroscopies and ESI-MS (Figures S35-S38). Figure 2 shows the overlaid FT-IR spectra of **TPP-Az-3AcMan**, **TPP-Az-3Man** and **TPP-3Man-CB7** for comparison. FT-IR spectrum of the **TPP-3Man-CB7** (Figure 2c) reveals the absence of azide stretching at 2100 cm^{-1} and the presence of strong carbonyl stretch at 1725 cm^{-1}, which supports the successful synthesis of **TPP-3Man-CB7**. Figure 1A shows the ^{1}H-NMR spectrum of **TPP-3Man-CB7** recorded in DMSO-d_6. As can be seen from the spectrum, the peaks for porphyrin and mannosyl protons are relatively sharp but the peaks due to CB protons are quite broad. In the ^{1}H NMR spectrum, the singlet at 8.49 ppm for the hydrogen of triazole ring formed during the second click reaction and the peak at 155.6 ppm for carbonyl carbon of CB in ^{13}C NMR further confirms the success of the reaction (Fig. S35, S37). In the ESI-MS spectrum, the related signals are readily assigned to corresponding molecular ions as shown in Figure S35.

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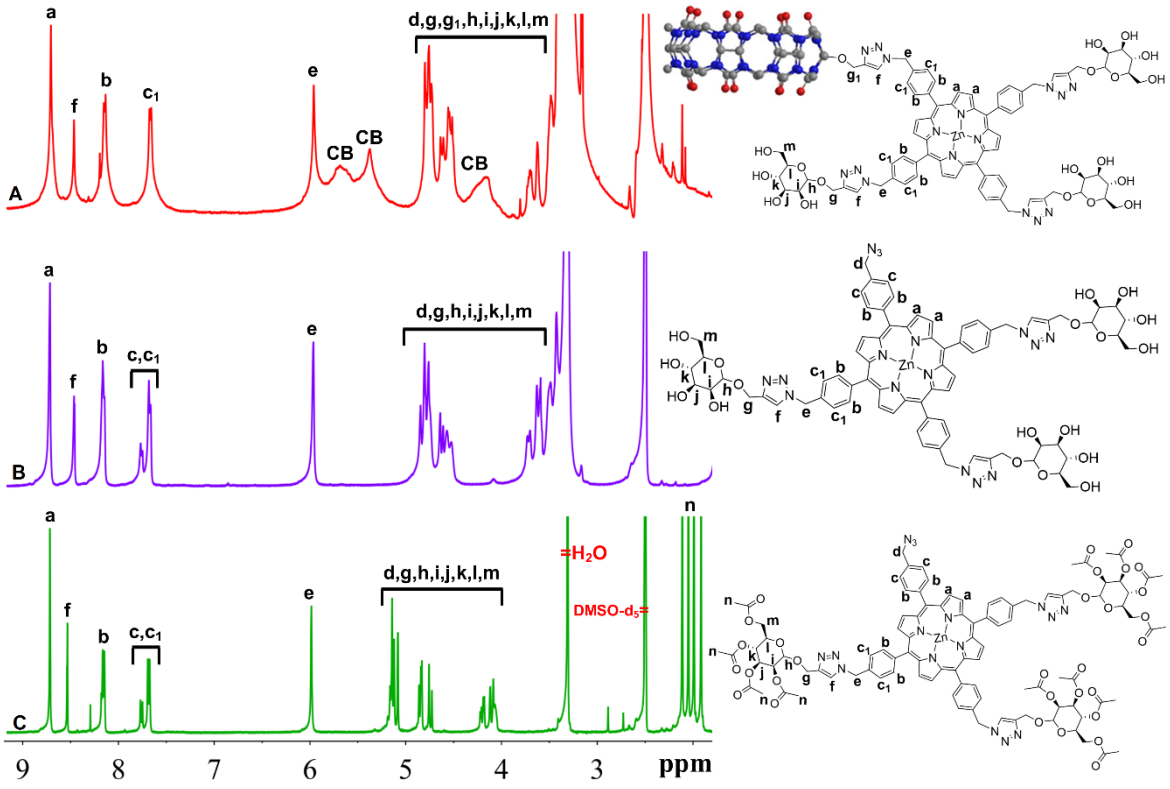

Figure 1. Overlay of the ^{1}H NMR (400 MHz, 25 °C) spectra of (A) TPP-3Man-CB7 (B) TPP-Az-3Man and (C) TPP-Az-3AcMan (Spectra were recorded in DMSO-d_6).

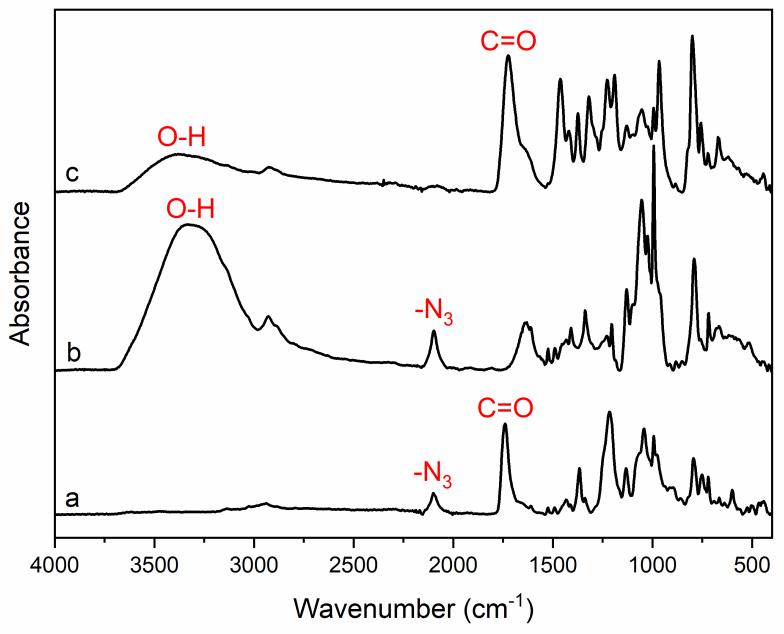

Figure 2. Overlay of the FT-IR spectra of (a) TPP-Az-3AcMan (b) TPP-Az-3Man (c) TPP-Az-3Man-CB7 in absorption mode.

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In order to find out whether CB7 will be available as a host in the assembly, 1,1'-(1,4-phenylenebis(methylene))-bis(3-methyl-1*H*-imidazol-3-ium) iodide (bisimidazolium), which is known to have high affinity toward CB7 was selected as a guest molecule and ^{1}H-NMR experiment was carried out. As can be seen from ^{1}H-NMR spectrum of bisimidazolium guest recorded in D_2O (Figure 3A), chemical shifts for the phenyl and imidazole protons (labelled as f and b/c, respectively) overlap and resonate at 7.5 ppm. However, upon addition of 1 equiv CB7-OH_1, the phenyl protons exhibit an upfield shift of around 1 ppm and imidazole protons (labelled as b and c) appear as two distinct peaks (Figure 3B). These changes indicate the encapsulation of phenyl moiety of the imidazole guest by CB7-OH_1 as the suggested inclusion complex structure shown on Figure 3B. We have also observed similar changes in the ^{1}H-NMR spectrum of the **TPP-3Man-CB7** (Figure 3C) when bisimidazolium solution in D_2O (1 equiv) was added to the NMR tube containing the DMSO-d_6 solution of **TPP-3Man-CB7**. Furthermore, the broadened CB7 peaks acquired their well-defined shapes after complexing with bisimidazolium guest. These observations confirm that CB7 is available as a host for complexation and there is no conformational restriction for CB7 in the assembly to exhibit its nature as being a receptor.

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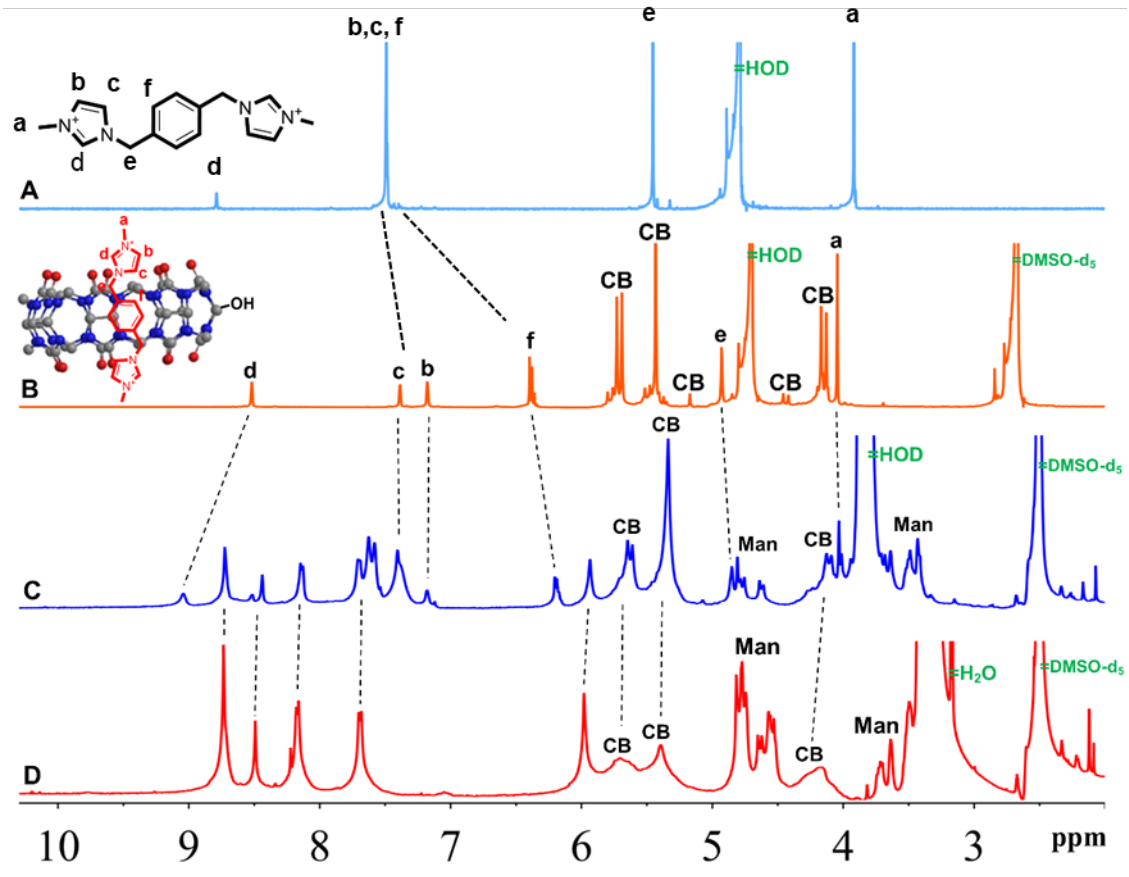

Figure 3. ^{1}H NMR (400 MHz, 25 °C) spectra of (A) 1,1'-(1,4-phenylenebis(methylene))bis(3-methyl-1H-imidazol-3-ium) iodide (bisimidazolium) (in D_2O); (B) CB7-OH_1+1 equiv bisimidazolium, (in DMSO-d_6:D_2O mixture, 1:2, v/v); (C) TPP-3Man-CB7+1 equiv bisimidazolium (1.2 mM, in DMSO-d_6:D_2O mixture, 2:1, v/v); (D) TPP-3Man-CB7 (1.2 mM, DMSO-d_6).

Photophysical properties of **TPP-3Man-CB7**, **TPP-Az-3AcMan** and **TPP-Az-3Man** in DMSO were also investigated. Figure 4 shows an overlay of the UV-Vis absorbance and fluorescence spectra of **TPP-Az-3AcMan**, **TPP-Az-3Man** and **TPP-3Man-CB7**. UV-vis absorbance spectra show no significant difference in a typical sharp Soret band (λ_{max}= 429 nm) and Q-bands (λ_{abs} = 561 and 600 nm). Similarly, emission spectra also do not show any significant difference (λ_{em} = 608 and 661 nm). The fluorescence quantum yields (Φ_f) of **TPP-3Man-CB7** and **TPP-Az-3Man** in DMSO were found to be 3.5 and 4.1, respectively. The

fluorescence lifetime (τ) is 1.8 ns for both **TPP-3Man-CB7** and **TPP-Az-3Man** (Fig. S34, S40).

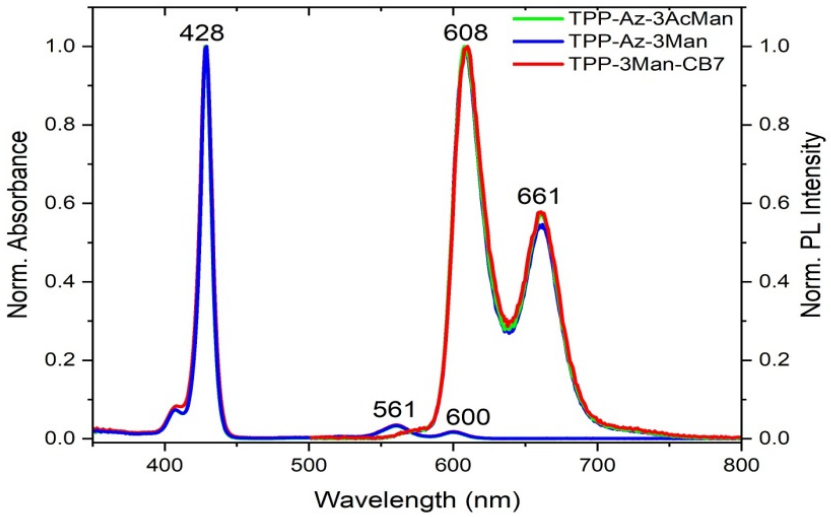

Figure 4. Normalized UV-Vis absorbance and fluorescence spectra of **TPP-Az-3AcMan** (green), **TPP-Az-3Man** (blue), and **TPP-3Man-CB7** (red) in DMSO.

Low fluorescence quantum yields of these compounds would suggest us that the excited molecules may follow nonradiative relaxation pathways, which could possibly increase their $^1O_2$ generation capacity. In order to prove this, a widely known indirect method for the determination of produced $^1O_2$ was employed. 1,3-diphenylisobenzofuran (DPBF) was used as $^1O_2$ trapping agent and time-dependent decrease in the absorbance of DPBF in the presence of photosensitizer upon irradiation was correlated with the amount of $^1O_2$ generated. For this experiment, the samples in DMSO were irradiated with 460 nm LED with 10 sec intervals. The reduction in the absorbance intensity of DPBF was monitored with the increasing irradiation time (Fig. S41). From the absorbance graphs, $-\ln[DPBF]/[DPBF]_0$ vs. time plots were extracted to indirectly calculate $^1O_2$ quantum yields of the samples using the equation below:

$$\Phi_{sam} = \Phi_{MB}(m_{sam}/m_{MB})(F_{MB}/F_{sam})$$

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where the subscripts 'MB' and 'sam' stand for methylene blue (Φ_{MB} = 0.52 in DMSO) and acetylated bis-mannose TPP, hydrolyzed bis-mannose TPP and TPP-3Man-CB[7], respectively. m is the slope of $-\ln[DPBF]/[DPBF]_0$ vs. time plot and F is the absorption correction factor that is given by $F=1-10^{-OD}$ (OD: optical density at the irradiation wavelength). The $^1O_2$ quantum yields of the corresponding samples can be order as:

TPP-Az-3Man ≅ TPP-3Man-CB7 > TPP-Az-3AcMan; [Φ_Δ = 0.77 ≅ 0.77 > 0.80]

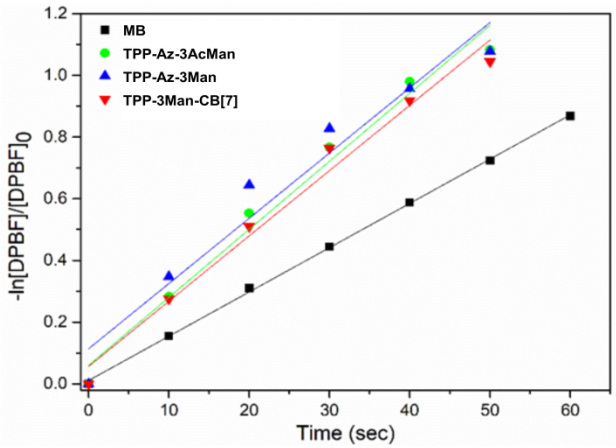

Figure 5 Linearized plots based on the decrease in the absorbance intensity of DPBF in the presence of methylene blue, TPP-Az-3AcMan, TPP-Az-3Man and TPP-3Man-CB7 irradiated at 460 nm with 10 sec intervals.

In the literature the $^1O_2$ quantum yield of unfunctionalized TPP was reported as 0.60 in DMF.[27] The synthesized novel materials were seen to have $^1O_2$ quantum yields around 80%, which are significantly higher than that of TPP. The reason of high $^1O_2$ quantum yields could be explained by reduced π-π interactions between the porphyrin cores resulted from the presence of bulky functional groups (mannosyl and CB7).

Conclusions

In summary, a multifunctional supramolecular assembly based on a photoactive glycosylated porphyrin and covalently attached mono-functionalized CB7 was synthesized first time and fully characterized successfully. With a CuAAC reaction of 1-α-propargyloxy mannose and **Zn-**

TPP-N3, first tri-mannosyl clicked porphyrin, **TPP-Az-3AcMan,** was synthesized and isolated from the other mono, di and tetra mannosyl analogues and subsequently hydrolyzed to obtain its deacetylated version. Tri-mannosyl clicked porphyrin was selected to be used for the construction of assembly because it allowed us to obtain well-defined and as result, well-characterized structure after its second CuAAC reaction with mono-propargyloxy-CB7. The resulting assembly dissolves in DMSO (10 mg/mL), in H_2O (0.2 mg/mL), in H_2O:DMSO mixture (4:1, v/v), 2 mg/mL) and in aqueous acid solution.

$^1O_2$ generation efficiencies of the synthesized compounds were investigated and they were found to be significantly higher than that of the unfunctionalized TPP. Moreover, the availability of the CB7s as a host in the assembly was confirmed by ^{1}H-NMR experiments in which the imidazole-based guest was observed to form inclusion complex with the CB7s of the assembly.

This photoactive supramolecular assembly has a potential to be used in the multimodal chemo and photodynamic therapies as its photoactive porphyrin core can act as a photosensitizer and in order to increase the efficiency of the therapy, anticancer drugs or antibiotics, respectively, can be further encapsulated and carried by CB7 units. This assembly could also be used for photocatalysis and energy harvesting in which CB units could encapsulate respectively, an analyte and donor/acceptor molecules for an efficient photocatalytic and energy transfer processes.

Experimental Section

Experimental details and procedures, characterization data and spectra provided in the supporting information part.

Acknowledgements

We thank The Scientific and Technological Research Council of Turkey-TÜBİTAK for funding (KBAG 215Z035).

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10.1002/chem.201804024

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Sugar coated porphyrin-cucurbituril host ready to serve: A novel multifunctional supramolecular assembly was synthesized by clicking an azide functionalized photoactive glycosylated porphyrin with mono-propargyloxy functionalized cucurbit[7]uril (CB7). This supramolecular assembly can serve as a host to bind with guests and an efficient photosensitizer for the generation of singlet oxygen.