

Spectroscopy and laser characterization of synthesized supramolecular host cucurbit[7]uril using aqueous Rhodamine B dye

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DOI: 10.1007/s12043-013-0675-4; ePublication: 12 February 2014

Abstract. Recent demonstration in augmenting the efficiency of aqueous Rhodamine dye lasers using cucurbit[7]uril (CB[7]), a deaggregating and photostabilizing host, has drawn interest in the synthesis and characterization of spectroscopic grade CB[7] in larger quantities. Synthesis of cucurbituril group of macrocycles always leads to the formation of various homologues of CB[n]s (n=5–7) with CB[7] as the minor product. The literature procedure has been optimized to get pure CB[7] in 12–14% yield by fractional crystallization and the purity was checked by NMR, MS and spectrophotometric titration. Laser performances of the synthesized and commercial CB[7] sample as an additive were evaluated using Nd-YAG (532 nm) pumped Rhodamine B aqueous dye lasers and comparable results were obtained.

Keywords. Macrocyclic host; cucurbit[7]uril; host–guest complex; Rhodamine B; aqueous dye lasers.

PACS No. 36.20.–r

1. Introduction

Understanding the weak non-covalent interactions in supramolecular chemistry for their suitable applications in various fields of research remained a major challenge. Of late, it has been demonstrated that supramolecular encapsulation of fluorescent molecules like Coumarin and Rhodamines, by a relatively recent macrocyclic host cucurbit[7]uril can improve their fluorescence properties and photochemical stability due to an altered micro-environment [1,2]. Cucurbit[n]urils are hollow barrel-shaped macrocyclic molecules possessing a pair of hydrophilic carbonyl portals (rim) at both ends and a hydrophobic cavity inside, which can bind a wider range of neutral and cationic guests in aqueous solutions by

non-covalent supramolecular interactions. Among the CB[n] family, CB[7] has substantially higher solubility in water than CB[6] and CB[8], larger voluminous cavity than its water soluble analogue CB[5], and thus has been used to form strong and stable inclusion complexes with many fluorescent dyes [3]. As an application, the same supramolecular strategy was recently adopted by us to demonstrate the operational efficiency and photostability of aqueous Rhodamine dye lasers, pumped by high-repetition-rate (12.5 kHz) CVL (at 578 nm) as well as low-repetition rate (10 Hz) Nd-YAG (at 532 nm) lasers [2].

The spectroscopic grade CB[7] needed for our dye laser studies is highly expensive (Rs.1.2 lakhs/g) with limited availability. Therefore, indigenous synthesis and characterization of highly pure CB[7] remained an important task for its applications in high-average power aqueous dye lasers. The detailed reaction conditions of synthesizing CB[7] are protected by many patents and are not available in open literatures. After many trials, we have optimized the synthetic route for CB[7] by acid-catalyzed condensation of formaldehyde and glycoluril over a temperature range of 75–100°C for a long reaction time (5 days). As synthesis of CB[7] was always accompanied by formation of its chemically similar homologues CB[5], CB[6] and CB[8], the isolation of pure CB[7] remained a daunting task. Also, determination of the purity of synthesized CB[7] sample is not yet clearly established in the literature and thus remains a big issue. None of the CB[n]s absorb/fluoresce in UV–vis region, and their IR spectra are almost similar due to the presence of similar functional groups (amide groups). In this report, we present the synthesis and estimation of the purity of CB[7] by different spectroscopic techniques such as high resolution (500 MHz) ^1H NMR, ^{13}C NMR, ESI-MS, MALDI-TOFMS and spectrophotometric titration. Finally, laser performances of both synthesized and commercial-grade samples of CB[7] were compared using Nd-YAG (532 nm) pumped Rhodamine B aqueous dye lasers. These results gave us confidence for the indigenous synthesis of CB[7] in relatively larger amount (10–20 g), needed for high-repetition-rate operations of tunable dye lasers, which required a large volume of dye solution.

2. Experimental

Cucurbit[7]uril is synthesized by the acid-catalysed condensation of formaldehyde and glycoluril over a temperature range of 75–100°C, shown schematically in figure 1.

Purity of the synthesized and commercial (Aldrich make) CB[7] samples was comparatively evaluated using different spectroscopy techniques such as FT-IR, ESI-MS,

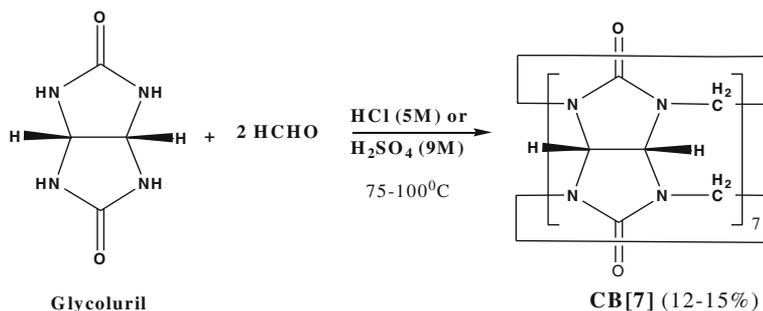


Figure 1. Synthesis scheme of cucurbit[7]uril (CB[7]).

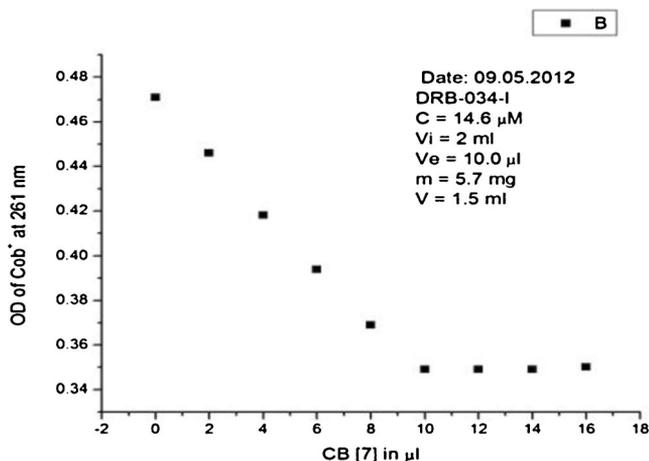


Figure 2. Spectrophotometric titration of CB[7] by Cob^+ .

MALDI-TOFMS, ^1H NMR (500 MHz), ^{13}C NMR (125 MHz) and UV-visible titration method. For these experiments, CB[7] samples were prepared in solid or solution matrix, according to the established literature procedures. UV absorption spectra of a highly binding (binding const. $K > 10^6$) guest molecule bis(cyclopentadienyl)cobalt(III) hexafluorophosphate ($\text{Cob}^+\text{PF}_6^-$) in water, in the presence of various CB[7] concentrations, were recorded to determine the purity (%) of the CB[7] sample by UV titration experiment. The plot of maximum absorbance of Cob^+ at 261 nm versus CB[7] concentrations clearly indicated quantitative complex formation, and the equivalence point of two intersecting straight lines was used to calculate the purity of CB[7] sample. Since Cob^+ is the UV active species, its concentration was maintained constant throughout the titration, so that any absorbance change is due to the formation of the less absorbing Cob^+ inclusion complex (figure 2).

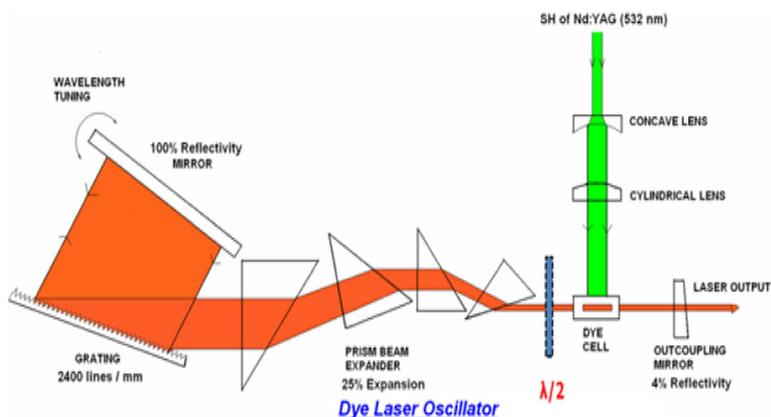


Figure 3. A schematic diagram of the dye laser set-up for characterizing laser performances of the synthesized CB[7] sample.

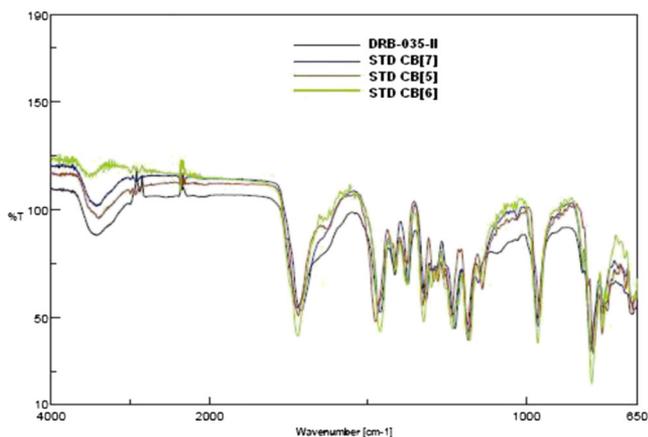


Figure 4. Comparative FT-IR spectra of CB[n]s.

Laser performances of the synthesized and standard CB[7] were compared using an indigenously constructed grazing incidence grating (GIG) configured narrow band ($\sim 0.1 \text{ cm}^{-1}$) pulsed dye (aqueous Rhodamine B) laser, transversely excited by second harmonic (at 532 nm) of a Q-switched Nd-YAG (prf 10 Hz, pulse width 6–8 ns) laser (figure 3).

3. Results and discussion

The chemical structure of CB[7] molecule is shown in figure 1. Comparison of FT-IR spectra of standard (Aldrich-make) CB[7], CB[6] and CB[5] with synthesized CB[7] samples are shown in figure 4. The almost identical spectra of all the CB[n]s, poses difficulty in determining the purity of CB[7] that can be explained by the presence of similar functional group such as amide. In contrast, chemical shift values in NMR spectra (^1H NMR and ^{13}C NMR) of various CB[n]s were found to be different. The identical ^{13}C NMR spectra for all three chemically different carbons of both standard and synthesized CB[7] samples in figure 5 indicated the high purity of synthesized samples.

The inclusion complex of CB[7] with coumarin 1 dye (7-diethylamino-4-methylcoumarin) was confirmed by MALDI-TOF mass spectrometry, wherein a peak at m/z

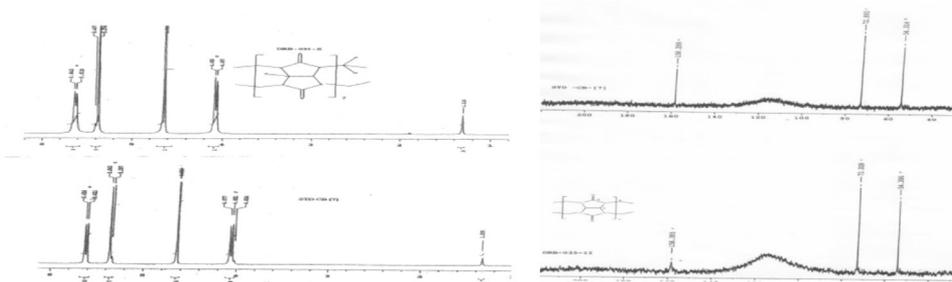


Figure 5. ^1H NMR and ^{13}C spectra of synthesized and standard CB[7].

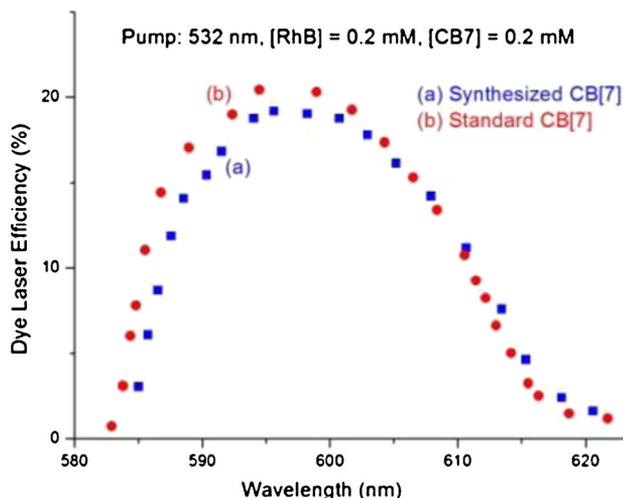


Figure 6. Laser performance of the synthesized and standard CB[7].

1394 confirms the presence of the supramolecular entity of CB[7]-coumarin-1. For UV titration experiment, the UV absorption band of aqueous Cob^+ at 261 nm is decreased by the gradual addition of CB[7]. The plot of absorbance vs. CB[7] concentrations in figure 2 clearly shows a behaviour characterized by two straight lines intersecting at the well-defined equivalence point, which was reached exactly upon addition of 1.0 equiv of CB[7]. The resulting UV titration data were used to calculate the purity ($\%p$) of CB[7] sample using the equation $\%p = [\text{MW} \cdot c (V_i + V_e) \times 100] / [m V_e / v]$, where MW is the molecular weight of the CB[7] host (1162 g/mol), c is the molar concentration of Cob^+ , v is the volume of c molar of Cob^+ solution in water with a weighed amount m of the CB[7] sample, V_i is the initial volume of the original Cob^+ solution taken for titration and V_e is the end (equivalence) point of titration. The comparative narrow-band laser performances of aqueous Rhodamine B (RhB) dye laser, using the synthesized and standard Aldrich-make CB[7] samples, showed comparable tuning range and peak efficiency, which is illustrated in figure 6.

4. Conclusion

The reported protocol for the synthesis of CB[7] has been optimized to get spectrally pure CB[7] in 12–15% yield. The purity of the synthesized CB[7] was established by comparing its NMR, MS, spectrophotometric and dye laser data with that of the commercial samples.

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