

Scientific paper

Preparation of Cu Nanocomposites from EDA, DETA, and Jeffamine Cored PAMAM Dendrimers with TRIS and Carboxyl Surface Functional Groups

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Abstract

This study presents the synthesis and UV-Vis characterization of Cu nanocomposites from ethylenediamine (EDA) (E), diethylenetriamine (DETA) (D), and Jeffamine® T-403 (P) cored PAMAM dendrimers (PAMAMs) with TRIS and carboxyl surface functional groups. Cu-PAMAM dendrimer encapsulated nanoparticles (Cu-DENs) were characterized by UV-Vis spectroscopy. Disappearance of the 680 nm *d-d* transition and 270–300 nm ligand to metal charge transfer (LMCT) peaks and the formation of monotonically increasing exponential band were used as the evidence of the successful synthesis of Cu-DENs in addition to immediate color change of dendrimer-metal mixture solutions from blue to golden brown by reduction. Synthesized Cu-DENs could be facilitated as novel alternatives to the existing nanomaterials used in a wide range of applications involving bio and chemical sensors, catalysis, hydrogenations, oxidations, semiconductors, noble metals, magnetic dendrimer nanocomposites, environmental cleanup and many others.

Keywords: TRIS and carboxyl terminated PAMAM dendrimers; Dendrimer encapsulated nanoparticles; EDA, DETA, Jeffamine, Cu nanocomposites

1. Introduction

Dendrimers are a new class of polymeric materials and cascade molecules with their spherical three-dimensional (3D) morphology, typically symmetric around a core. There has been a growing interest toward dendrimers due to their controllable structures, globular shapes and definite monodisperse nanosizes.¹ In particular, controllable synthesis of dendrimers allows them to be architecturally designed with the desired physical and chemical properties for the desired applications.² Design variables of dendrimers are a core, repeating branches emanating from the core, and surface-groups. Selectivity on these variables makes dendrimers proper host and candidate for guest molecules so that various metal nanoparticles have been successfully stabilized using dendrimers as templates with tunable solubility and surface reactivity.³

Dendrimer encapsulated nanoparticles (DENs) are used as templates to control size, stability and solubility of nanoparticles in the range of 1 nm to up to 4–5 nm.⁴ Crooks et al.⁴ announced dendrimers as good hosting metal nanoparticles because of their uniform structures leading to well-defined nanoparticles, availability to participate in catalytic reactions, resistance to agglomeration, and selectivity to control encapsulation of small substrate molecules.

DENs have gained great interest in the field of chemical sensors in molecular recognition,⁵ biochemistry, catalysis,^{6,7} optoelectronics,⁸ application areas of semiconductors, noble metals, magnetic dendrimer nanocomposites, and environmental cleanup.⁹ First DENs were reported by Crooks et al.¹⁰ and followed parallel by Tomalia.⁹ Different types of Pt, Pd, Au, Ag, Cu, Ni, Ru, Mn, and Fe DENs were prepared in the literature^{4,11–15} by using dendrimers with amine, carboxyl, and hydroxyl surface-groups.^{16–21}

Modification of surface-groups of dendrimers is an important process to gain the desired solubility. TRIS is the abbreviation of the common known organic compound, tris(hydroxymethyl) aminomethane, with the chemical formula of $(\text{HOCH}_2)_3\text{CNH}_2$. It is widely used in biochemistry, molecular biology, and is highly water-soluble. Surface modified dendrimers with TRIS are highly water soluble.²² In our recent study, we have shown the microwave-assisted fast, facile and one-pot synthesis of a series of TRIS-terminated poly(amidoamine) PAMAM (PAMAM-TRIS) dendrimers with ethylenediamine (E), diethylenetriamine (D), and Jeffamine (P) core.²³ Here, we have introduced the synthesis of generation-3 (G3) and -4 (G4) E, D, and P cored PAMAM dendrimers (PAMAMs) with TRIS and carboxyl end groups, and later used these templates for the preparation of Cu nanocomposites. Indeed, this study is the first study presenting the synthesis and UV-Vis characterization of G3 and G4, D and P cored PAMAM-COOH dendrimers templates, and Cu-PAMAM-TRIS and Cu-PAMAM-COOH nanocomposites. Synthesized Cu-DENs can take a potential use in the future studies with a wide range of applications.

2. Experimental

2.1. Materials and Apparatus

Jeffamine[®] T403 Mn 440, diethylenetriamine (DETA), methyl acrylate, ethylenediamine (EDA), methanol, n-butanol, tris(hydroxymethyl) aminomethane (TRIS), NaOH, 37% HCl, NaH_2PO_4 , NaCl, potassium hydrogen phthalate (KHP), $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, and NaBH_4 were supplied from Merck. All solutions were prepared by 18.2 M Ω Millipore Milli-Q deionized water. NaOH solutions were used as titrant after standardized with a primary grade KHP. Standardized HCl against KHP was used as excess acid in order to adjust initial pH of dendrimer solutions. Dendrimer solutions were stored at 4 °C. Unless otherwise stated all the chemicals were in analytical grade and used without further purification.

Spectroscopic titrations were carried out automatically by using TitroLine[®] 7000 (SI Analytics GmbH, Hattenbergstraße, Germany) autotitrator equipped with thermostated titration vessel under nitrogen media and PG TG 70 UV-Vis spectrophotometer equipped with UVWin5 Software v5.0.5.

2.2. Synthesis of PAMAMs

PAMAM-TRIS (Cn.TRIS) dendrimers were synthesized according to our recent study.²³ C refers to dendrimer core, which are ethylenediamine (E), diethylenetriamine (D), and Jeffamine (P) while n is the generation number. PAMAM-COOH dendrimers (Cn.COOH) were prepared by the slight modification of literature procedure,²⁴ and our previous study.²⁵ During the synthesis of PAMAM-

COOH dendrimers, briefly, a methanolic solution of ester-terminated PAMAM dendrimers (PAMAM-OCH₃) (Cn.5) dendrimers was mixed with 1.5 M equiv. of NaOH per terminal ester. The final mixture was stirred for 24 h. Excess amount of solvent was removed under vacuum at bath temperature 65 °C. The remaining oil was dissolved in methanol and again evaporated in vacuo. Drying under vacuum resulted in a white powder product. Yields were 100%. The detailed experimental, characterization data were given in the supporting information (Table S1). Synthesized G3-G4 E, D and P cored PAMAM-COOH, and PAMAM-TRIS dendrimers were used for the preparation of dendrimer encapsulated Cu nanomaterials (Cu-DENs).

2.3. Spectroscopic Titrations of PAMAMs with Cu²⁺ Ions and Synthesis of Cu(II)-PAMAM Dendrimer Complexes

The maximum number of Cu²⁺ ions, PAMAMs can complex and to be used in the synthesis of Cu-DENs, were determined via spectroscopic titrations. We have shown the microwave-assisted synthesis, characterization and Cu(II) intra-dendrimer complexes of E, D, and P cored G3, G4 PAMAM-TRIS dendrimers in our recent study.²³ By using the same procedure, we have performed the spectroscopic titrations of E, D, and P cored G3, G4 PAMAM-COOH dendrimers and their Cu(II) complexes. Concentrations used to titrate aqueous solutions of PAMAM-COOH dendrimers with Cu²⁺ ions were given in Table 1.

Table 1. Concentrations used to titrate aqueous solutions of PAMAM-COOH dendrimers with Cu²⁺ ions.

Dendrimers	Dendrimer Conc. of	Conc. (mM) CuSO ₄ (mM)	Increment of CuSO ₄ (μL)
E3.COOH	0.637	80.14	44.00
E4.COOH	0.321	80.14	44.00
D3.COOH	0.549	79.86	44.00
D4.COOH	0.268	80.50	44.00
P3.COOH	0.454	79.86	55.00
P4.COOH	0.200	79.86	52.00

2.4. Preparation of Cu-DENs Using PAMAM-COOH and PAMAM-TRIS Dendrimer Templates

Syntheses of Cu-DENs were adapted from the literature.^{10,26} In general, 10.0 mL of 5.0 μM aqueous dendrimer solutions were prepared. This concentration was kept constant for all dendrimer solutions. The pH of the aqueous dendrimer solution was adjusted to pH ~8. Correct amount of aqueous CuSO₄ (pH ~4.62) (Table 1) was added to each dendrimer solution. The final pH of the solu-

tion was about pH ~5. The solution was then stirred for 30 minutes to allow the complexation of Cu²⁺ ions with the inner tertiary amines of dendrimers. Afterwards, chemical reduction of TRIS and carboxyl terminated Cu²⁺ loaded Cu²⁺/dendrimers with 20 molar excess NaBH₄ in 0.10 M NaOH was resulted in intradendrimer Cu-DENs. Then, pH was adjusted to pH ~8 at where Cu-DENs are most stable²⁶ with a negligible amount of dropwise addition of 0.01–0.10 M HCl and NaOH solutions. The formation of Cu-DENs was monitored with UV-Vis spectroscopy.

3. Results and Discussion

3. 1. Synthesis of PAMAMs

Microwave-assisted synthesis of PAMAM-TRIS dendrimers with E, D and P core from half generation PAMAM-OCH₃ dendrimers, were performed according to our previous studies²⁷ and,²³ respectively. On the other hand, PAMAM-COOH dendrimers were prepared by slight modification of the literature procedure²⁴ and our recent study.²⁵ The results were in good agreement with the literature.^{23,27} General procedures for the preparation and characterization PAMAM-COOH dendrimers were given in the supplementary material. Molecular weights of the synthesized dendrimers were in the ranges of 2584 and 13647 g/mol. The prepared dendrimers were stored in methanolic solution and stored at ± 4 °C. Some selected properties and characterization data of dendrimers were presented in Table 2.

3. 2. Characterization of PAMAMs

Synthesized water-soluble dendrimers could easily be characterized via ¹H NMR and ¹³C NMR. Figure 1

show the sample ¹H NMR spectrum monitoring of the conversion of D3.5 to D4.COOH, and D4.TRIS. All the expected signals are at the correct intensities and places. The resonances from methyl ester at 3.78 ppm are no longer visible and confirm the complete conversion of the ester groups to acids (D4.COOH, middle in Figure 1) while formation of a new singlet at 3.71 ppm, resulting from re-

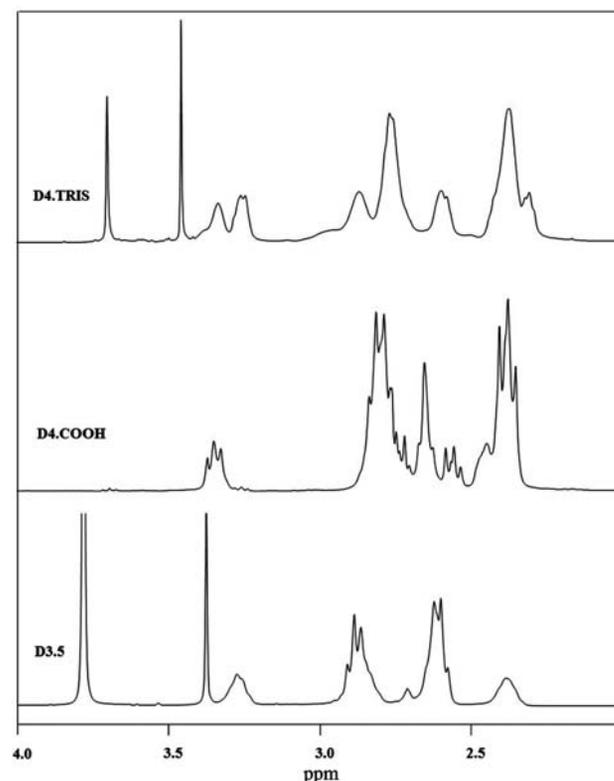


Figure 1. ¹H NMR spectrum monitoring of the conversion of D3.5 (bottom) to D4.COOH (middle) and D4.TRIS (Top).

Table 2. The theoretical characteristic data of synthesized PAMAM dendrimers.

Dendrimer	Mw (g/mol)	Number of tertiary amines (NR ₃)	Number of terminal hydroxyls (OH)	Number of terminal carboxyls (COOH)
<i>TRIS-terminated^a</i>				
E3.TRIS	4234	14	48	–
E4.TRIS	8865	30	96	–
D3.TRIS	5230	18	60	–
D4.TRIS	11109	38	120	–
P3.TRIS	6700	21	72	–
P4.TRIS	13647	45	144	–
<i>Carboxyl-terminated</i>				
E3.COOH	2584	14	–	16
E4.COOH	5564	30	–	32
D3.COOH	3258	18	–	20
D4.COOH	6983	38	–	40
P3.COOH	4226	21	–	24
P4.COOH	8696	45	–	48

^aData for PAMAM-TRIS dendrimers were taken from the study of Ertürk et al.²³

sonances of new methylene protons adjacent to the terminal hydroxyl groups, indicates full conversion to D4.TRIS (top in Figure 1). Moreover, formation of the 181.61, 181.46, 174.86 ppm peaks corresponding to acids and interior amides prove the fully conversion of D3.5 to D4.COOH. Likewise, ^1H NMR, the strong resonances corresponding to the methyl groups of terminal methyl group at 173.13(C=O) and 51.87(COOCH₃) ppm in the ^{13}C NMR are no more available (see supplementary file characterization data). Similar spectral changes were observed during the synthesis of E, D, and P cored water-soluble dendrimers.

In ^{13}C NMR of TRIS-terminated conversions, the formation of 56.67(NHCR₃) and 63.6 (CH₂OH) ppm bands were indicated the fully formation of TRIS-terminated PAMAMs.²³ Therefore, ^1H NMR and ^{13}C NMR spectroscopy evaluations prove a good purity.

In ATR spectroscopy, the disappearance of esteric peak at 1730 cm⁻¹ and formation of two asymmetrical stretching at 1650–1550 cm⁻¹ and a weaker, symmetrical band near 1400 cm⁻¹ also prove the complete conversion of ester terminated D3.5 to D4.COOH (Figure 2). Similar spectral deconvolutions were observed during the synthesis of E, D, and P cored water-soluble dendrimers.

3. 3. Spectroscopic Titrations of TRIS and Carboxyl-Terminated PAMAMs

In order to learn about Cu²⁺ binding capacity of different generation TRIS and carboxyl-terminated E, D and P cored PAMAMs (Table 2), spectroscopic titration studies were performed. Figure 3 shows the sample spectro-

scopic titration spectra of carboxyl-terminated E4.COOH, D4.COOH, and P4.COOH dendrimers. Investigation of the Figure 3 reveals that absorbances of Cu²⁺/DEN complexes increases with the addition of the increasing amount of Cu²⁺.

In their former studies, Crooks et al.^{10,26} declared that the number of tertiary amines are important to determine the exact number of the maximum metal loading capacity of PAMAMs. In our intra-dendrimer complexation studies, we have observed a sudden deep-blue color change with the addition Cu²⁺ ions over PAMAM-TRIS and PAMAM-COOH dendrimer solutions. We have characterized this color change by UV-Vis spectroscopy, and observed a common broad absorption band at $\lambda_{\text{max}} = 680$ nm for E, D, and P cored PAMAM-TRIS and PAMAM-COOH dendrimers (Figure 3). This band (*d-d transition*) indicates the formation of tetradentate (1:4 dendrimer to tertiary amine molar ratio) complexes between the tertiary amine groups of PAMAMs and Cu²⁺ ions.^{23,28}

Figure 4 shows the spectroscopic titration curves of E4.COOH, D4.COOH and P4.COOH dendrimers with Cu²⁺ ions. The experimental end points derived from these curves were presented in Table 3 regarding absorbance at $\lambda_{\text{max}} = 680$ nm versus Cu²⁺/DENs molar ratio plots. Indeed, maximum molar excess of Cu²⁺ ions that can be loaded to dendrimers were calculated from these plots. Results showed that PAMAM-COOH dendrimers used in this study absorb the number of Cu²⁺ ions equivalent the number of tertiary amine numbers, and the structure of these dendrimers are at the desired monodispersity similar to those of PAMAM-TRIS dendrimers, we reported in our recent study.²³

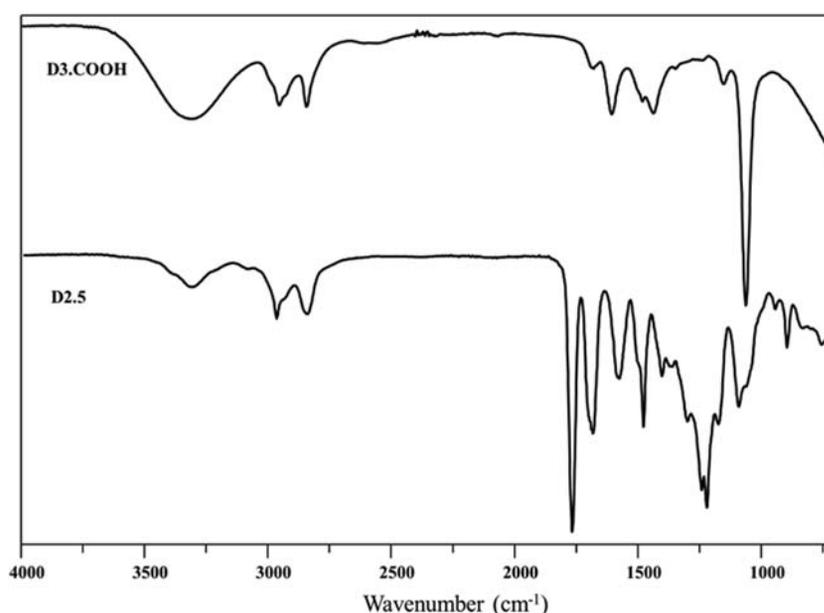


Figure 2. ATR monitoring and time dependency from ester to amide (D2.5 to D3.COOH).

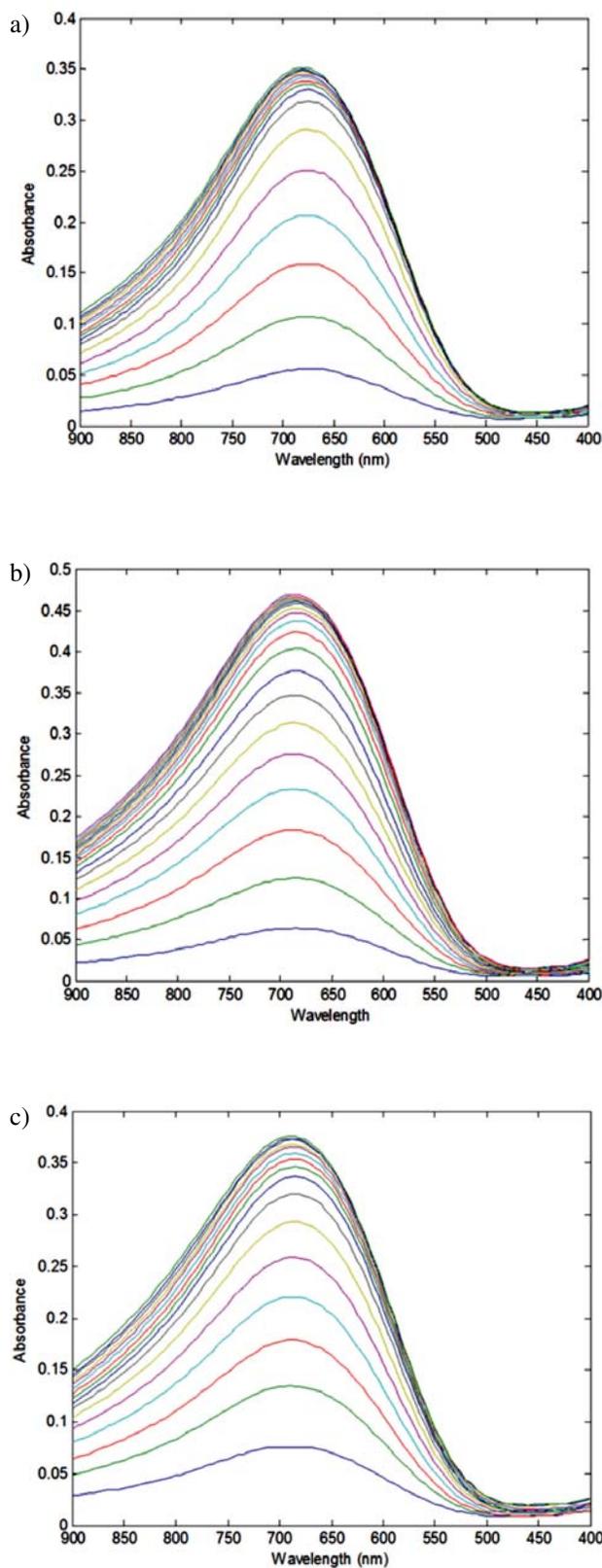


Figure 3. Absorption spectra (at 680 nm) of (a) E4.COOH dendrimer (0.321 mM) solution titrated with Cu^{2+} (80.14 mM), (b) D4.COOH dendrimer (0.268 mM) solution titrated with Cu^{2+} (80.50 mM), (c) P4.COOH dendrimer (0.200 mM) solution titrated with Cu^{2+} (79.86 mM).

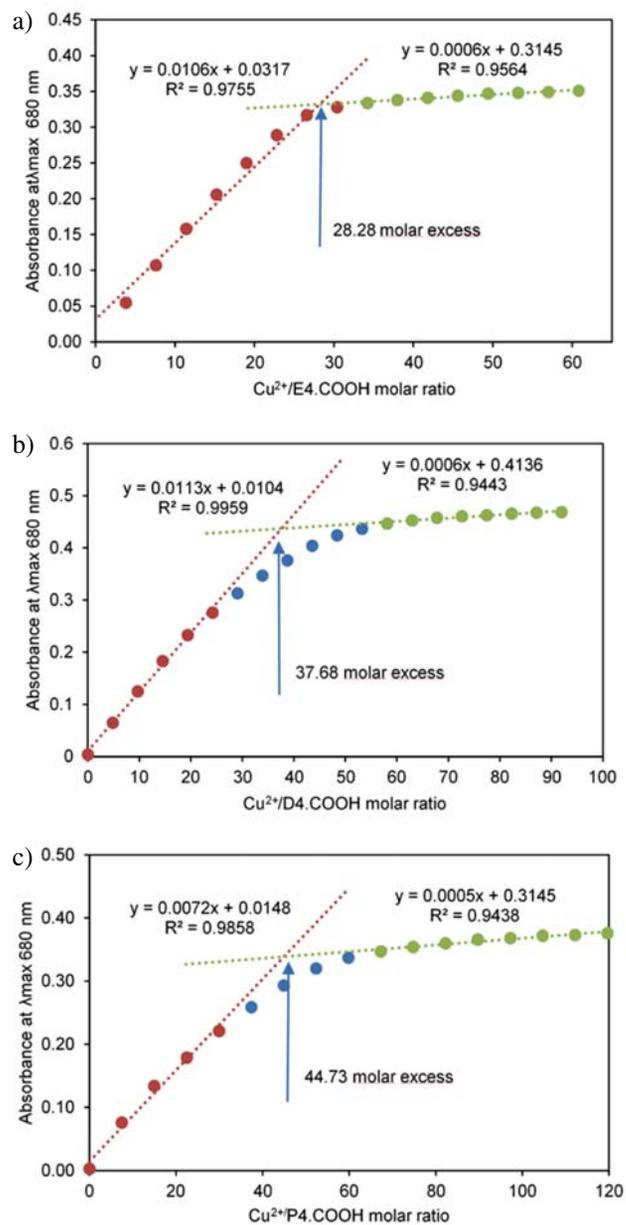


Figure 4. Spectroscopic titration curve of (a) E4.COOH; (b) D4.COOH; (c) P4.COOH with Cu^{2+} ions at $\lambda_{\text{max}} = 680$ nm.

Table 3. Number of amine groups on carboxyl-terminated PAMAMs available for binding with Cu^{2+} ions.

Dendrimer	Calculated end point	Experimentally obtained end point ^a
E3.COOH	14	14.00
E4.COOH	30	28.28
D3.COOH	18	17.80
D4.COOH	38	37.68
P3.COOH	21	20.59
P4.COOH	45	44.73

^aEach end point has been calculated as an average value of three experimental runs and see for the experimental values of PAMAM-TRIS dendrimers.²³

3. 4. Synthesis and UV-Vis Characterization of Cu-DENs

Most common procedure for the synthesis of DENs involves first the determination of the appropriate number of metal ion ratio to be complexed with dendrimer solutions under pH control, and then this is followed by the reduction of metal ions inside the dendrimer by an appropriate reducing agent.¹⁰ Sodium borohydride (NaBH_4) is used as the reducing agent. Appropriate chemical excess of NaBH_4 leads to zerovalent intradendrimer metal nanoparticles. Immediate change in metal ion dendrimer aqueous solution color indicates the reduction. In the case of Cu, LMCT peak at around 300 nm arising from Cu-DENs are replaced with a monotonically increasing absorbance band toward shorter wavelength. This indicates the formation of small nanoparticles. In addition, an absence of plasman peak at around 570–590 nm proves that Cu clusters are smaller than 4 nm.^{29,30} Transition d-d complex band resulting from the coordination of internal amine groups of ethanol amine-terminated PAMAMs were reported at λ_{max} at 605 nm.¹⁰ This band reported in the range of 600–800 nm depending on surface modification with TRIS.²⁸

Syntheses of Cu-DENs were adapted from the literature.^{10,26} After the number of Cu^{2+} ions that can be loaded to E, D and P cored PAMAM-TRIS dendrimers were determined from binding studies reported in our recent study,²³ similar synthetic procedures were applied for the synthesis Cu(II) intra-dendrimer complexes of E, D, and P cored PAMAM-COOH dendrimers.

A straightforward evidence for the reduction of Cu^{2+} ions into dendrimer cavity comes from the immediate change in solution color from blue to golden brown as being parallel to literature^{10,26} (Figure 6). Upon the addition of appropriate molar ratio of calculated CuSO_4 solutions to the aqueous dendrimer solutions, strong bands at around 270–280 nm for carboxyl (Figure 7) and 280–300 nm for TRIS-terminated (Figure 8) PAMAMs were occurred, respectively. These bands are assigned to LMCT bands.^{31–33} In addition, *d-d* copper transition band at around 680 nm for all Cu^{2+} /DEN complex solutions were observed (Figure 7, 8). This band could not be observable for low concentrations. After the addition of excess reducing agent NaBH_4 , LMCT peak at around 300 nm and *d-d* transition band at 680 nm in all Cu^{2+} /DENs were immediately disappeared and replaced with a nearly exponen-

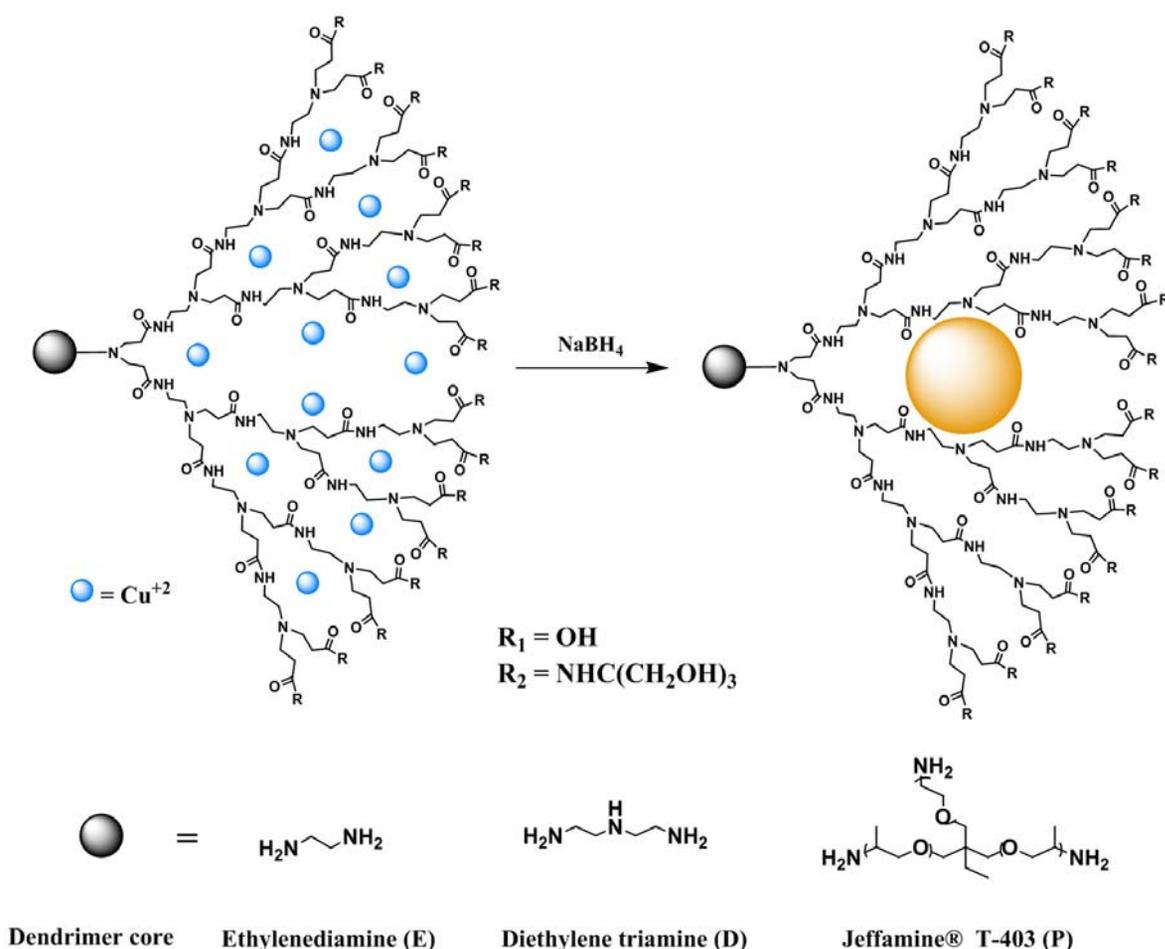


Figure 5. Synthetic route for E, D and P core PAMAM-COOH and PAMAM-TRIS Cu-DENs.

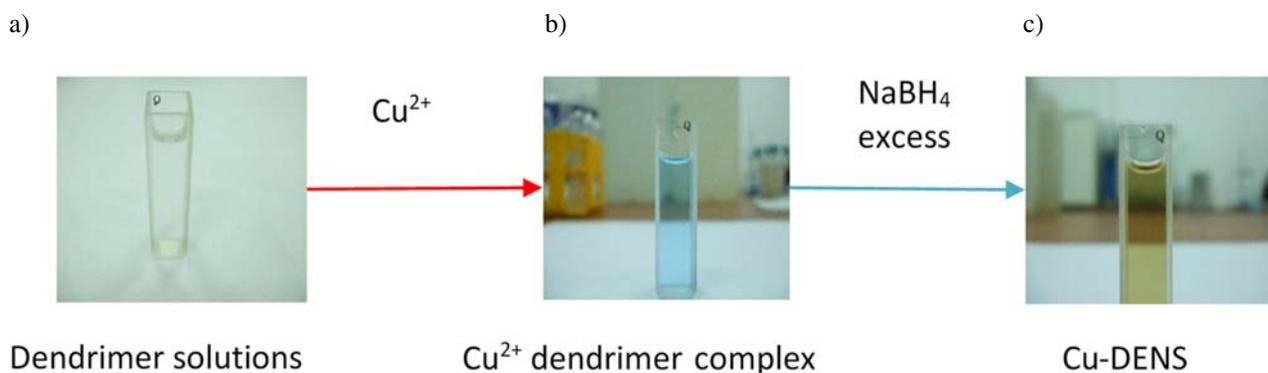


Figure 6. Change in color during the synthesis of Cu-DENS. (a) aqueous dendrimer solutions, (b) Cu²⁺ dendrimer complex solution, (c) Cu-DENS solution.

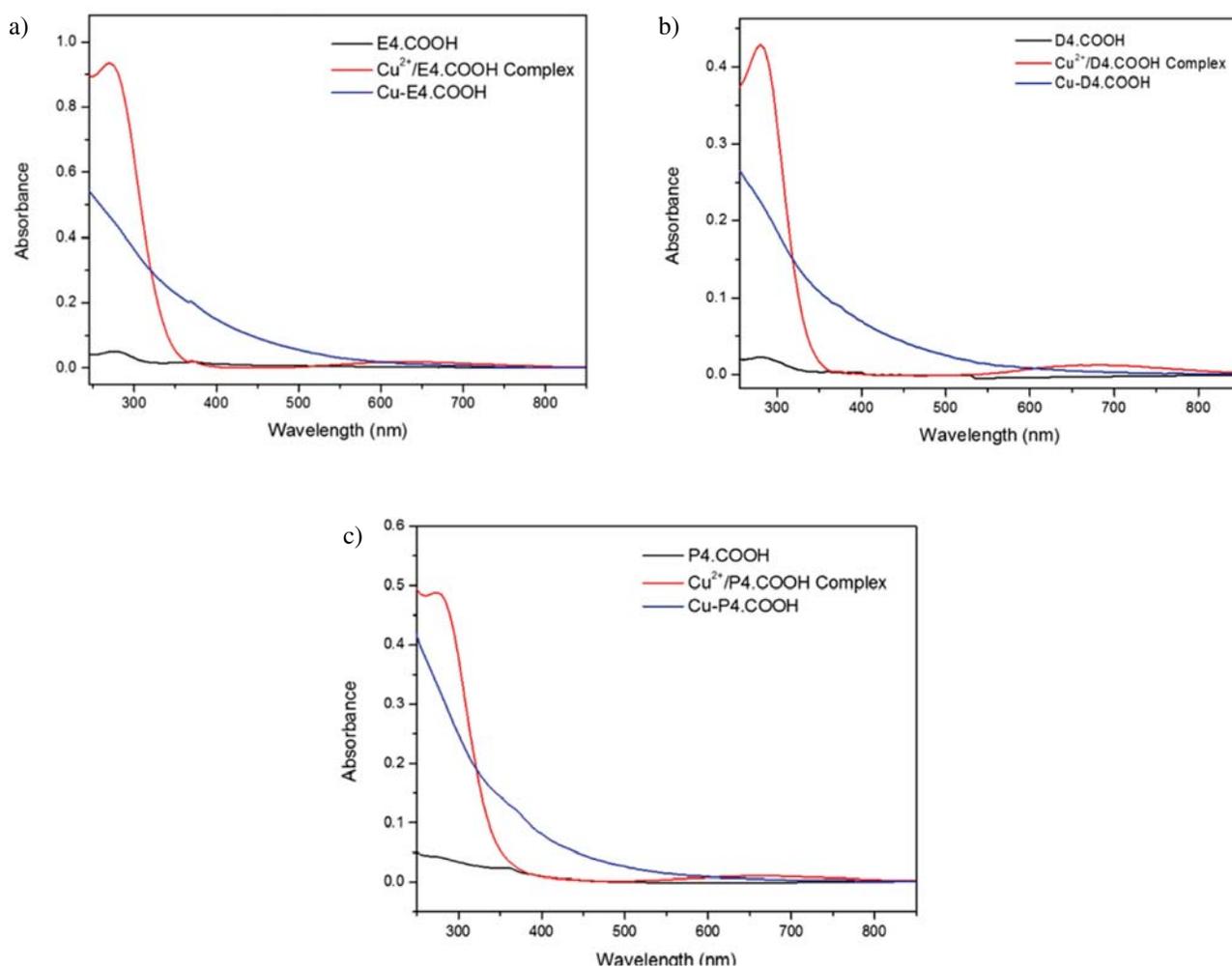


Figure 7. UV-Vis absorption spectra of the formation of (a) Cu-E4.COOH; (b) Cu-D4.COOH, and (c) Cu-P4.COOH.

tial monotonically increasing spectrum towards to shorter wavelengths (Figure 7, 8). Moreover, the size of Cu clusters can be understood from the absence of a Mie plasman peak at around 570 nm in UV-Vis spectra (Figure 8).

The absence of this band indicates that Cu clusters within the dendrimer cavity are smaller than 5 nm.¹⁰ Results of the UV characterizations are in good agreement with the previously reported Cu-DENS.^{10,26}

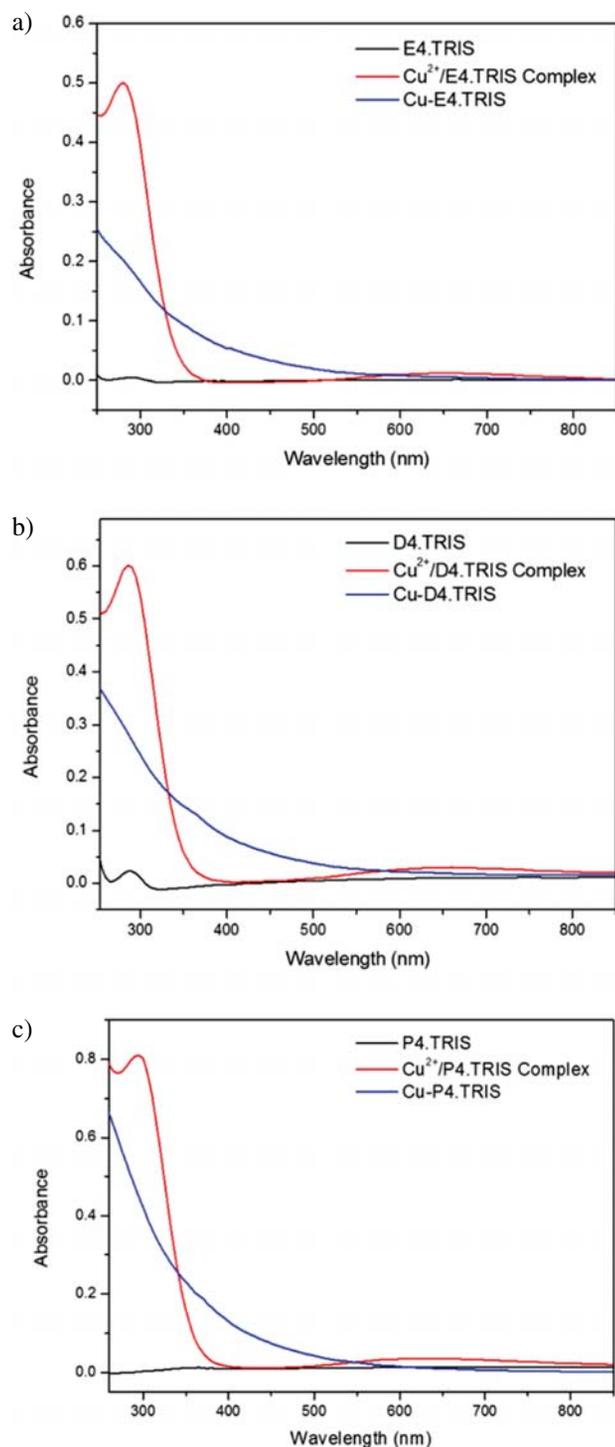


Figure 8. UV-Vis absorption spectra of the formation of (a) Cu-E4.TRIS; (b) Cu-D4.TRIS, and (c) Cu-P4.TRIS.

4. Conclusions

In this study, TRIS and Carboxyl surface modified E, D and P cored G3-G4 PAMAM dendrimers were synthesized as macromolecular templates, and used in the synthesis of Cu-DENDs. In particular, G3 and G4, D and P

cored PAMAM-COOH dendrimer templates, and Cu-PAMAM-TRIS and Cu-PAMAM-COOH nanocomposites were prepared and characterized for the first time.

Investigations of the maximum metal loading capacity of PAMAM-TRIS and PAMAM-COOH dendrimers were determined by the spectroscopic titrations with Cu^{2+} ions and optimum molar ratios were calculated. The most sparingly evidence of the successfully synthesis of Cu-DENDs came from the color change from blue to golden brown. UV-Vis evidence of this color change was the disappearance of d-d complexation band at ~ 680 nm and formation of monotonically increasing exponential absorption band towards to low wavelengths. The size of Cu clusters can be understood from the absence of a Mie plasmon peak at around 570 nm in UV-Vis spectra. The absence of this band indicates that Cu clusters are smaller than 5 nm.¹⁰ All of these observations indicated the successful synthesis of Cu-DENDs. Catalytic properties of these novel series of Cu-DENDs might be interesting for catalytic evaluation in organic synthesis, and in a wide range of future studies.

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Povzetek

V prispevku je predstavljena sinteza in UV-Vis karakterizacija Cu nanokompozitov iz etilendiamina (EDA) (E), dietiltriamina (DETA) (D) in Jeffamine® T-403 (P) PAMAM (poli(amidoamin)) dendrimerov s TRIS (tris(hidroksimetil)aminometan) in karboksilnimi funkcionalnimi skupinami na površini. Cu-PAMAM dendrimeri z enkapsuliranimi nanodelci (Cu-DENs) smo karakterizirali z UV-Vis spektroskopijo. Kot dokaz za uspešno sintezo Cu-DENs nanokompozitov lahko navedemo izginotje vrhov pri 680 nm (d-d prenos) in 270–300 nm (prenos naboja med ligandom in kovino (LMCT)) in formiranje eksponentnega pasu. Dodaten dokaz uspešne sinteze je tudi takojšnja sprememba barve raztopine dendrimer-kovina iz modre v zlato rjavo, ki je posledica redukcije Cu²⁺ ionov. Tako pripravljene Cu-DENs nanokompozite bi bilo mogoče uporabiti kot novo alternativo obstoječim nanomaterialom, ki se uporabljajo v številnih aplikacijah: biološki in kemični senzorji, kataliza, hidrogenacija, oksidacija, polprevodniki, plemenite kovine, magnetni dendrimeri nanokompoziti, okoljska problematika in mnoge druge.