

Supporting Information

Preparation of Long Supramolecular Carbon Nanotubes

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Shortening of MWCNTs

MWCNTs were purified and shortened according to reported procedures in literature [1]. Briefly, MWCNTs (2 g) were added to 40 ml of sulfuric/nitric acid mixture (3:1) in a reaction flask and refluxed for 24 h at 120 °C. The mixture was cooled and diluted by distilled water and then it was filtrated. The product (SCNTs) was washed by distilled water and dried at 60 °C for 3 h by vacuum oven.

Preparation of ABA type linear-dendritic copolymers containing PEG as B block and PAMAM with periphery amino functional groups as A blocks (LDNH₂)

For preparation of linear-dendritic copolymer, first polyethyleneglycol was functionalized by triazine. A solution of polyethylene glycol (4 g) and sodium hydroxide (0.32 g) in 10 mL of water was added to a solution of cyanuric chloride (3.69 g) in 50 mL dichloromethane at 0 °C. Mixture was stirred at 0 °C for 1 h, and then it was stirred at room temperature for 1 h and finally was refluxed for additional 6 h. Then mixture was cooled and filtered off and solvent was evaporated. The crude product was dissolved in 10 mL dichloromethane and was precipitated in diethyl ether at 0 °C several times. The purified product was obtained as a white solid. Therefore it was reacted with ethylenediamine and was used as core for synthesizing PAMAM blocks according to reported procedure in literature [2] (scheme 1).

Preparation of ABA type linear-dendritic copolymers containing PEG as B block and PAMAM with aromatic functional groups as A blocks (LDAr)

In order to synthesis LDAr, ligand (2- chloro 4,6- di phenoxy- 1,3,5- triazine) (compound A) was synthesized by using reaction between cyanuric chloride and phenol in the presence of sodium hydroxide according to reported procedures in literature [3].

Then a solution of LDNH₂ (2 g) in 5 mL of dry methanol was added to a solution of compound A (1.82 g) in 10 mL of dry dichloromethane, dropwise at 0 °C. Mixture was stirred at room temperature for 1 h and then was refluxed for additional 12 h. Mixture was cooled

and filtered off and product was dissolved in 5 mL methanol and then it was precipitated in diethyl ether. Purified compound was obtained as a dark brown viscose solid. (scheme 2).

Preparation of palladium complex of LDAr (LDAr-Pd)

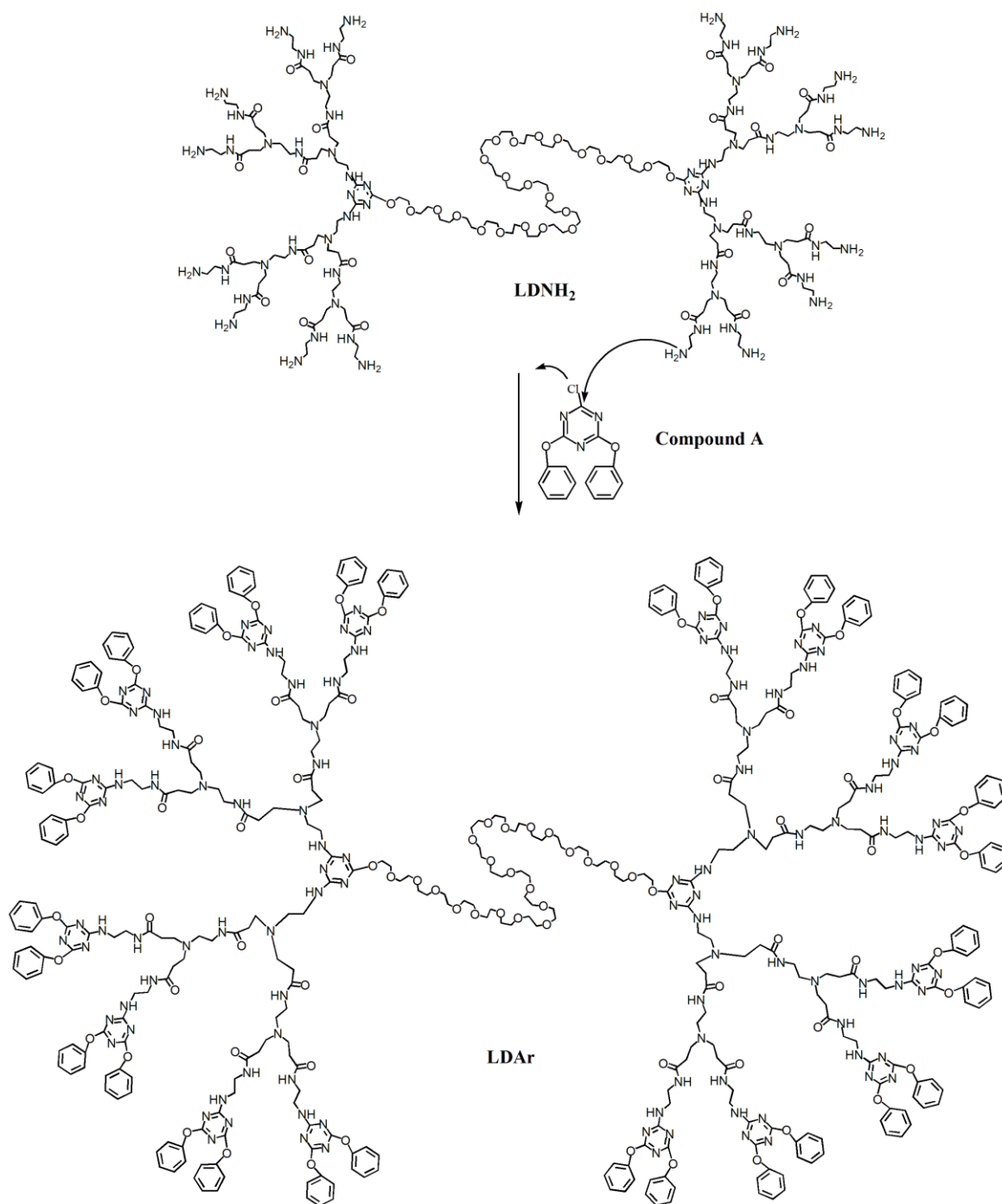
For preparation of these linear-dendritic copolymers, first was synthesized of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ complex. Therefore 0.1g (0.56 mmol) of PdCl_2 with 35ml acetonitril was refluxed for 1 h was cooled and solution was obtained as a orange solution. Then insitu added to 1.2g (1.1mmol) LDAr. Mixture was stirred at room temperature for 24 h then was filtered off. The crude precipitation was washed in acetonitril for several times. Purified compound was obtained as a yellow solid. (scheme 3).

Preparation of Pd bis [(2- chloro 4,6 di naphtoxy- 1,3,5- triazine)]₂Cl₂ (Ligand X).

First ligand 2-chloro-4,6-di naphtoxy-1,3,5- triazine (compound B) was synthesized by using reported procedure in literature [3]. $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ was added to 0.36 g (1.1 mmol) of compound B and mixture was stirred at room temperature for 24 h and then it was filtered off. Crude product was washed by acetonitril several times and final product was obtained as a light brown solid.

Preparation of LDCNTs

For preparation of LDCNTs ,0.1 g of opened CNT was added to an aqueous solution of LDAr (0.1 g in 10 ml water) or LDAr-Pd and it was sonicated for 5 minutes at room temperature. Then solution was stirred at room temperature over night. The solution was filtered and centrifuged to precipitate the final product.



Scheme S11. ABA type linear-dendritic copolymers containing periphery a) amino and b) aromatic groups.

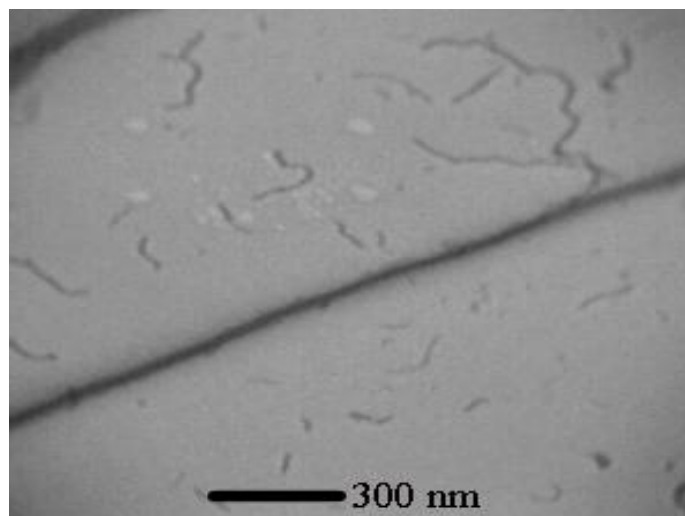


Figure SI1. TEM image of pristine MWCNTs after refluxing in acid and purification process (SCNTs).

SEM images show a network-like assembly for SCNTs interacted with the LDNH₂. Diameter of SCNTs shielded by linear-dendritic copolymers is around 50 nm. Since diameter of pristine SCNTs is 25-30 nm, diameter of assembled linear-dendritic copolymers onto the surface of carbon nanotubes is 25 nm.

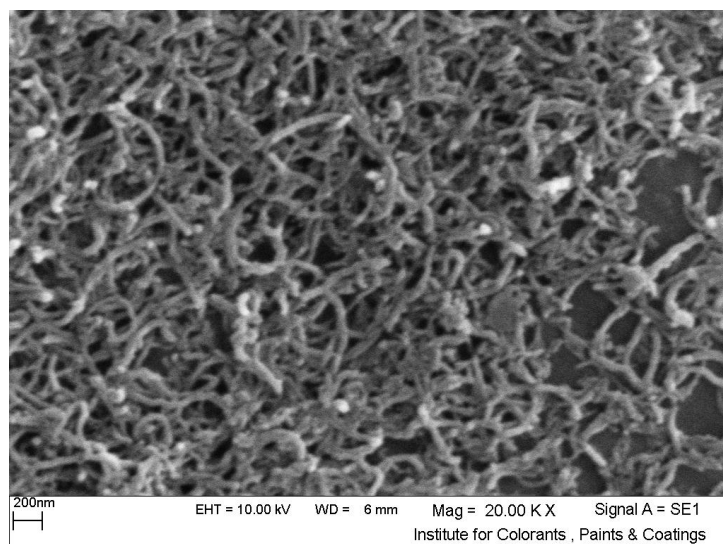
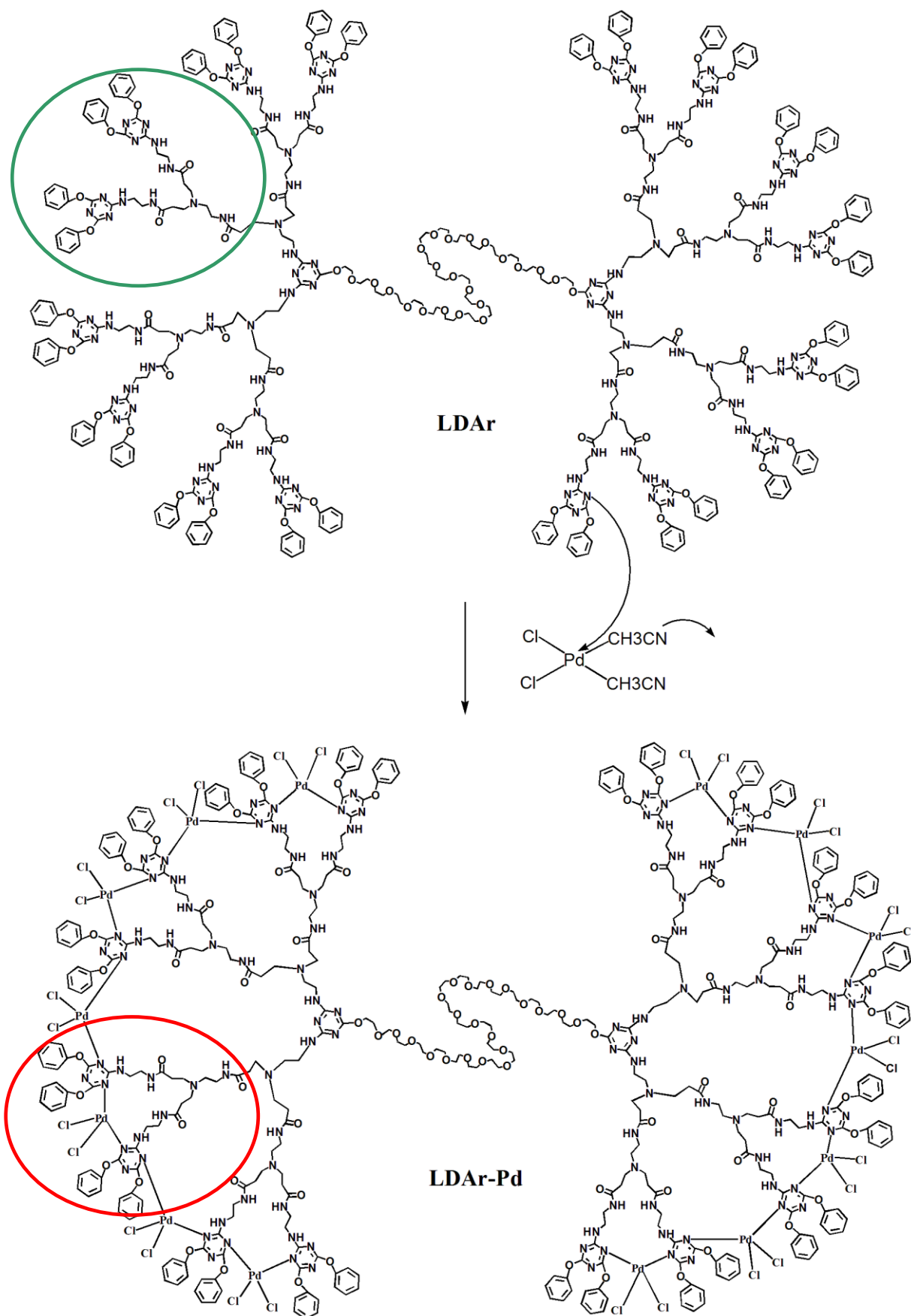


Figure SI2. SEM images of SCNTs interacted with LDNH₂ noncovalently.



Scheme SI2. Reaction between hetero atoms of dendritic blocks of LDAr and palladium chloride to produce a complex with planar and rigid aromatic domains.

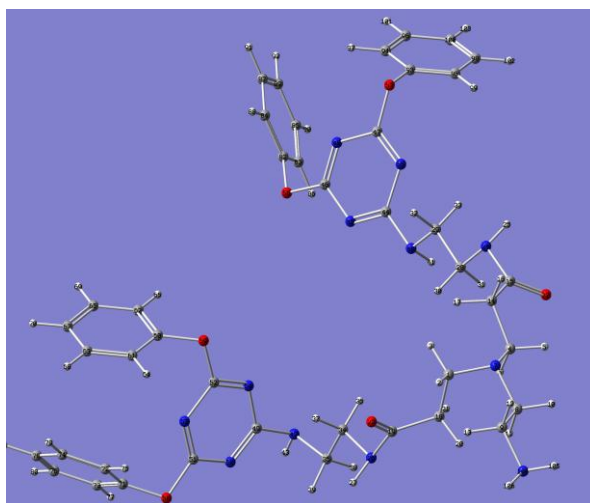
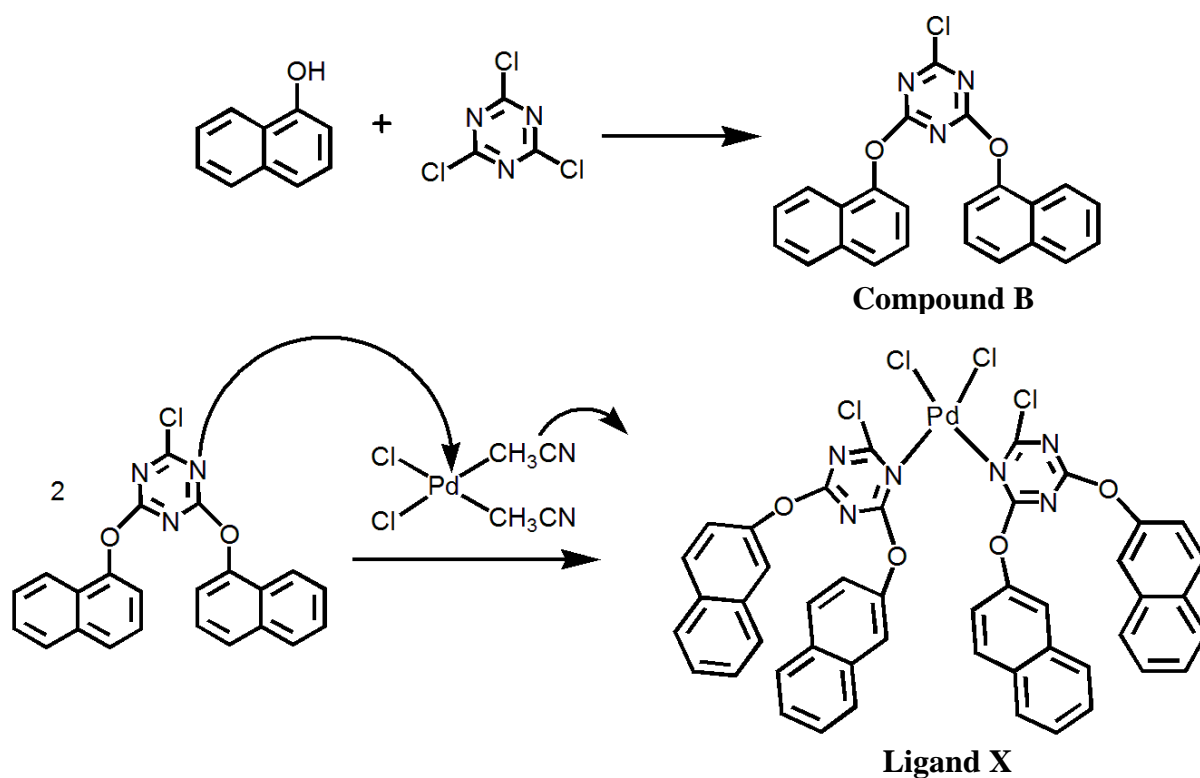


Figure SI3. Three dimensional structure for highlighted part of LDAr in scheme SI2 (green circle).



Scheme 3. Synthesis of palladium complex of 2-chloro 4,6-di Naphthoxy-1,3,5-triazine.

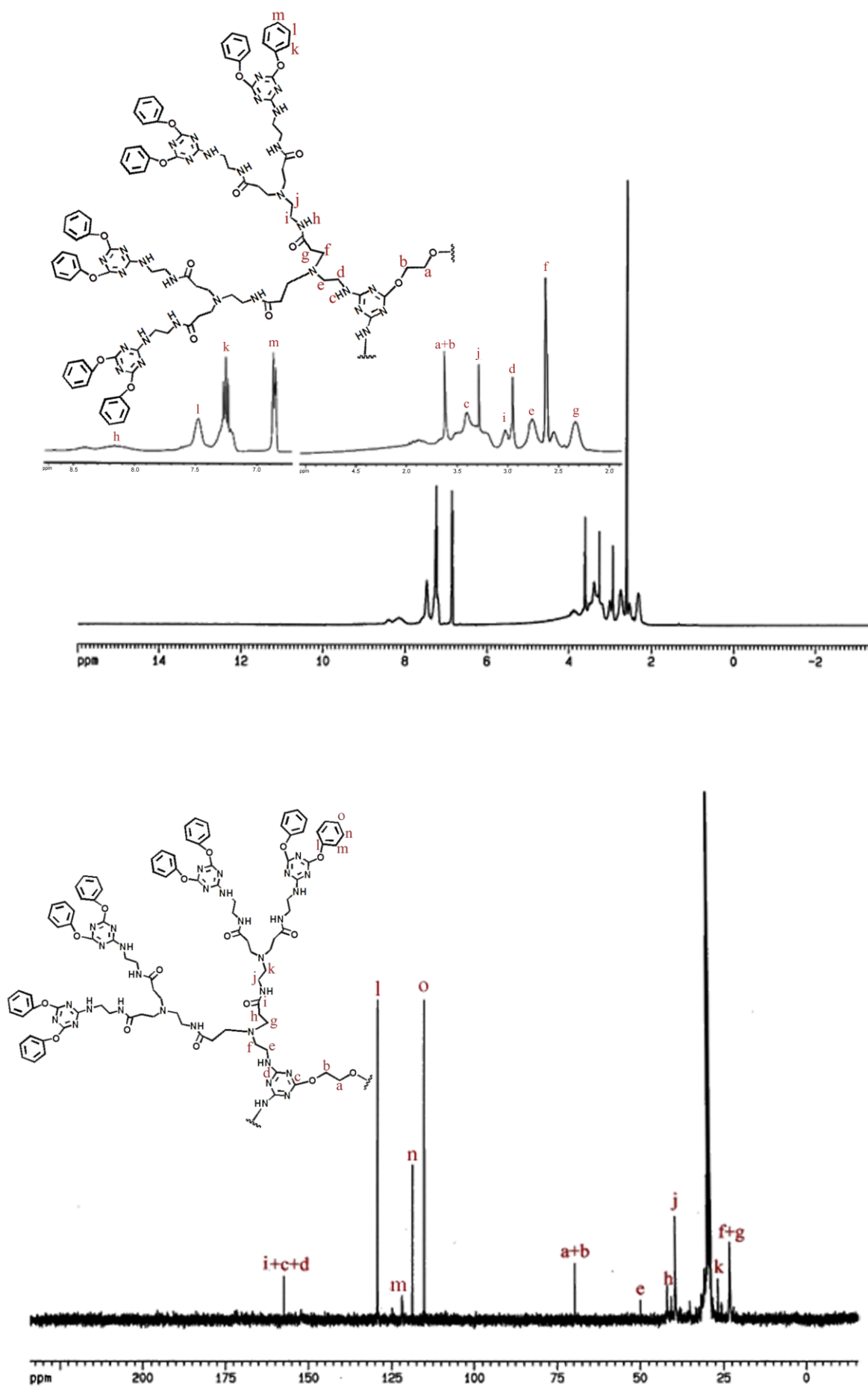


Figure SI4. ^1H , ^{13}C NMR spectra of LDAr.

The integral ratio of aliphatic protons of PEG to the aromatic part of the LDAr is 1.8 (in comparison to 1.7 as a theoretical calculation). This is an evidence, which shows growth of linear-dendritic copolymer has been accomplished completely (Figure SI6).

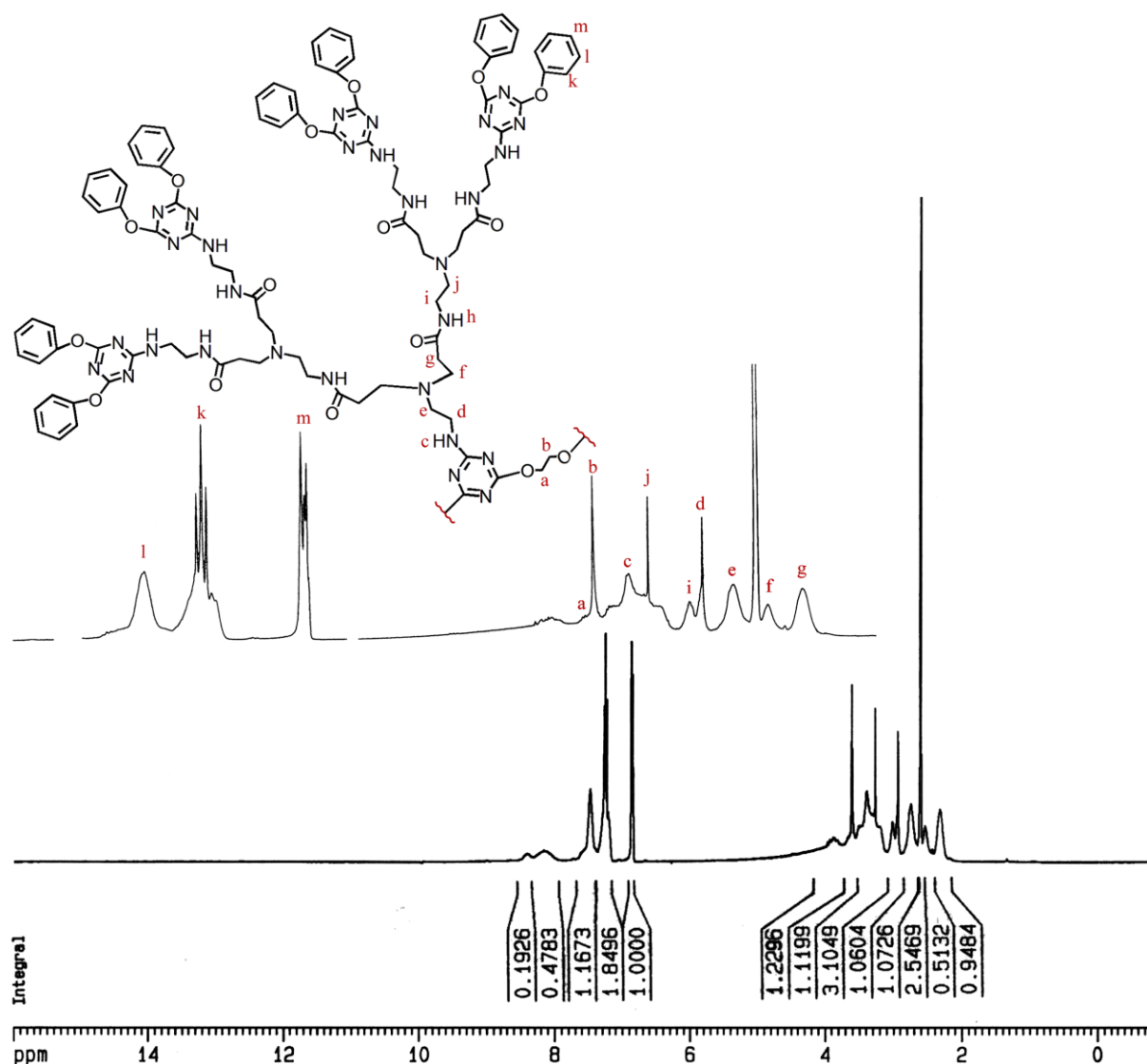


Figure SI5. The integral ratio of protons of polyethylene glycol to aromatic end groups is in agree with the calculated ratio.

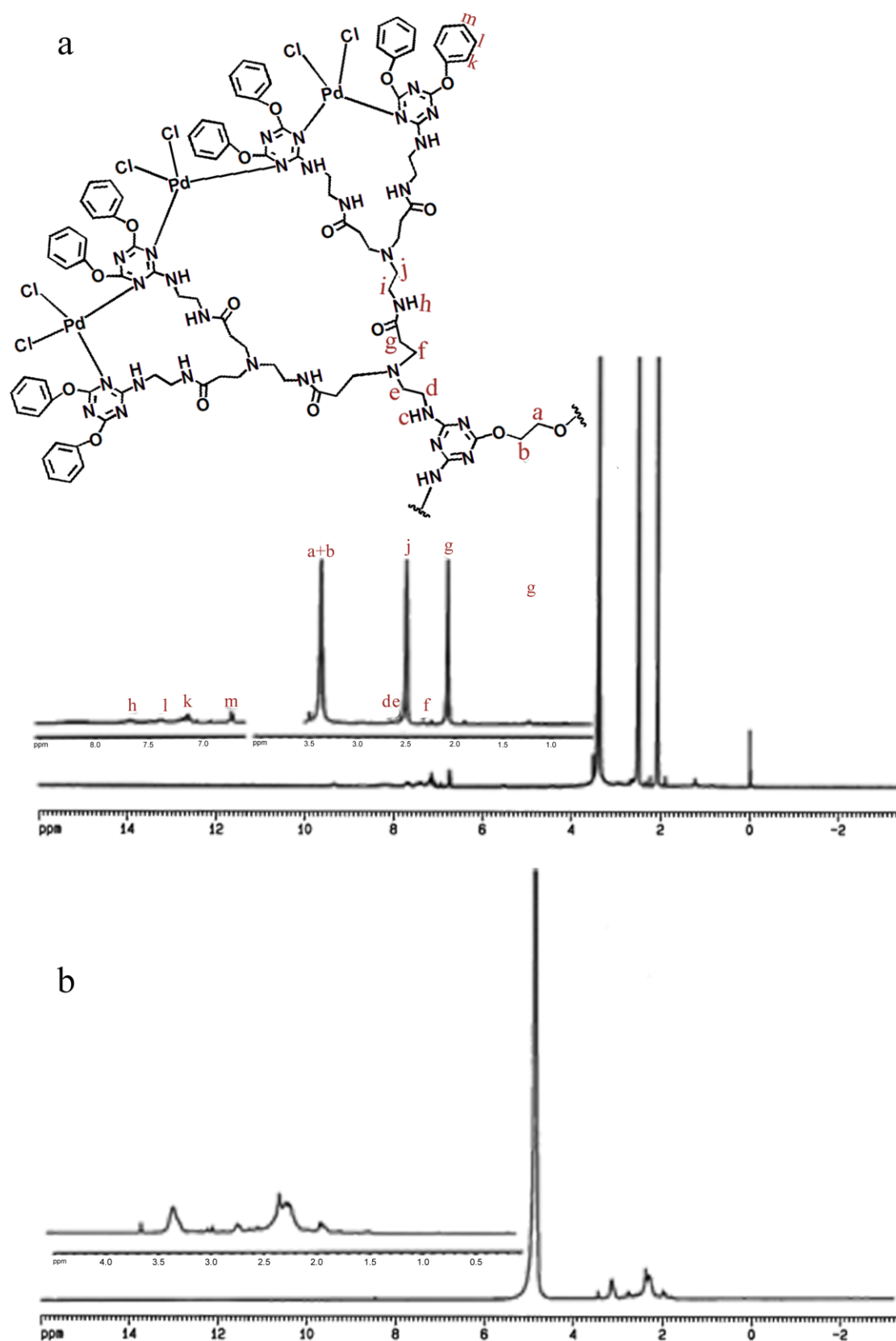


Figure SI6. ^1H NMR spectra of a) LDCNT b) LDCNT-Pd/CNT (LDCNTs).

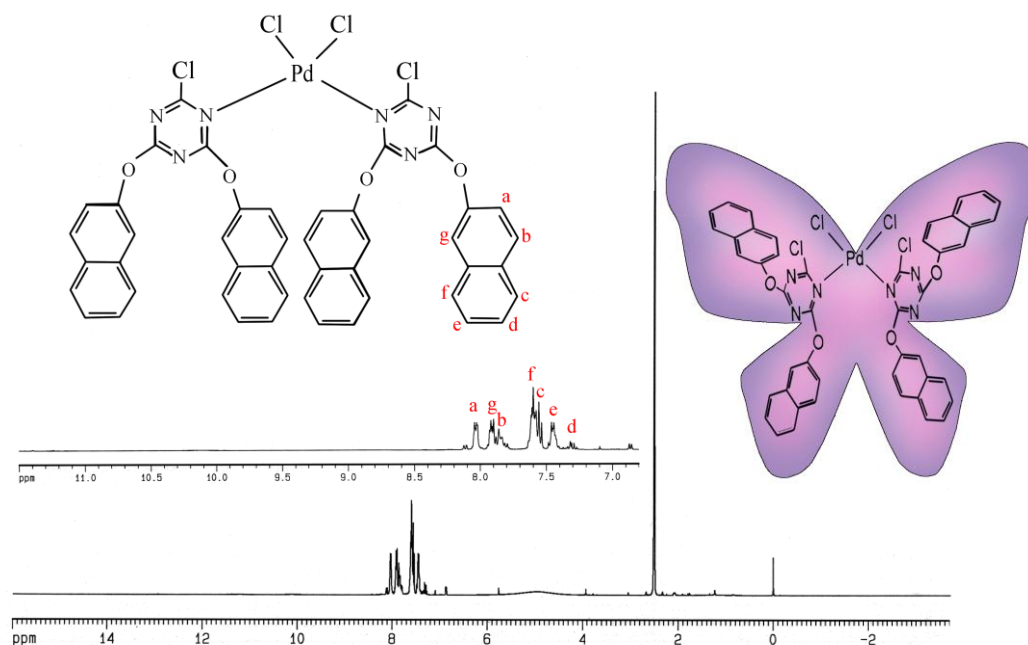


Figure SI7. ^1H NMR spectra of Ligand X.

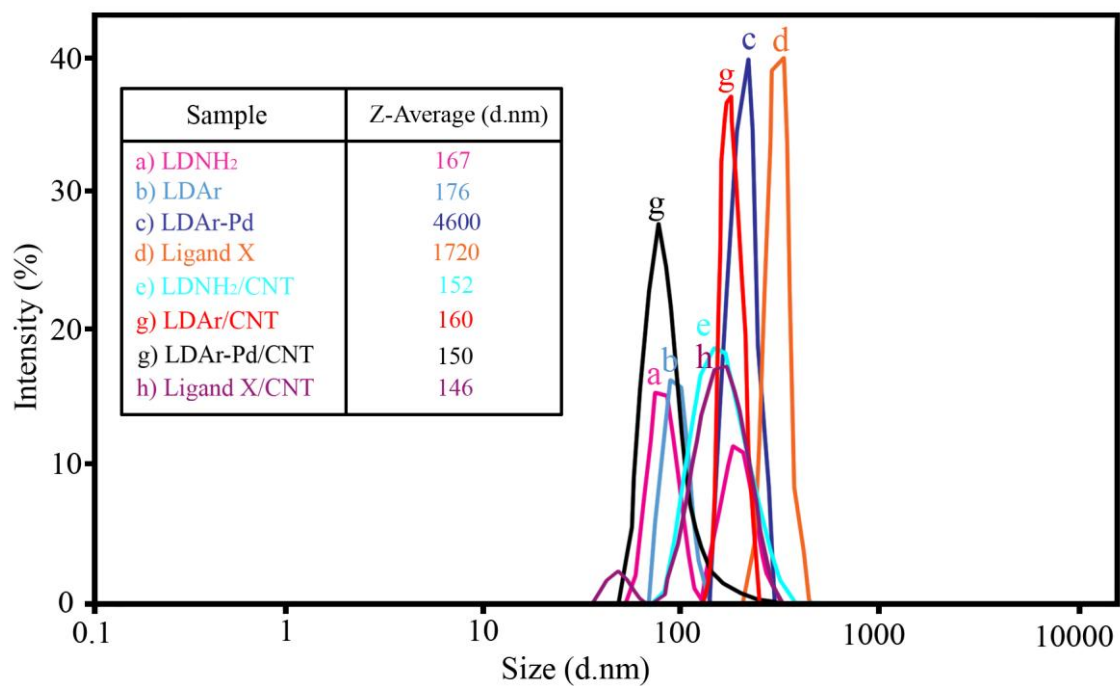


Figure SI8. DLS diagrams of ligands and linear-dendritic copolymers used in this research work.

Sample	Zeta Potential(mV)
LDAr-Pd	-0.941
Ligand X	-0.557
LDAr-Pd/CNT	-6.21
Ligand X/CNT	-7.01

Figure SI9. Zeta potential of LDAr-Pd, ligand X, LDAr-Pd/CNT, Ligand X/CNT.

References:

- [1] Adeli, M.; Bahari, A.; Hekmatara, H. *NANO: Brief Reports and Reviews*. **2008**, 3, 37-44.
- [2] Kim, T.; See, H.; Ch. J.; Jang, H-S.; et al. *Biomacromolecules*. **2004**, 5, 2487-2492.
- [3] Namazi, H.; Adeli, M. *polymer*. **2005**, 46, 10788–10799.