# Supporting Information

## Hybrid CdSe Nanoparticles in Carbazole Dendron Boxes: Electropolymerization and Energy Transfer Mechanism Shift[**]

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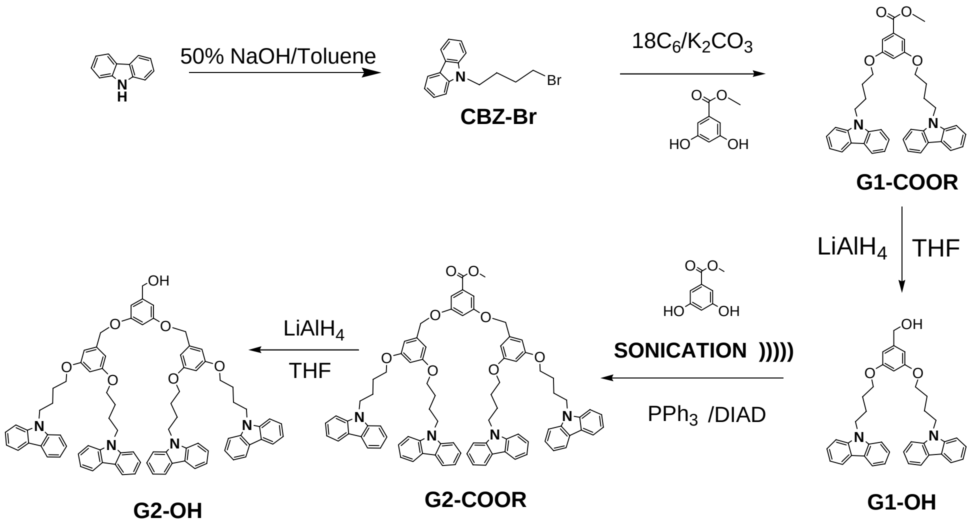
**Structural Design and Synthesis of Dendron Precursors.** The synthetic route for the generation one (G1) and two (G2) carbazole terminated dendrons are shown in Scheme 1. The synthesis was started using carbazole and 1,4-dibromobutane to produce 9-(4-bromobutyl)-9H-carbazole (CBZ-Br) in a modified procedure used previously by Shen et al (*J. Macromol. Chem. Phys.* **1998**),

Similarly, we have also modified the synthesis of (G1) dendron ester (G1-COOR) reported earlier by Bo et.al (*Macromolecules* **2004**, *37*, 6395). in a synthetically useful yield of 70%. The purification of G1-COOR does not require any column chromatography. It can be easily purified by recrystallization using ethyl acetate.



**S. I. Scheme 1.** Synthesis route to G-OH

The G1-COOR was then reduced using lithium aluminium hydride (LAH) to produce the G1 dendron alcohol (G1-OH) in 90 % yield. The G1-OH dendron was then dissolved in minimal THF along with $PPh_3$, methyl 3,5-dihydroxybenzoate and DIAD was slowly added under sonication conditions to produce G2-COOR in 84 % yield within 75 min. (Caution: Water in the sonicator turns very hot if used for prolonged periods of time) The amount of THF is very important. It should only be used to barely dissolve the starting alcohol. Excess THF, temperature fluctuations in the sonication bath, and scaling above 6g caused significant lowering in the yields. The G2-COOR was further reduced to G2-OH

**Synthesis of 9-(4-bromobutyl)-9H-carbazole [CBZ-Br].** (Scheme 1) The synthesis of 9-(4-bromobutyl)-9H-carbazole was accomplished by a modified method as reported by Shen *et al.* A mixture of 10.32 g (61.72 mmol) carbazole in toluene (100 mL) containing 1,4-dibromobutane 118.2 g (547.4 mmol) and tetrabutylammonium bromide (TBAB) 2g, was stirred at 45 $^{o}$C for 3h and then left overnight. After the aqueous layer was removed and washed three times with water and brine, the organic layer was dried over $Na_2SO_4$. The organic solvent was evaporated and unreacted 1,4-dibromobutane was removed by vacuum distillation. The residue was recrystallized from ethanol to give 16.7 g (89.5 %) of the product. The characterization was found to be consistent with the literature.

**Synthesis of methyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzoate [G1-COOR].** (Scheme 1) In a literature modified process as reported by Bo *et al.*,[11d] a mixture of 15.22 g (50.37 mmol) of CBZ-Br, 21.0 g of $K_2CO_3$, 3.94 g (23.4 mmol) of methyl 3,5-dihydroxybenzoate, 500 mL of acetone, and 45 mg of 18-crown-6 was stirred and reflux under nitrogen atmosphere for 72h. Acetone was evaporated under vacuum, and the residue was partitioned between water (400 mL) and $CH_2Cl_2$ (500 mL). The organic layer was separated and the aqueous layer was extracted three times with $CH_2Cl_2$ (250 mL). Finally, the combined organic layer was dried over $Na_2SO_4$. After removal of the solvent, the residue was recrystallized from ethyl acetate to give a white solid product in 70 % yield. The characterization data was found to be consistent with the literature.

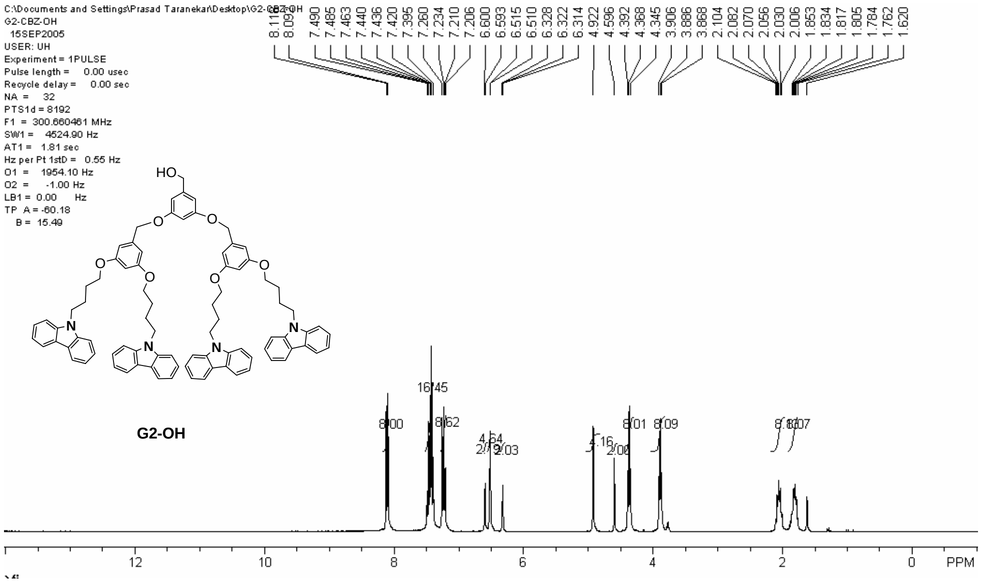
**General method for Lithium Aluminum hydride (LAH) reduction of aromatic esters to benzylic alcohols (Method [A]).** The aromatic ester was added drop wise to a suspension of LAH in THF cooled to 0 $^{o}$C with an ice bath. The suspension was then allowed to warm to room temperature and stirred until the reaction was complete as indicated by TLC. The reaction was quenched by adding water, and the THF removed under reduced pressure in a rotary evaporator. The resulting layer was brought to a neutral pH with the addition of 2 N HCl solution and extracted with $CH_2Cl_2$. The organic layer were combined, washed with water, dried over sodium sulfate, filtered and concentrated under reduced pressure. The product was purified by silica gel flash column chromatography using a 20 / 4 / 1 : $CH_2Cl_2$ / hexane / ethyl-acetate eluent.

**General method for etherification reactions (Method [B]).** The Mitsunobu etherification and esterification method was performed using sonication. The mixture of alcohol, phenol (or aromatic carboxylic acid) and triphenylphosphine ($PPh_3$) in *minimal* THF was cooled to 5 $^{o}$C with an ice bath and sonicated for 5 min. Under sonication, a solution of diisopropyl-azodicarboxylate (DIAD) was added drop wise under nitrogen. The water temperature was allowed to warm to room temperature and precautions were taken to maintain the temperature. (Caution: Water in the sonicator turns very hot, if sonicated for a long time) Sonication was performed until the reaction was completed as indicated by TLC. The product was purified using 4/1 $CH_2Cl_2$/hexane as an eluent by silica gel column chromatography. *Note:* In the case of G4-dendrimer (G4-D), sonication did not yield the desired product and therefore a reflux condition was used to get the final product. The product was purified using neutral alumina and 6/1 ratio of $CH_2Cl_2$/hexane.

**Synthesis of (3,5-bis(4-(9H-carbazol-9-yl)butoxy)phenyl)methanol [G1-OH].** (Scheme 1) Following the general synthesis method A as described above, the reaction of 1.0g (23.3mmol) of LAH in 300ml of THF with a solution of 9.5g (15.5mmol) of G1-COOR in 400ml THF afforded white solid in 90% yield. $^{1}$H NMR ($CDCl_3$): δ (ppm) 8.10 (d, 4H, *J* = 7.5 Hz), 7.53-7.42 (m, 8H), 7.25-7.22 (m, 4H), 6.45 (d, 2H, *J* = 2.1 Hz), 6.28 (t, 1H, *J* = 2.1 Hz), 4.59 (s, 2H), 4.39 (t, 4H, *J* = 6.9 Hz), 3.91 (t, 4H, *J* = 6.2 Hz), 2.02-2.12 (m, 4H), 1.87-1.78 (m, 4H). $^{13}$C NMR ($CDCl_3$): δ (ppm) 160.26, 144.33, 140.38, 128.4, 125.7, 122.89, 120.44, 118.89, 108.69, 105.19, 100.57, 67.58, 65.34, 42.75, 27.02, 25.91. Anal. Calcd.: C, 80.38; H, 6.57; N, 4.81. Found: C, 80.12; H, 6.44; N, 4.95.

**Synthesis of methyl 3,5-bis(3’,5’-bis(4-(9H-carbazol-9-yl)butoxy)benzyloxy) benzoate [G2-COOR].** (Scheme 1) Following the general synthesis method B as described above, a pre-cooled solution of 0.86g (5.15mmol) of methyl 3,5-dihydroxybenzoate, 6g (10.3mmol) of G1-OH, and 2.7g (10.3mmol) of $PPh_3$ in THF under sonication was treated with a solution of DIAD 2.08g (10.3mmol) in 3ml THF under nitrogen. The solution was sonicated for 1.5h to afford a white solid product in 84% yield after purification. $^1$H NMR ($CDCl_3$): δ (ppm) 8.09 (d, 8H, *J* = 7.5 Hz), 7.48-7.39 (m, 16H), 7.27-7.21 (m, 8H), 7.19(d, 2H, *J* = 2.1 Hz), 6.76 (t, 1H, *J* = 2.1 Hz), 6.50 (d, 4H, *J* = 2.1 Hz), 6.31 (t, 2H, *J* = 2.1 Hz), 4.94 (s, 4H), 4.37 (t, 8H, *J* = 7.5 Hz), 3.91-3.87 (m, 11H), 2.08-2.03 (m, 8H), 1.85-1.78 (m, 8H). $^{13}$C NMR ($CDCl_3$): δ (ppm) 166.70, 160.22, 159.87, 140.32, 138.72, 132.02, 125.63, 122.84, 122.47, 120.38, 118.82, 110.03, 108.63, 108.33, 107.34, 105.82, 100.87, 70.11,69.98, 67.98, 67.53, 52.27, 42.67, 26.93, 25.84, 25.62. Anal. Calcd.: C, 79.60; H, 6.21; N, 4.32. Found: C, 79.53; H, 6.12; N, 4.60.

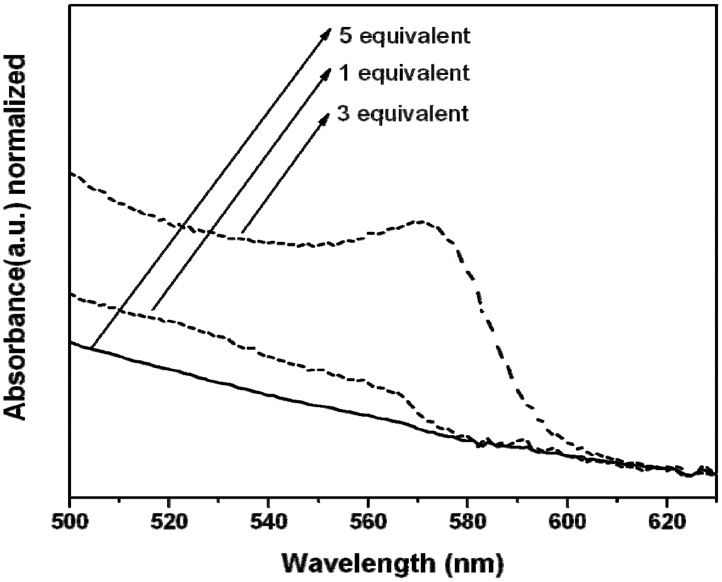
**Synthesis of (3,5-bis(3’,5’-bis(4-(9H-carbazol-9-yl)butoxy)benzyloxy)phenyl) methanol [G2-OH].** (Scheme 1) Following the general synthesis method A as described above, the reaction of 0.2g (5.5mmol) of LAH in 100ml of THF with a solution of 4.2g (3.2mmol) of G2-COOR in 25ml THF afforded a white solid product in 90% yield. $^1$H NMR ($CDCl_3$): δ (ppm) 8.15 (d, 8H, *J* = 7.5 Hz), 7.53-7.42 (m, 16H), 7.31-7.25 (m, 8H), 6.59 (d, 2H, *J* = 2.1 Hz), 6.50-6.52 (m, 5H), 6.32 (t, 2H, *J* = 2.1 Hz), 4.95 (s, 4H), 4.59 (s, 2H), 4.36 (t, 8H, *J* = 6.9 Hz), 3.88 (t, 8H, *J* = 5.7 Hz), 2.11-2.00 (m, 8H), 1.87-1.76 (m, 8H). $^{13}$C NMR ($CDCl_3$): δ (ppm) 160.25, 160.09, 143.39, 140.37, 139.2, 125.69, 122.88, 120.4, 118.86, 108.66, 105.84, 105.72, 101.33, 100.81, 69.98, 67.57, 65.3, 42.72, 26.96, 25.88. Anal. Calcd.: C, 80.41; H, 6.35; N, 4.41. Found: C, 80.48; H, 6.30; N, 4.60.



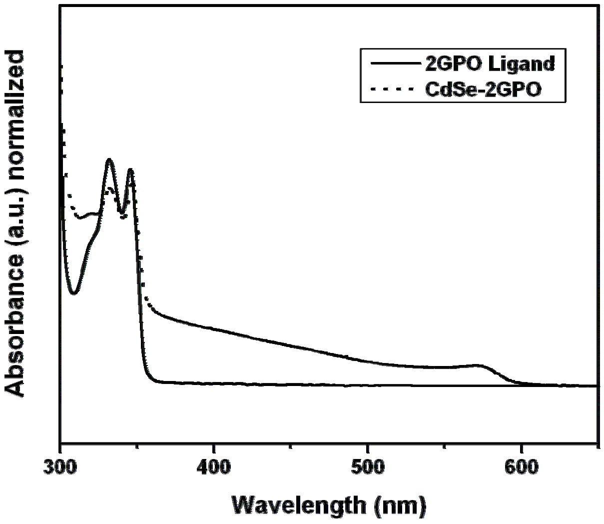
**S.I. Figure 1.** NMR Spectrum of G2-OH

| | 2GPO | Cadmium acetate | Dodecylamine | HPA | Selenium/TOP(0.1/2) |
|---|---|---|---|---|---|
| *1 | 50mg | 0.748mg | 100mg | 1.6mg | 1.7ml |
| *3 | 50mg | 2.244mg | 300mg | 4.8mg | 5ml |
| *5 | 50mg | 3.74mg | 500mg | 8mg | 8.5ml |

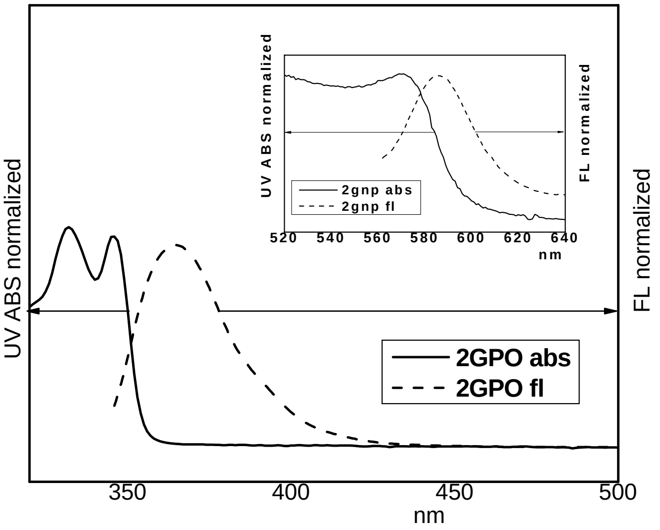
**S.I Table 1 . The equivalent ratio for the nanoparticle synthesis**



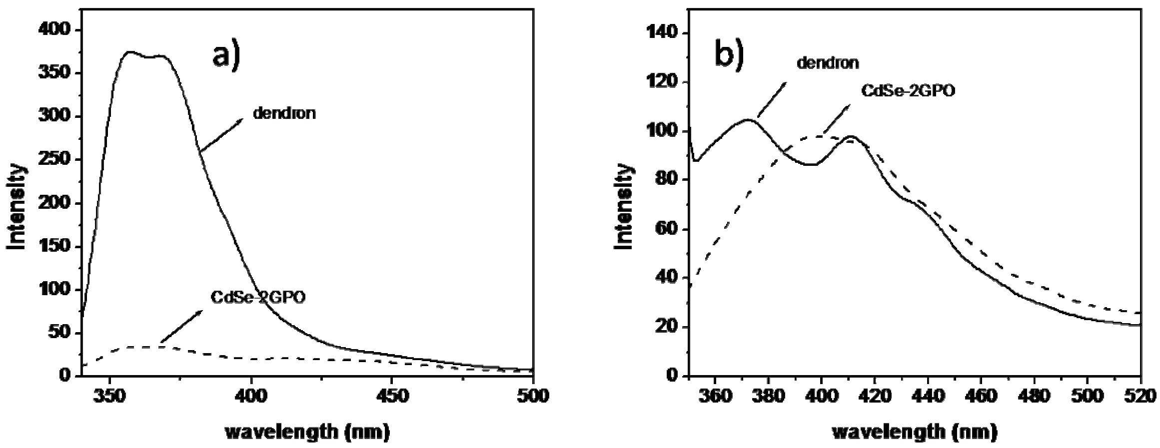
**S.I Figure 2.** UV of the nanoparticles depend on the different equivalent ratio against the fixed amount of 2GPO



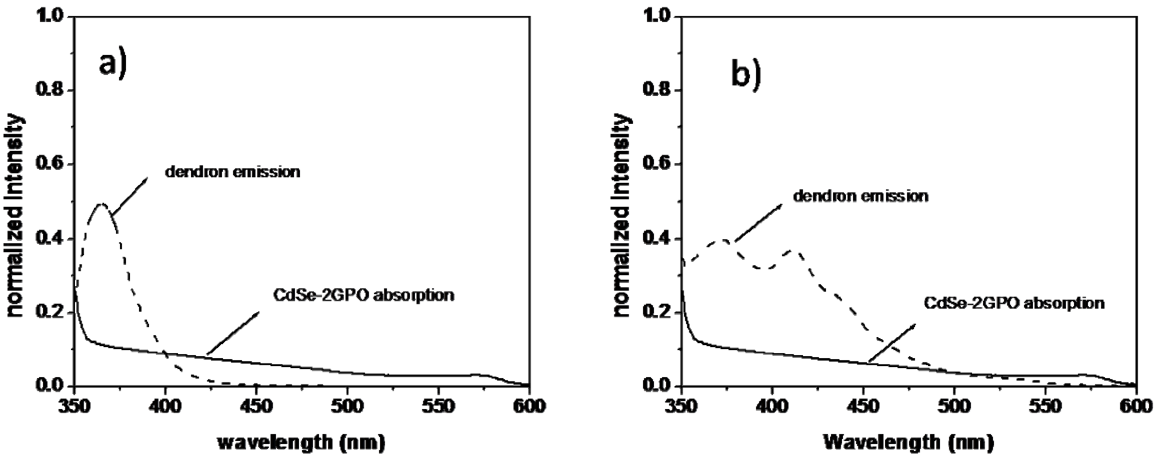
**S.I Figure 3.** UV-vis spectra of the ligands (solid) and CdSe-2GPO (dotted).



**S.I Figure 4.** UV and Fluorescence of 2GPO and nanoparticles which are capped with 2GPO

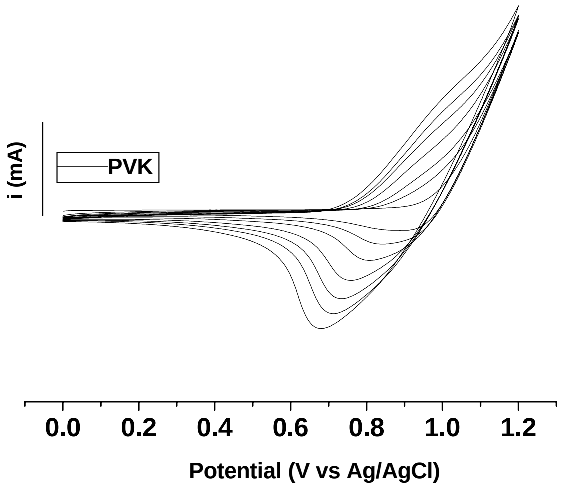


**S.I Figure 5.** Fluorescence overlap of dendron itself and CdSe-2GPO nanoparticles (donor itself and donor-acceptor pair) a) before and b) after electropolymeriztion.



**S.I Figure 6.** Spectral overlap function of dendron itself emission and absorption of CdSe-2GPO nanoparticles  a) before and b) after electropolymeriztion.

**Electrochemical polymerization/crosslinking of PVK.** The precursor PVL was electropolymerized for comparision using the cyclic voltammetry (CV) technique. In a three electrode cell, 0.1M tetra butyl ammonium perchlorate (TBAP) was taken as a supporting electrolyte along with 1mM of each dendrimer dissolved in 4ml methylene chloride in separate cells. The electropolymerization of the precursor polymer was performed by sweeping the voltage at a scan rate of 20mV/s from 0 to 1.2V against Ag/AgCl as a reference electrode and platinum as a counter electrode. The ITO or gold coated slides were used as a working electrode and also as a substrate.



**S.I Figure 7.** CV of PVK Precursor Polymer