Supporting Information

Dendronized carbon nanoparticles: the effect of light antenna

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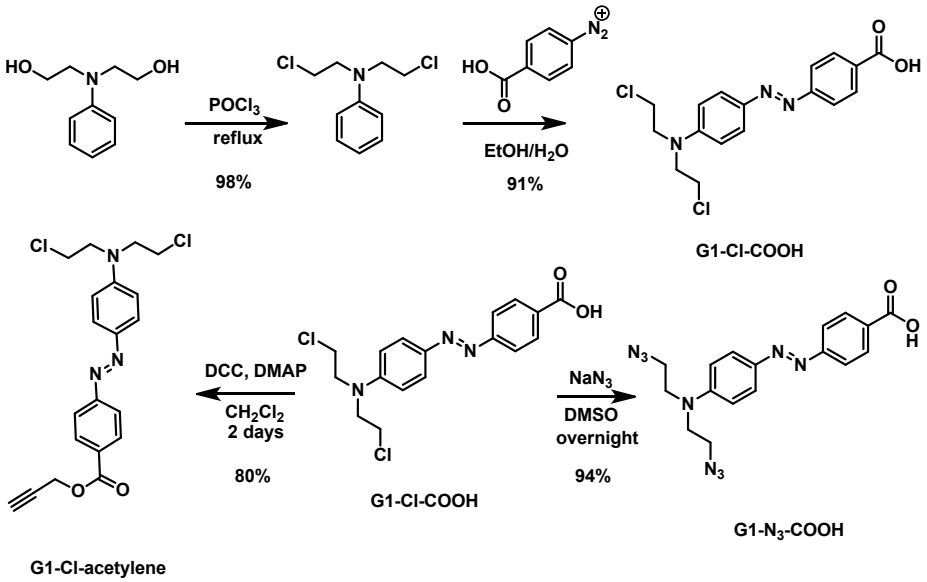
A. Sample preparations

Preparation of CNPs

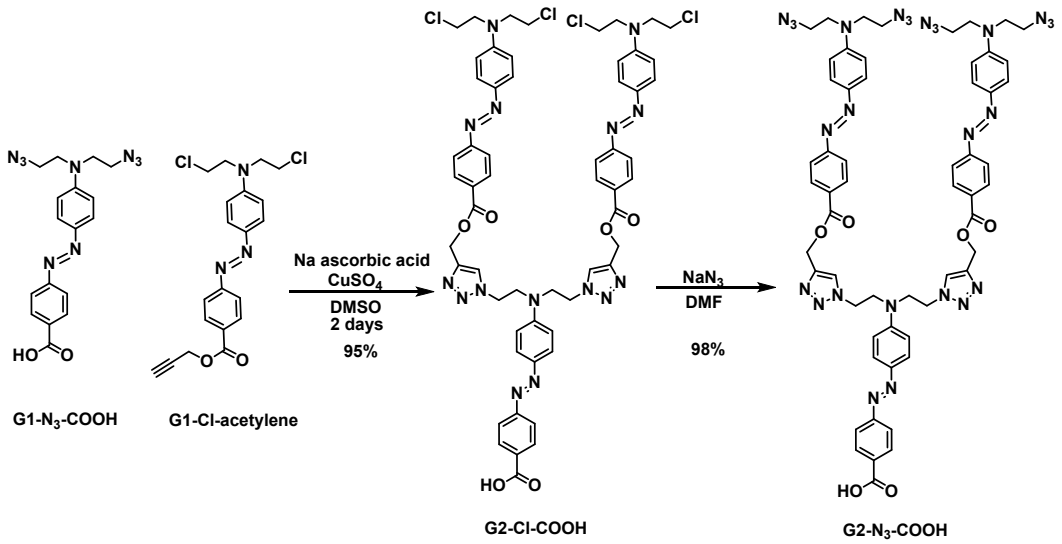
3 g of citric acid and 3 g of urea were added in 10 mL deionized water. The mixture was then heated in a microwave oven operated at 800 W for 3-4 min. The resultant dark brown solid obtained was put into a vacuum oven for heating at 60 ºC for 1 h and re-suspended in 100 mL deionized water. The solution was centrifuged at 10000 rpm for 15 min to remove the agglomerated particles. CNPs were obtained through the freeze drying.

Preparation of azobenezene dendrons

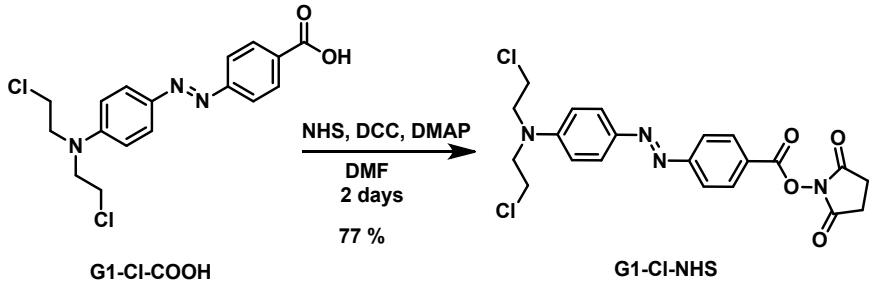
Chemicals were purchased from Aldrich and used without further purification. Reactions were performed under nitrogen unless otherwise stated. Deionized H_2O was obtained from Barnstead RO pure system. Chromatography purifications were performed on silica gel (SiO_2) with the indicated eluents. All other solvents and reagents were of reagent grade and used as received without purification. ^1H and ^{13}C NMR spectra for structural characterization were recorded with Bruker Avance 400 (^1H: 400 MHz; ^{13}C: 101 MHz) spectrometer at 297 K. All NMR samples were prepared in $CDCl_3$ unless otherwise stated. Spectra were calibrated internally using the solvent residual peak (e.g., for residual $CHCl_3$ in $CDCl_3$, ^1H: $\delta = 7.26$; ^{13}C: $\delta = 77.16$ ppm). Electrospray ionization (ESI) mass spectra were measured on a Bruker SolariX 9.4T mass spectrometer using CH_3OH/CH_2Cl_2 (1:1) as solvent.



Scheme S1. Preparation of azide (G1-N_3-COOH) and acetylene (G1-Cl-Acetylene) precursors.

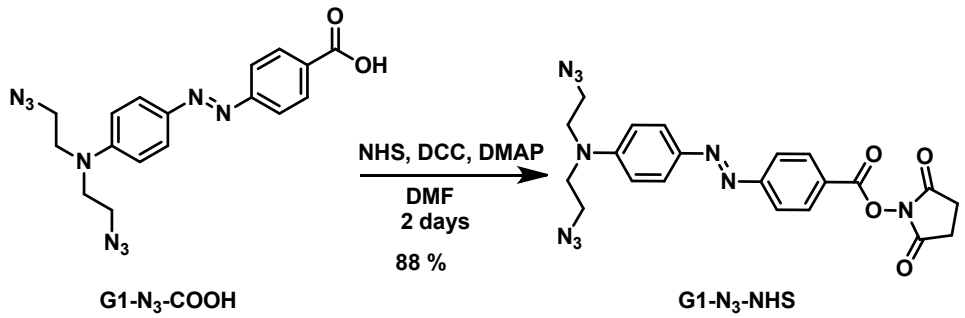


Scheme S2. Preparation of azide (G2-N_3-COOH) precursor.



G1:

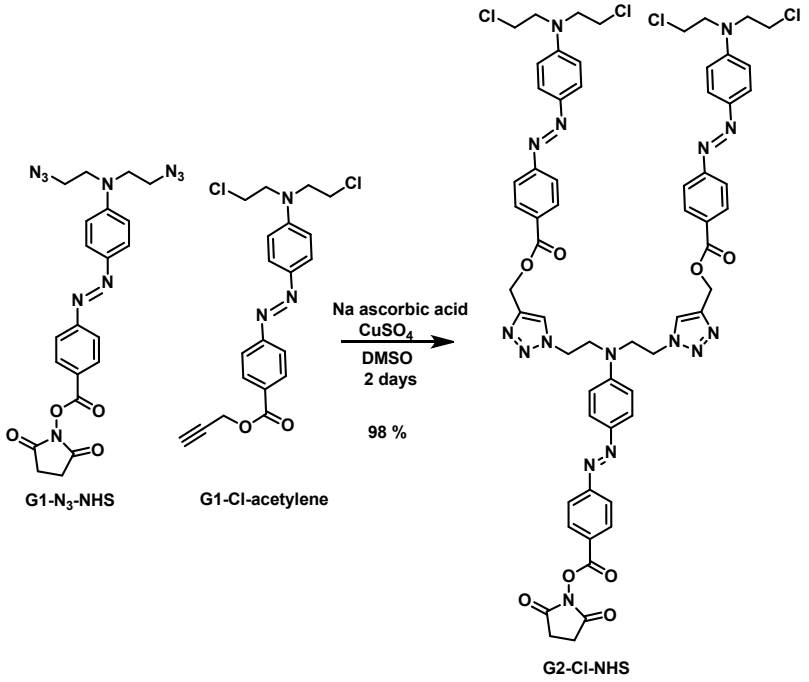
G1-Cl-COOH (2.00 g, 5.48 mmol), *N,N′*-dicyclohexylcarbodiimide (4.85 g 23.5 mmol) and *N*-hydroxysuccinimide (1.3 g, 11.3 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL). Catalytic amount of 4-dimethylaminopyridine was added to the reaction mixture. The reaction was carried out for 2 d and monitored by TLC. The insoluble solid was removed by filtration and the filtrate was dried by anhydrous $MgSO_4$. The mixture was filtrated and then concentrated in vacuo. The residue was purified by column chromatography with CH_2Cl_2 as the eluent. The product was an orange solid (1.95 g, 77%). ^{1}H NMR ($CDCl_3$): 2.93 (s, 4H, $COCH_2$), 3.69–3.73 (t, J = 7.0 Hz, 4H, NCH_2), 3.85–3.89 (t, J = 6.9 Hz, 4H, $ClCH_2$), 6.78–6.80 (d, J = 9.1 Hz, 2H, ArH), 7.93–7.97 (m, 4H, ArH), 8.24–8.26 (d, J = 8.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): 25.9, 40.4, 53.6, 111.8, 122.7, 125.4, 126.2, 131.8, 144.8, 149.6, 156.9, 161.7, 169.4. HRMS (ESI): $C_{21}H_{21}Cl_2N_4O_4$ $[M+H]^+$ calcd: 463.09344, found: 463.09489.



G1-N_3-NHS

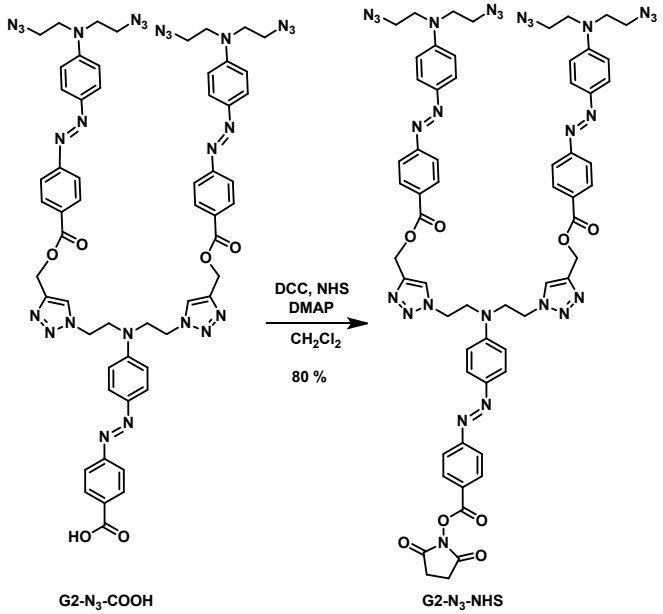
G1-N_3-COOH (3.23 g, 8.54 mmol), *N,N′*-dicyclohexylcarbodiimide (3.21 g, 15.6 mmol) and *N*-hydroxysuccinimide (2.00 g, 17.3 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL). Catalytic amount of 4-dimethylaminopyridine was added to the reaction mixture. The reaction

was carried out for 2 d and monitored by TLC. The insoluble solid was removed by filtration and the filtrate was dried by anhydrous $MgSO_4$. The mixture was filtrated and then concentrated in vacuo. The residue was purified by column chromatography with CH_2Cl_2 as the eluent. The product was an orange solid (3.60 g, 88%). ^{1}H NMR ($CDCl_3$): 2.92 (s, 4H, $COCH_2$), 3.56–3.59 (t, J = 6.2 Hz, 4H, N_3CH_2), 3.68–3.71 (t, J = 5.8 Hz, 4H, NCH_2), 6.79–6.81 (d, J = 9.2 Hz, 2H, ArH), 7.92–7.94 (d, J = 8.6 Hz, 4H, ArH), 8.23–8.25 (d, J = 8.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): 25.8, 48.9, 50.9, 112.0, 122.7, 125.2, 126.2. 131.8. 144.6, 149.8, 156.9, 161.7, 169.4. HRMS (ESI): $C_{21}H_{21}N_{10}O_4$ $[M+H]^+$ calcd: 477.17418, found: 477.17468.



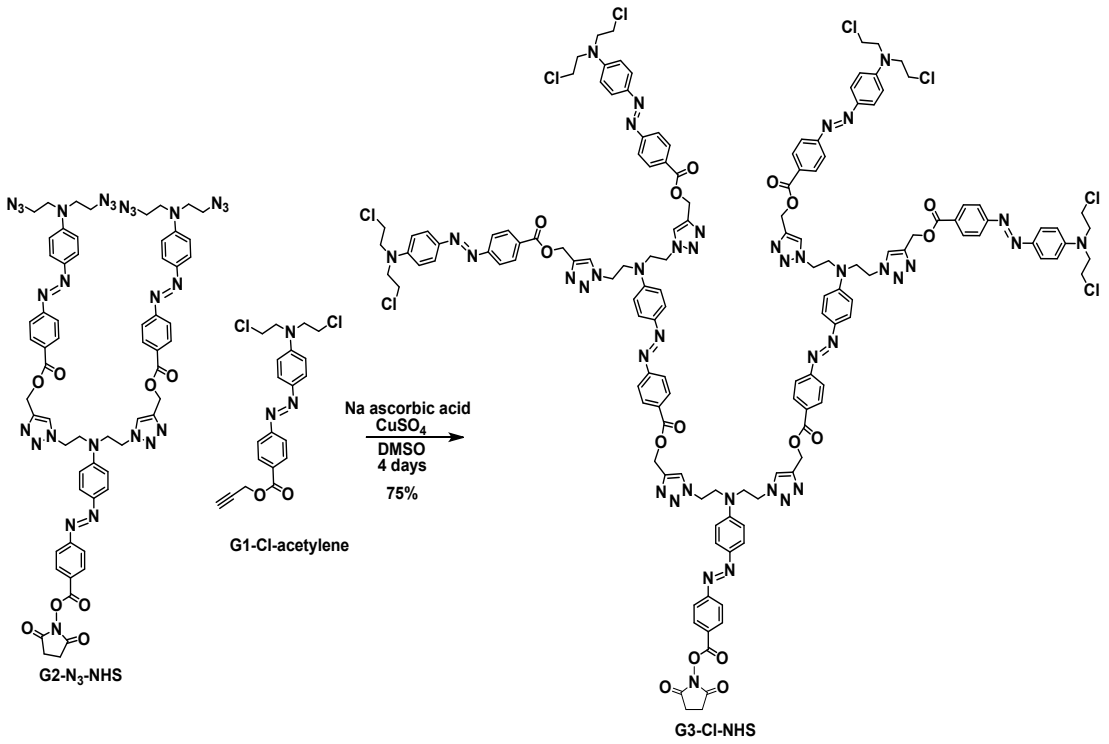
G2:

G1-N_3-NHS (0.77 g, 1.6 mmol) and G1-Cl-acetylene (1.6 g, 4.0 mmol, 2.5 eqv.) were dissolved in DMSO (15 mL). Sodium ascorbic acid (0.17 g) and $CuSO_4 \cdot 5H_2O$ (0.09 g) was added to the reaction mixture. The reaction was carried out for 2 d and monitored by TLC. The reaction mixture was transferred into water and an orange solid was precipitated. The crude product was collected by filtration. Then, it was purified by column chromatography with $CHCl_3$, then gradient to ethyl acetate as the eluents. The product was an orange solid (2.0 g, 98%). ^{1}H NMR ($CDCl_3$): 2.93 (s, 4H, $COCH_2$), 3.69–3.77 (m, 12H, NCH_2CH_2), 3.84–3.87 (t, J = 6.8 Hz, 8H, $ClCH_2$) 4.46 (s, 4H, $COOCH_2$), 5.43 (s, 4H, NCH_2), 6.56–6.58 (d, J = 9.1 Hz, 1H, ArH), 6.65–6.67 (d, J = 8.8 Hz, 1H, ArH), 6.76–6.77 (d, J = 9.2 Hz, 4H, ArH), 7.54 (s, 2H, CH=C), 7.64–7.89 (m, 12H, ArH), 8.06–8.08 (d, J = 8.6 Hz, 4H, ArH), 8.15–8.17 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): 25.8, 31.0, 40.3, 47.4, 53.5, 58.2, 111.7, 112.0, 122.3, 122.8, 125.4, 125.9, 130.0, 130.7, 131.7, 143.4, 144.6, 149.3, 155.9, 166.0, 169.4. HRMS (ESI): $C_{61}H_{59}Cl_4N_{16}O_8$ $[M+H]^+$ calcd: 1285.34363, found: 1285.34495.



G2-N_3-NHS

G1-N_3-COOH (1.45 g, 1.26 mmol), *N,N′*-dicyclohexylcarbodiimide (0.51 g, 2.48 mmol) and *N*-hydroxysuccinimide (0.27 g, 2.35 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL). Catalytic amount of 4-dimethylaminopyridine was added to the reaction mixture. The reaction was carried out for 2 d and monitored by TLC. The insoluble solid was removed by filtration and the filtrate was dried with anhydrous $MgSO_4$. The mixture was filtrated and then concentrated in vacuo. The residue was purified by column chromatography with $CHCl_3$ as the eluent. The product was an orange solid (1.32 g, 80%). ^{1}H NMR ($CDCl_3$): 2.88 (s, 4H, $COCH_2$), 3.58–3.60 (m, 8H, N_3CH_2), 3.69–3.75 (m, 12H, NCH_2CH_2), 4.45 (s, 4H, $COOCH_2$), 5.44 (s, 4H, NCH_2), 6.58–6.61 (d, J = 9 Hz, 2H, ArH), 6.77–6.81 (d, J = 8.8 Hz, 4H, ArH), 7.54 (s, 2H, CH=C), 7.76–7.89 (m, 12H, ArH), 8.06–8.08 (d, J = 8.4 Hz, 4H, ArH), 8.16–8.19 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): 25.8, 47.3, 49.8, 50.8, 51.4, 58.1, 111.9, 122.3, 122.8, 125.3, 125.9, 126.1, 129.9, 130.7, 131.6, 143.4, 144.5, 144.9, 149.5, 155.8, 156.5, 161.6, 166.0, 169.4. HRMS (ESI): $C_{61}H_{59}N_{28}O_8$ $[M+H]^+$ calcd: 1311.50652, found: 1311.50840.



G3:

$G2\text{-}N_3\text{-}NHS$ (0.31 g, 0.24 mmol) and G1-Cl-acetylene (0.39 g, 0.97 mmol, 4.1 eqv.), were dissolved in DMSO (15 mL). Sodium ascorbic acid (0.17 g) and $CuSO_4 \cdot 5H_2O$ (0.09 g) was added to the reaction mixture. The reaction was carried out for 2 d and monitored by TLC. The reaction mixture was transferred into water and orange solid was precipitated. The crude product was collected by filtration. Then, it was purified by column chromatography with $CHCl_3$, then gradient to ethyl acetate as the eluents. The product was an orange solid (0.51 g, 75%). ^1H NMR ($CDCl_3$): 2.88 (s, 4H, $COCH_2$), 3.66–3.73 (m, 28H, NCH_2), 3.80–3.84 (m, 16H, $ClCH_2CH_2$), 4.43 (s, 12H, $COOCH_2$), 5.41 (s, 12H, NCH_2), 6.49–6.53 (d, J = 8.8 Hz, 2H, ArH), 6.62–6.64 (d, J = 8.7 Hz, 4H, ArH), 6.73–6.75 (d, J = 9,2 Hz, 8H, ArH), 7.57 (s, 6H, CH=C), 7.68–7.87 (m, 28H, ArH), 7.98–8.11 (d, J = 8.4 Hz, 14H, ArH). ^{13}C NMR ($CDCl_3$): 40.4, 47.5, 51.6, 53.6, 58.2, 111.8, 112.2, 122.4, 122.5, 125.4, 126.0, 130.1, 130.8, 144.7, 149.4, 155.9, 166.1. HRMS (ESI): $C_{141}H_{136}Cl_8N_{40}O_{16}$ $[M+2H]^{2+}$ calcd: 1464.92769, found: 1464.93071.

Preparation of dendronized CNPs (*d*-CNPs)

2 mg of azobenzene dendrons (G1, G2 or G3) was dissolved in 50 mL THF. 10 ml of 700 μg/mL aqueous dispersion of CNPs was added and the resultant mixture was allowed to stand for 30 min. In all cases, azobenzene dendrons used were in excess. Based on the space occupied by each dendron G1, G2 and G3, and also the surface area of a 10-nm CNP, the maximum number of dendrons that can reside onto each CNP can be found. With these numbers, excessive G1, G2 or G3 were prepared for reaction with CNPs. As dendrons can readily attach onto the available space on CNP surface because the reaction between –NHS on dendritic azobenzene and $–NH_2$ on CNP surface is a well-known and well-established coupling reaction with high yield and stability. As such, full coverage by G1, G2 or G3 on CNP were expected when excessive G1, G2 or G3 were used.

Preparation of CH_3COOH treated CNPs (*a*-CNPs)

104 mg of *N*-hydroxysuccinimide (NHS) and 58 mg of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) were separately dissolved in 30 mL of deionized water to give a NHS and an EDC solution. 38 μL of CH_3COOH was added to 50 mL

deionized water to give a CH_3COOH solution. 10 µL of NHS solution and 10 µL of EDC solution were added to 10 mL of CH_3COOH solution. The mixture was thoroughly stirred for 15 min. Then, 10 mL of 700 µg/mL aqueous dispersion of CNPs was added to the mixture. NHS, EDC, CH_3COOH and CNPs in the mixture were allowed to react completely under stirring for 1 h.

B. XPS analysis of CNP

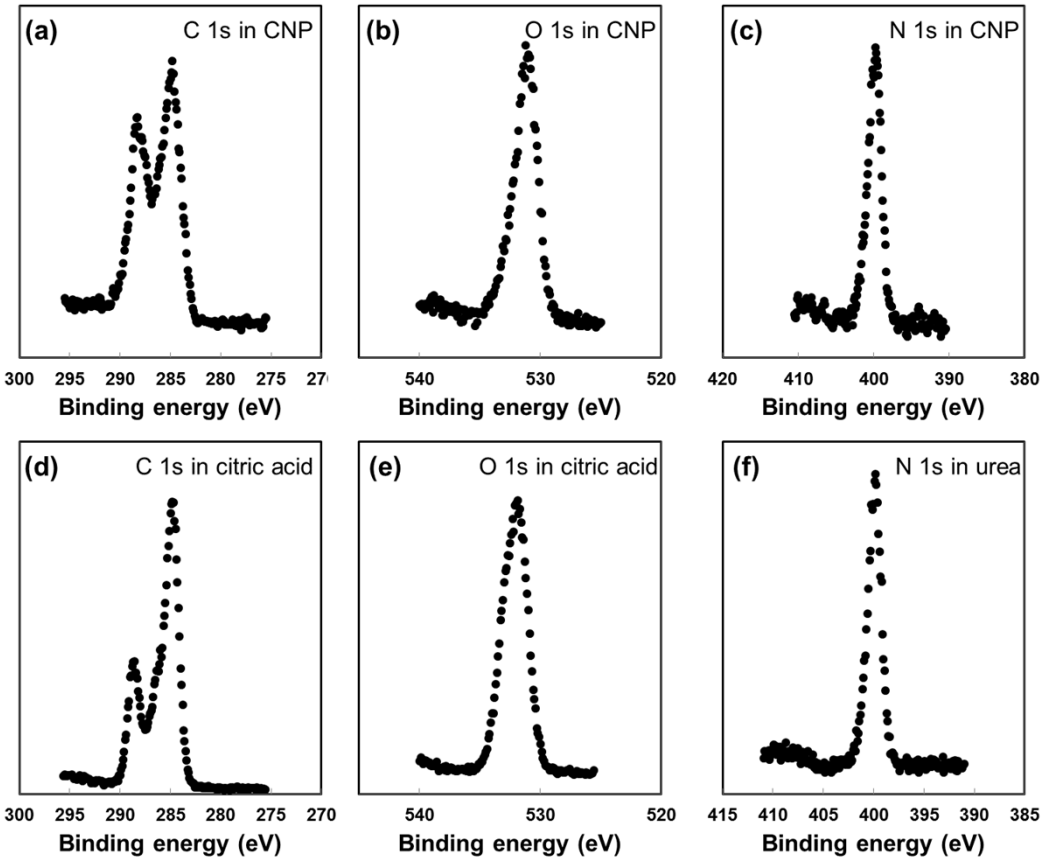


Figure S1. XPS signals of a) C 1s in CNP, b) O 1s in CNP, c) N 1s in urea, d) C 1s in citric acid, e) O 1s in citric acid, and f) N 1s in urea.

XPS analyses were performed with PHI Quantum 2000 Scanning ESCA Microprobe. All spectra were referenced to 284.8 eV of C 1s from adventitious surface hydrocarbon. Evidently from the XPS C 1s spectrum of CNP, the peak at ~288 eV matches well with the signal component from –COOH group of citric acid. Also, the O 1s signals from both CNP and citric acid show the same spectral feature. These confirm the presence of carboxylic acid (-COOH) groups in CNP. On the other hand, the peak position of N 1s in CNP is the same as the N 1s in pure urea that has $–NH_2$ groups as the only nitrogen source. As such, the nitrogen present in the prepared CNP should be in the form of $–NH_2$.