Supporting Information

Amidoamine Dendron-Based Co-adsorbents: Improved Performance in Dye-Sensitized Solar Cells

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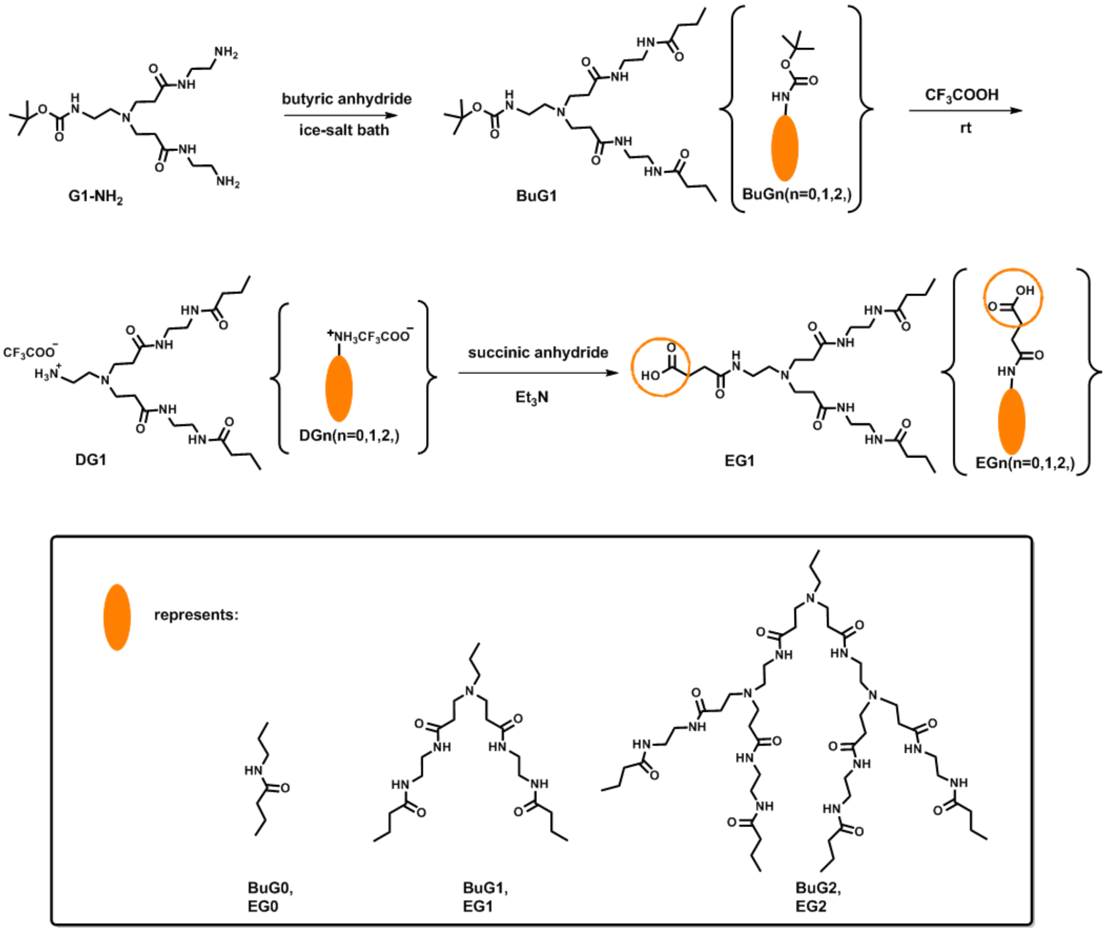

Scheme S1. The synthetic procedures of dendritic molecules EG0, EG1 and EG2.

Synthetic procedures and structural characterization

The synthetic procedures of dendritic molecules EG0, EG1 and EG2 are shown in Scheme S1. Three targeted molecules were prepared by the similar strategies. Therefore, for convenience, only the synthetic methods of EG1 are given in detail in the following section.

Synthesis and characterization of BuGn

The dendron G1-NH_2 (3.64 g, 9.38 mmol) was dissolved in the solvent of $CHCl_3$. The *n*-butyric anhydride (5.93 g, 37.50 mmol)/$CHCl_3$ mixed solution was dropwise added into the G1-NH_2 solution in an ice-salt bath. The reaction solution was stirred for 48 h (24h for the synthesis of BuG0) at room temperature and then evaporated under vacuum to remove excess solvent. The pure BuG1 was obtained by precipitation in diethyl ether and isolation using a silica column. The synthesis of BuG0 and BuG2 employed the similar process as that of BuG1.

BuG1: Yield: white solid, 45.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 2H, $\mathrm{CON}H$), 7.54 (s, 1H, $\mathrm{CON}H$), 7.15 (s, 1H, $\mathrm{CON}H$), 5.57 (s, 1H, $\mathrm{OCON}H$), 3.36 (s, 8H, $\mathrm{CONHC}H_2\mathrm{C}H_2\mathrm{NHCO}$), 3.18 (d, 2H, $\mathrm{CONHC}H_2\mathrm{CH_2}$), 2.69 (s, 4H, $\mathrm{-N(C}H_2\mathrm{)C}H_2$), 2.53 (s, 2H, $\mathrm{CONHCH_2C}H_2\mathrm{N}<$), 2.43 – 2.26 (m, 4H, $>\mathrm{NCH_2C}H_2\mathrm{CONH}$), 2.18 (t, 4H, $\mathrm{NHCOC}H_2\mathrm{CH_2CH_3}$), 1.78 – 1.55 (m, 4H, $\mathrm{NHCOCH_2C}H_2\mathrm{CH_3}$), 1.39 (d, 9H, $\mathrm{(C}H_3\mathrm{)_3OCO}$), 0.96 (dt, 6H, $\mathrm{NHCOCH_2CH_2C}H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.28, 173.37, 156.20, 79.20, 52.56, 50.20, 39.67, 39.28, 38.43, 33.81, 28.41, 19.11, 13.76. ESI MS: Calcd for $C_{25}H_{48}N_6O_6$: 528.36; Found: 529.4 $(M+H)^+$, 551.4 $(M+Na)^+$.

BuG0: Yield: white solid, 44.4%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (s, 1H, $\mathrm{CON}H\mathrm{CH_2}$), 5.24 (s, 1H, $\mathrm{CH_2N}H\mathrm{CO}$), 3.43 – 3.31 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{NHCO}$), 3.32 – 3.16 (m, 2H, $\mathrm{CONHC}H_2\mathrm{CH_2}$), 2.16 (t, 2H, $\mathrm{COC}H_2$), 1.74 – 1.57 (m, 2H, $\mathrm{COCH_2C}H_2$), 1.44 (s, 9H, $\mathrm{(C}H_3\mathrm{)_3CO}$), 0.94 (t, 3H, $\mathrm{CH_2CH_2C}H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.85, 156.96, 79.51, 40.41 (d), 38.56, 28.34, 19.10, 13.71. ESI MS: Calcd for $C_{11}H_{22}N_2O_3$: 230.16; Found: 231.2 $(M+H)^+$, 253.2 $(M+Na)^+$, 269.1 $(M+k)^+$.

BuG2: Yield: white solid, 44.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 – 7.70 (m, 5H, $\mathrm{CON}H$), 7.22 (s, 4H, $\mathrm{CON}H$), 5.66 (s, 1H, $\mathrm{OCON}H$), 3.35 (s, 16H, $\mathrm{CONHC}H_2\mathrm{C}H_2\mathrm{NHCO}$), 3.26 (s, 4H, $\mathrm{CONHC}H_2\mathrm{CH_2N}<$), 3.22 – 3.14 (m, 2H, $\mathrm{OCONHC}H_2\mathrm{CH_2}$), 2.88 – 2.66 (m, 12H, $>\mathrm{NC}H_2\mathrm{CH_2CONH}$), 2.64 – 2.49 (m, 6H, $\mathrm{CONHCH_2C}H_2\mathrm{N}<$), 2.36 (t, 12H, $>\mathrm{NCH_2C}H_2\mathrm{CONH}$), 2.19 (dd, 8H, $\mathrm{NHCOC}H_2\mathrm{CH_2CH_3}$), 1.71 – 1.56 (m, 8H, $\mathrm{NHCOCH_2C}H_2\mathrm{CH_3}$), 1.43 (s, 9H, $\mathrm{(C}H_3\mathrm{)_3OCONH}$), 0.94 (q, 12H, $\mathrm{NHCOCH_2CH_2C}H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.35, 173.44, 172.70, 156.40, 79.19, 52.73, 50.54, 39.57, 39.38, 38.42, 37.68, 34.10, 28.48, 19.14, 13.78. ESI MS: Calcd for $C_{53}H_{100}N_{14}O_{12}$: 1124.76; Found: 1125.8 $(M+H)^+$, 1147.8 $(M+Na)^+$.

Synthesis and characterization of DGn

The dendron BuG1 (1.24 g, 2.35 mmol) was dissolved in the solvent of $CHCl_3$. Trifluoroacetic acid (3.48 mL, 46.96 mmol) was gradually dropped into the solution. After the mixed solution was stirred at room temperature for 2 h (prolonged time for the preparation of DG2), the excess trifluoroacetic acid and the solvent were removed by evaporation under vacuum. The crude product was precipitated in diethyl ether to afford DG1. DG0 and DG2 were prepared according to the same procedures as DG1.

DG1: Yield: white solid, 99%. ^{1}H NMR (400 MHz, D_2O): δ = 3.47 (s, 4H, $\mathrm{NH_3^+C}H_2\mathrm{C}H_2\mathrm{N}<$), 3.41 (t, 4H, $>\mathrm{NC}H_2$), 3.32 – 3.23 (m, 8H, $\mathrm{CONHC}H_2\mathrm{C}H_2\mathrm{NHCO}$), 2.72 (t, 4H, $>\mathrm{NCH2C}H_2\mathrm{CONH}$), 2.27 – 2.07 (m, 4H, $\mathrm{NHCOC}H_2\mathrm{CH_2CH_3}$), 1.65 – 1.44 (m, 4H, $\mathrm{NHCOCH_2C}H_2\mathrm{CH_3}$), 0.97 – 0.75 (m, 6H, $\mathrm{NHCOCH_2CH_2C}H_3$).

DG0: Yield: white solid, 99%. ^1H NMR (400 MHz, D_2O): δ = 3.51 (t, 2H, $NH_3^+C\mathit{H}_2CH_2NH$), 3.13 (dd, 2H, $NH_3^+CH_2C\mathit{H}_2NH$), 2.38 – 2.16 (m, 2H, $NHCOC\mathit{H}_2CH_2$), 1.76 – 1.47 (m, 2H, $NHCOCH_2C\mathit{H}_2$), 1.07 – 0.74 (m, 3H, $CH_2CH_2C\mathit{H}_3$).

DG2: Yield: white solid, 99%. ^1H NMR (400 MHz, D_2O): δ = 3.56 (t, 4H, >$NC\mathit{H}_2CH_2CONH$), 3.41 (t, 8H, >$NC\mathit{H}_2CH_2CONH$), 3.29 (dd, 4H, $CONHC\mathit{H}_2CH_2N$<), 3.28 – 3.15 (m, 18H, $CONHC\mathit{H}_2C\mathit{H}_2NHCO$, $CF_3COO^-NH_3^+C\mathit{H}_2CH_2$), 3.01 (s, 6H, $C\mathit{H}_2N(CH_2)CH_2$), 2.67 (t, 8H, >$NCH_2C\mathit{H}_2CONH$), 2.53 (t, 4H, >$NCH_2C\mathit{H}_2CONH$), 2.11 (t, 8H, $NHCOC\mathit{H}_2CH_2CH_3$), 1.57 – 1.41 (m, 8H, $NHCOCH_2C\mathit{H}_2CH_3$), 0.79 (t, 12H, $NHCOCH_2CH_2C\mathit{H}_3$).

Synthesis and characterization of EGn

The above prepared DG1 (1.27 g, 2.34 mmol) was dissolved in $CHCl_3$ solution containing triethylamine (0.71 g, 7.02 mmol). The $CHCl_3$ solution of succinic anhydride (0.35 g, 3.51 mmol) was dropwise added into DG1 solution. The reaction solution was stirred at room temperature for 48 h (24 h for the synthesis of EG0) and then evaporated under vacuum to remove redundant triethylamine and solvent. The crude product was washed by $CHCl_3$ and sequentially purified by a silica column to obtain the targeted molecule EG1. The compounds EG0 and EG2 were prepared based on the similar synthetic procedures as EG1.

EG1: Yield: white solid, 58.2%. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.01 (s, 2H, $CON\mathit{H}$), 7.90 (s, 2H, $CON\mathit{H}$), 7.78 (t, 1H, $HOOCCH_2CH_2CON\mathit{H}$), 3.15 – 3.02 (m, 10H, $CONHC\mathit{H}_2C\mathit{H}_2NHCO$, $CONHC\mathit{H}_2CH_2N$<), 2.64 (t, 4H, >$NC\mathit{H}_2CH_2$), 2.42 (t, 2H, $CONHCH_2C\mathit{H}_2N$<), 2.39 – 2.33 (m, 2H, $HOOCC\mathit{H}_2CH_2$), 2.29 (t, 2H, $HOOCCH_2C\mathit{H}_2$), 2.18 (t, 4H, >$NCH_2C\mathit{H}_2CONH$), 2.03 (t, 4H, $NHCOC\mathit{H}_2CH_2CH_3$), 1.59 – 1.38 (m, 4H, $NHCOCH_2C\mathit{H}_2CH_3$), 0.84 (t, 6H, $NHCOCH_2CH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.16, 171.55, 52.20, 49.65, 38.32 (d), 37.34, 36.96, 33.41, 30.71, 18.57, 13.58. ESI MS: Calcd for $C_{24}H_{44}N_6O_7$: 528.33; Found: 529.3 $(M+H)^+$, 551.3 $(M+Na)^+$.

EG0: Yield: white solid, 55.6%. ^1H NMR (400 MHz, DMSO-d_6): δ = 7.86 (s, 1H, $CON\mathit{H}$), 7.76 (s, 1H, $CON\mathit{H}$), 3.08 (dd, 4H, $CONHC\mathit{H}_2C\mathit{H}_2NHCO$), 2.42 (t, 2H, $HOOCC\mathit{H}_2CH_2$), 2.29 (t, 2H, $CH_2C\mathit{H}_2CONH$), 2.02 (t, 2H, $NHCOC\mathit{H}_2CH_2CH_3$), 1.58 – 1.42 (m, 2H, $NHCOCH_2C\mathit{H}_2CH_3$), 0.84 (t, 3H, $NHCOCH_2CH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.80, 172.10, 171.09, 38.42, 38.22, 37.34, 30.03, 29.11, 18.55, 13.58. ESI MS: Calcd for $C_{10}H_{18}N_2O_4$: 230.13; Found: 231.1 $(M+H)^+$, 253.2 $(M+Na)^+$, 269.1 $(M+k)^+$.

EG2: Yield: white solid, 47.7%. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.18 (s, 4H, $CON\mathit{H}$), 8.03 (s, 4H, $CON\mathit{H}$), 7.92 (s, 2H, $CON\mathit{H}$), 7.76 (t, 1H, $HOOCCH_2CH_2CON\mathit{H}$), 3.08 (s, 22H, $CONHC\mathit{H}_2C\mathit{H}_2NHCO$, $CONHC\mathit{H}_2CH_2N$<), 2.64 (t, 12H, >$NC\mathit{H}_2CH_2CONH$), 2.43 (t, 6H, $CONHCH_2C\mathit{H}_2N$<), 2.27 (s, 4H, $HOOCC\mathit{H}_2C\mathit{H}_2CONH$), 2.20 (dd, 12H, >$NCH_2C\mathit{H}_2CONH$), 2.03 (t, 8H, $CONHC\mathit{H}_2CH_2CH_3$), 1.49 (dd, 8H, $CONHCH_2C\mathit{H}_2CH_3$), 0.83 (t, 12H, $CONHCH_2CH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.13, 171.52, 171.36, 52.70, 49.71, 38.40, 38.28, 37.33, 36.88, 33.48, 33.33, 18.59, 13.59. ESI MS: Calcd for $C_{52}H_{96}N_{14}O_{13}$: 1124.73; Found: 1125.7 $(M+H)^+$, 1147.7 $(M+Na)^+$.

Figures

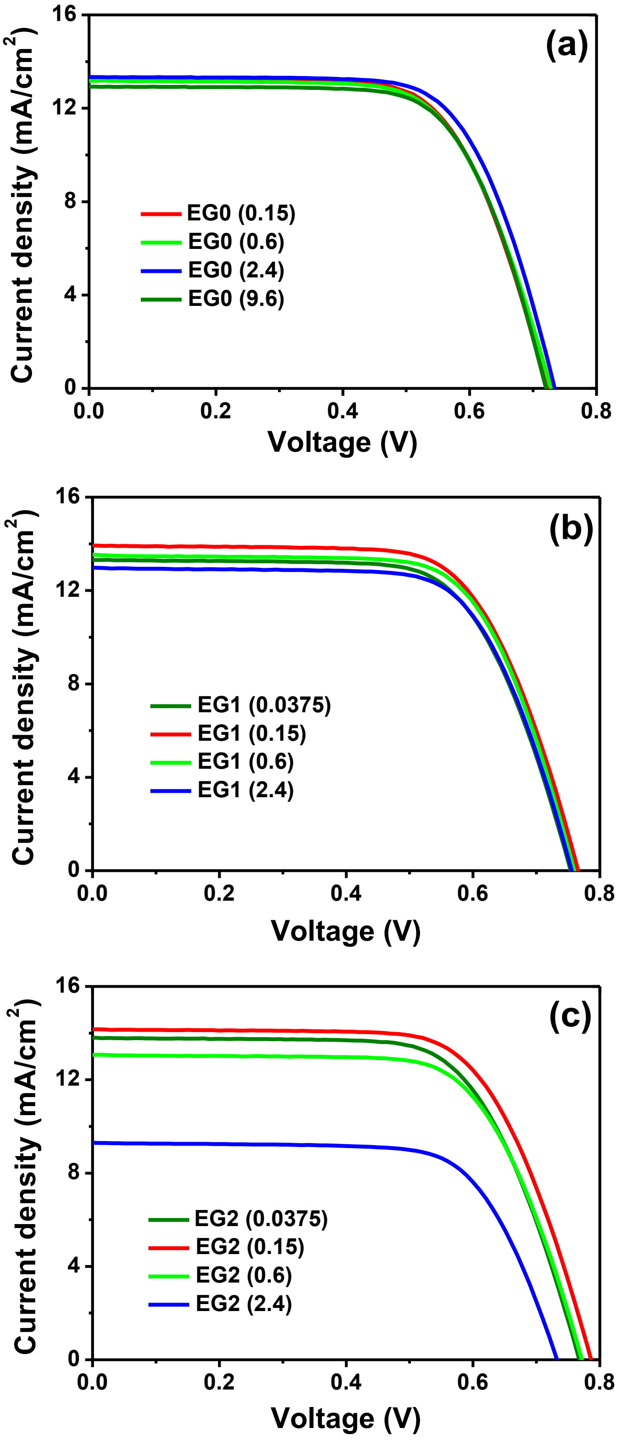

Figure S1. The *J-V* plots of the devices using dendritic molecule EG0 (a), EG1 (b) or EG2 (c) as the co-adsorbent at different concentrations (0.15, 0.6, 2.4 or 9.6 mM for EG0, and 0.0375, 0.15, 0.6, or 2.4 mM for both EG1 and EG2) under AM 1.5 simulated sunlight illumination.

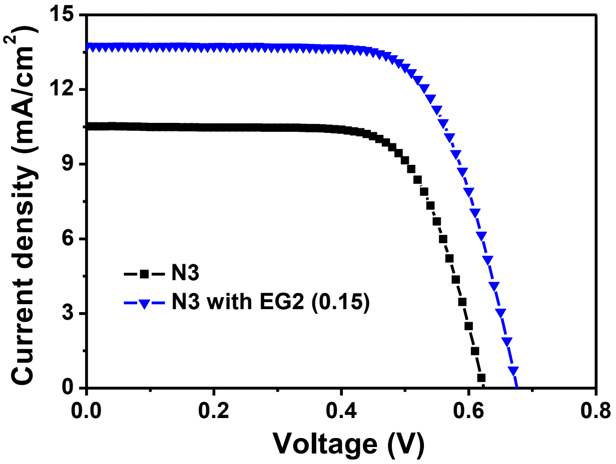

Figure S2. The *J-V* plots of N3-sensitized solar cells with and without co-adsorbent EG2 at the concentration of 0.15 mM under AM 1.5 simulated sunlight illumination.

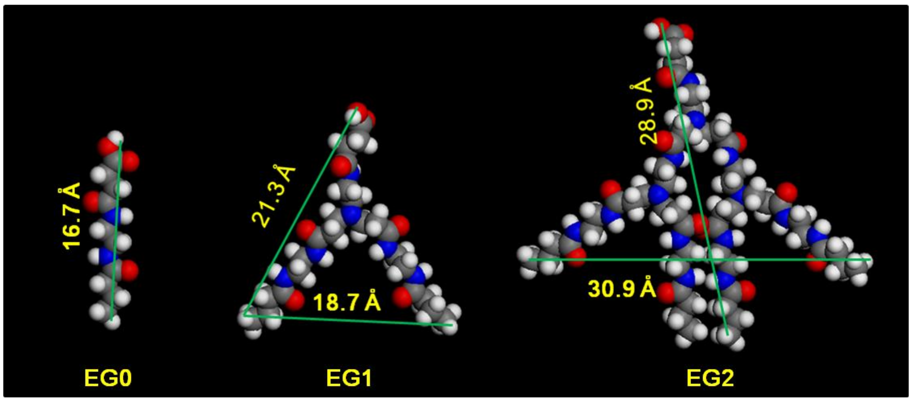

Figure S3. The optimized structures of EG0, EG1 and EG2 in CPK type.