

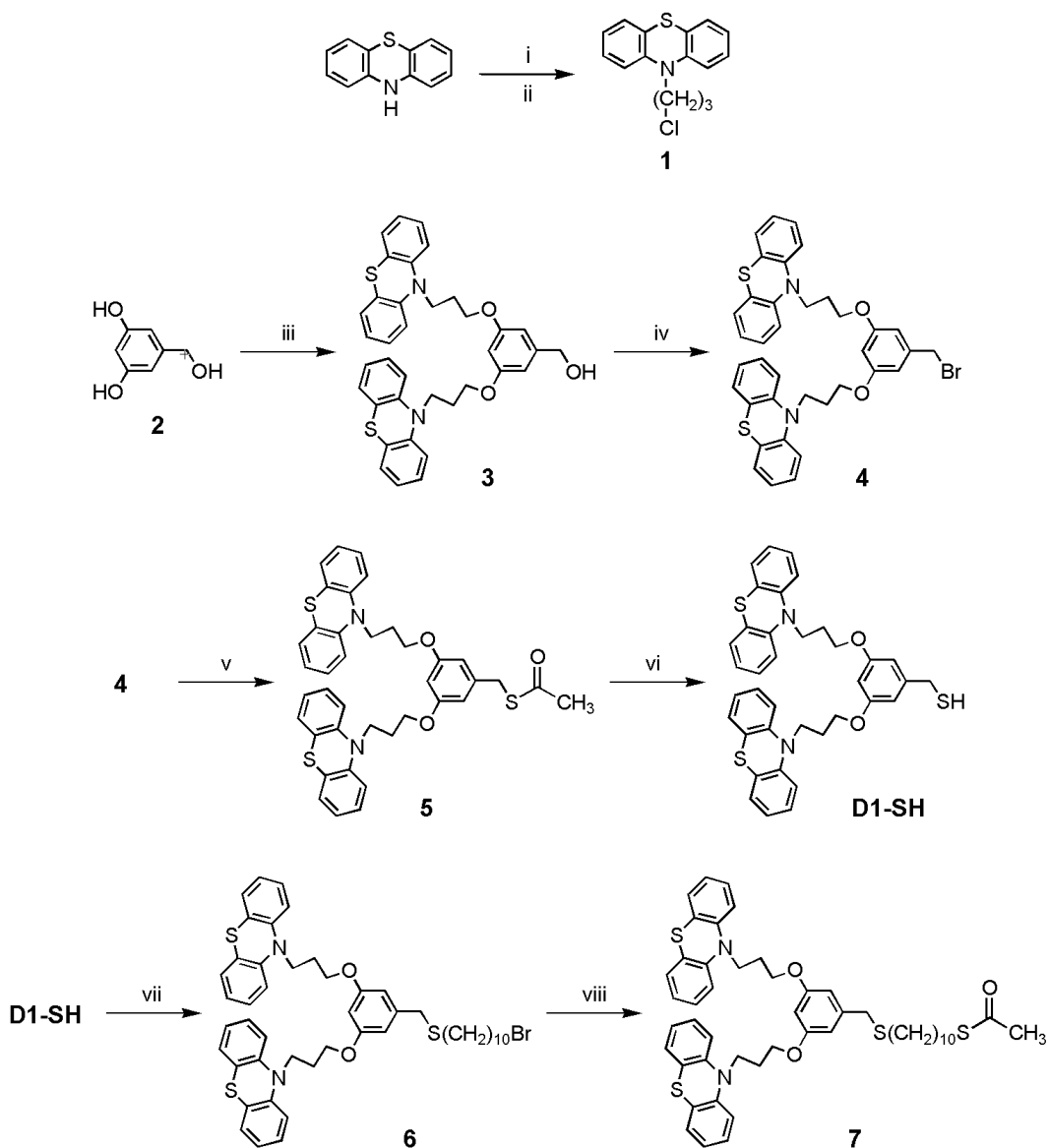
ESI (Electronic Supplementary Information)

Dendritic Effects on the Ordered Assembly and the Interfacial One-Electron Oxidation of Redox-active Dendron-functionalized Gold Nanoparticles

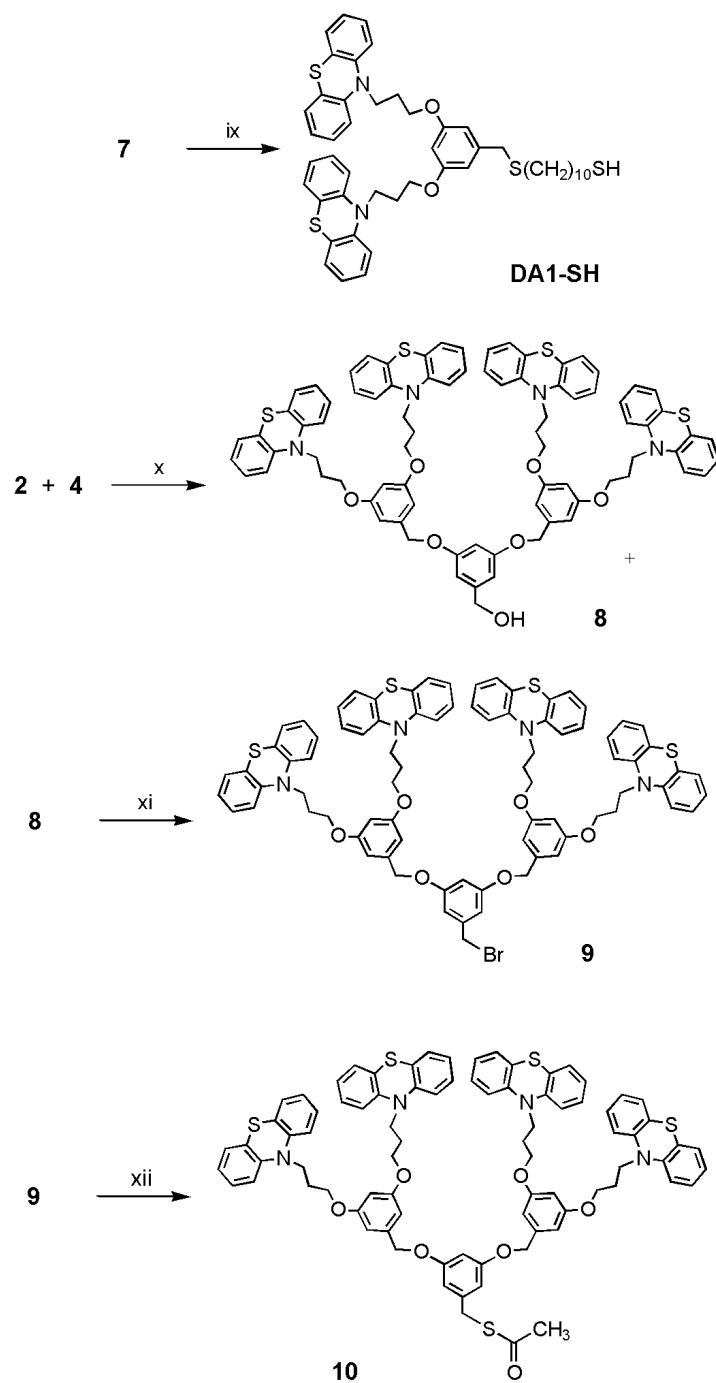
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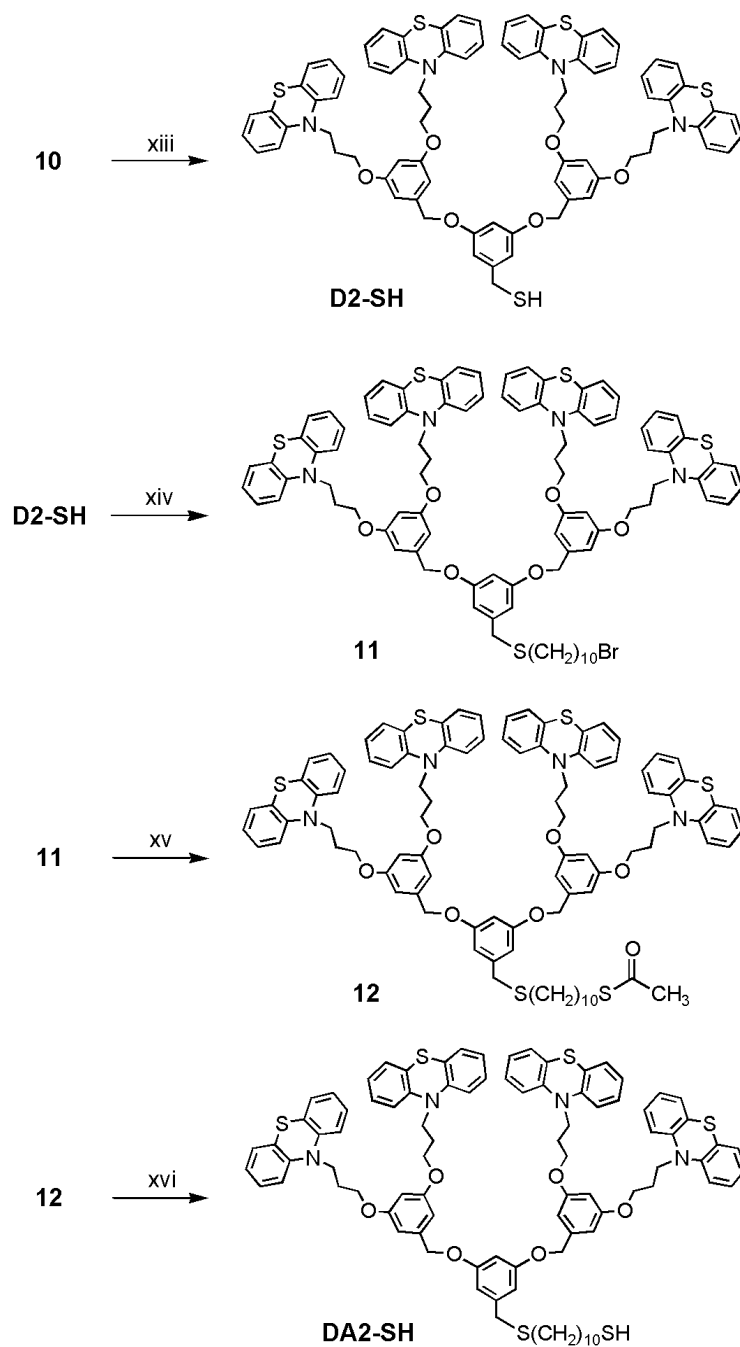
Synthesis of dendron-thiols. The dendron-thiols were synthesized according to Scheme S1, S2, and S3.



Scheme S1. Reagents and conditions. i, NaH, THF, 0 °C, 1 h; ii, Br(CH₂)₃Cl, THF, room temp., 24 h; iii, **1**, K₂CO₃, MeCN, reflux, 24 h; iv, CBr₄, PPh₃, THF, room temp., 1 h; v, MeCOSK, MeCN-C₆H₆, reflux, 1 h; vi, K₂CO₃, MeOH-C₆H₆, room temp., 1 h; vii, NaH, Br(CH₂)₁₀Br, THF, reflux, 5 h; viii, MeCOSK, MeCN-C₆H₆, reflux, 3 h.



Scheme S2. Reagents and conditions. ix, K_2CO_3 , MeCN- C_6H_6 , room temp., 1 h; x, K_2CO_3 , MeCN, reflux, 24 h; xi, CBr_4 , PPh_3 , THF, room temp., 1 h; xii, MeCOSK, MeCN- C_6H_6 , room temp., 1 h.



Scheme S3. Reagents and conditions. xiii, K_2CO_3 , THF, room temp., 1 h; xiv, NaH, $\text{Br}(\text{CH}_2)_{10}\text{Br}$, THF, reflux, 4 h; xv, MeCOSK , $\text{MeCN}-\text{C}_6\text{H}_6$, reflux, 2 h; xvi, LiAlH_4 , THF, room temp., 1 h.

Spectral data for M-SH, D1-SH, DA1-SH, D2-SH, and DA2-SH.

M-SH: FT-IR (cm^{-1} , KBr) 2572 (S-H); ^1H -NMR (CDCl_3) δ 7.13-6.87 (m, 8H, ArH), 3.81 (t, 2H, NCH_2), 2.49 (q, 2H, SCH_2), 1.78 (q, 2H, NCH_2CH_2), 1.57 (q, 2H, SCH_2CH_2), 1.46-1.20 (m, 13H, CH_2 , SH). MS, m/z 371 (M^+).

D1-SH: ^1H -NMR (C_6D_6) δ 7.10-6.37 (m, 19H, ArH), 3.69 (t, 4H, OCH_2), 3.64 (t, 4H, NCH_2), 3.26 (d, 2H, CH_2SH), 1.88 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.49 (t, 1H, SH); ^{13}C -NMR (CDCl_3) δ 160.0, 145.1, 143.3, 128.3, 127.5, 122.6, 115.6, 106.9, 100.3, 65.4, 43.8, 29.1, 26.7. Exact mass calcd. for $\text{C}_{37}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_3$: 634.178. Found: 634.176.

DA1-SH: ^1H -NMR (C_6D_6) δ 7.16-6.30 (m, 19H, ArH), 3.69 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.50 (s, 2H, ArCH_2S), 2.37 (t, 2H, SCH_2), 2.19 (q, 2H, CH_2SH), 1.96-1.82 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.53 (m, 2H, SCH_2CH_2), 1.44-1.08 (m, 14H, CH_2), 1.11 (t, 1H, SH); ^{13}C -NMR (CDCl_3) δ 159.9, 145.0, 141.0, 128.3, 127.5, 127.2, 125.4, 122.6, 115.6, 108.0, 100.2, 65.4, 43.9, 34.5, 32.2, 31.5, 29.4, 29.2, 29.1, 29.0, 28.8, 28.3, 26.7, 24.6. Exact mass calcd. for $\text{C}_{47}\text{H}_{54}\text{N}_2\text{O}_2\text{S}_4$: 806.307. Found: 806.307.

D2-SH: ^1H -NMR (C_6D_6) δ 7.11-6.40 (m, 41H, ArH), 4.72 (s, 4H, CH_2O), 3.74-3.65 (m, 16H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.32 (d, 2H, CH_2SH), 1.88 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.53 (t, 1H, SH); ^{13}C -NMR (C_6D_6) δ 160.66, 160.62, 145.6, 143.9, 139.8, 127.9, 127.4, 126.0, 122.9, 115.9, 107.8, 106.4, 101.7, 101.4, 70.3, 65.5, 44.1, 29.5, 27.1. Exact mass calcd. for $\text{C}_{81}\text{H}_{72}\text{N}_4\text{O}_6\text{S}_5$: 1356.405. Found: 1356.403.

DA2-SH: ^1H -NMR (C_6D_6) δ 7.12-6.41 (m, 41H, ArH), 4.75 (s, 4H, CCH_2O), 3.75-3.65 (m, 16H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.55 (s, 2H, CCH_2S), 2.35 (t, 2H, SCH_2CH_2), 2.18 (q, 2H, CH_2SH), 1.88 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.51 (q, 2H, SCH_2CH_2), 1.40-1.06 (m, 15H, CH_2 , SH); ^{13}C -NMR (C_6D_6) δ 160.62, 160.58, 145.5, 141.8, 139.8, 127.9, 127.4, 125.9, 122.8, 115.9, 108.5, 106.4, 101.7, 101.4, 70.6, 65.5, 44.1, 37.1, 34.5, 32.0, 29.98, 29.97, 29.75, 29.72, 29.5, 29.3, 28.8, 27.0, 24.8. Exact mass calcd. for $\text{C}_{91}\text{H}_{92}\text{N}_4\text{O}_6\text{S}_6$: 1528.534. Found: 1528.528.

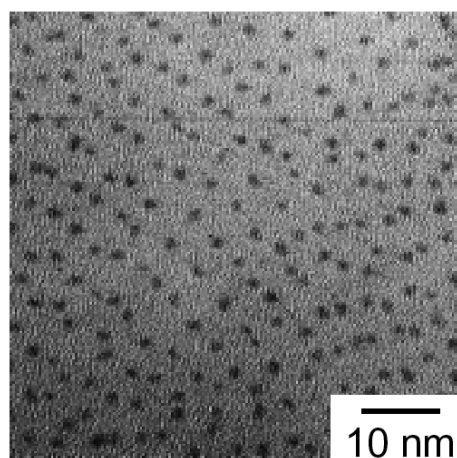


Figure S1. TEM micrograph of the other domain of DA2-Au.

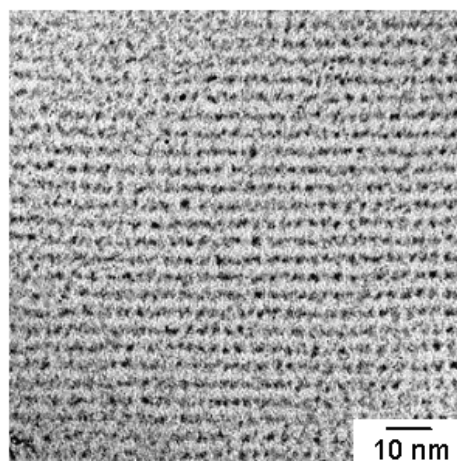


Figure S2. TEM micrograph at lower magnification of DA2-Au.