Electronic Supplementary Material (ESI) for Materials Advances.

Direct evidence of mesogenic dendrons with free void space by Brunauer-Emmett-Teller (BET) isotherms

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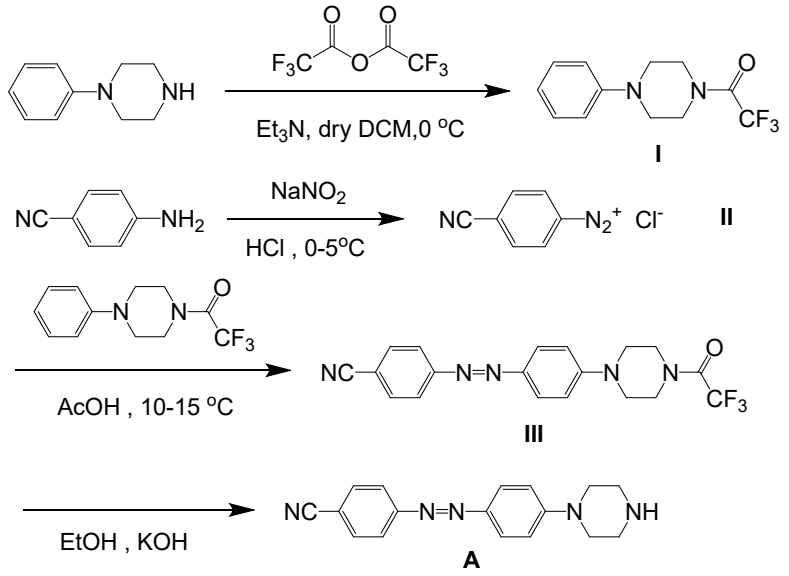
Supporting information

Experimental section

Synthesis of core **A**

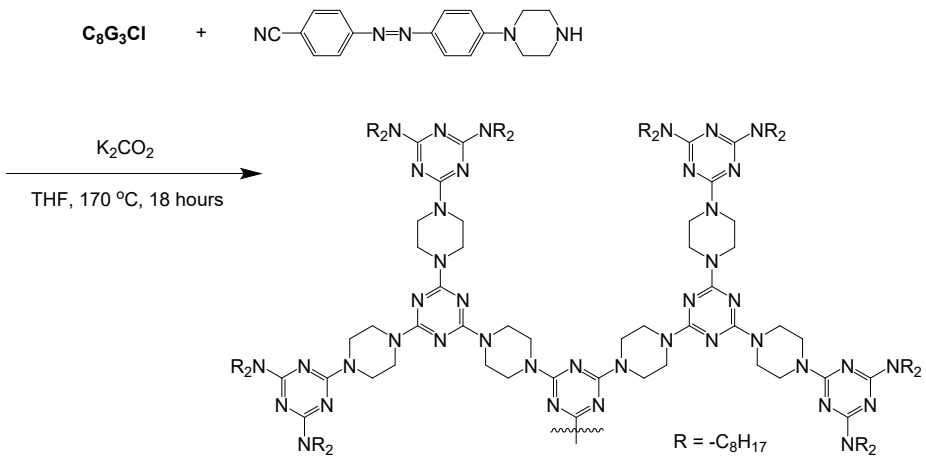


Compound **I** (2.58 g, 10.0 mmol), prepared according to the literature (Wilson, D. et. al., WO2007075895A2, 2007), was added to diazonium salt **II**, prepared from reaction of 4-aminobenzonitrile (0.50 g, 4.4 mmol) with Sodium nitrite (0.36 g, 5.2 mmol) in acetic acid solution (25 mL) and the resulting mixture was stirred at 5°C for 4 hours. Water (250 mL) was added and solid which had precipitated was filtered and dried under air. Recrystallization of the solid by dichloromethane and n-hexane (1:20), to give **III** in 72.4% (1.23 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.45 (t, *J* = 5.1, 4H, 2×CH_2), 3.79 (t, *J* = 5.1, 2H, 1×CH_2), 3.85 (t, *J* = 5.1, 2H, 1×CH_2), 6.96 (d, *J* = 9.0, 2H, 2×CH), 7.72 (d, *J* = 8.7, 2H, 2×CH), 7.88 (d, *J* = 8.7, 2H, 2×CH), 7.89 (d, *J* = 9.0, 2H, 2×CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ_C 42.6, 45.3, 47.3, 47.9, 112.8, 114.0, 116, 118.8, 122.3, 124.7, 132.3, 134.1, 145.8, 153.0, 154.9 ppm. MS cacld. for $C_{17}H_{16}N_5$ $[M\text{-}COCF3]^-$: 290.4; found 290.3.

A solution of potassium hydroxide (1.12 mg, 20.0 mmol) in ethanol (35 mL) was added to **III** (1.23 g, 3.2 mmol) and then refluxed for 4 hours. Solvent was removed at reduced pressure and the solid residue was extracted by dichloromethane and

water (1:2). The organic layer was dried over anhydrous magnesium sulfate and concentrated at reduced pressure to give compound **A** in 94.7 % yield (0.88 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.03-3.06 (m, 4H, 2×CH_2), 3.36-3.39 (m, 4H, 2×CH_2), 6.96 (d, *J* = 9.2, 2H, 2×CH), 7.76 (d, *J* = 8.5, 2H, 2×CH), 7.90 (2d, *J* = 9.2 and 8.5, 4H, 4×CH), ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ_C 46.1, 47.3, 47.5, 48.8, 112.6, 115.3, 119.1, 122.3, 125.0, 132.5, 134.2, 145.1, 154.4, 155.4 ppm. MS cacld. for $C_{17}H_{18}N_5$ $[M+H]^+$: 292.4; found 292.1.

Synthesis of dendron **1:**



A solution of **C_8G_3Cl** (0.60 g, 0.2 mmol) and core **A** (0.17 g, 0.6 mmol) were dissolved in tetrahydrofuran (5 mL). Potassium carbonate (1.0 g, 1.0 mmol) was then added, and the resulting mixture was heated at 110°C for 17 hours. The mixture was extracted with dichloromethane (50 mL) and dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure to give a solid, which was further purified by column (10x2.6 cm; eluates: CH_2Cl_2/ethyl acetate in a 50:1 ratio), to give dendron **1** in 37.8% yield (0.25 g) after recrystallization from dichloromethane and methanol (1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.89 (s, br., 48H, 16×CH_3), 1.29 (s, br., 160H, 80×CH_2), 1.59 (s, br., 32H, 16×CH_2), 3.46 (s, br., 36H, 18×CH_2), 3.80+3.83 (2s, 48H, 24×CH_2), 3.97 (s, br., 4H, 2×CH_2), 6.99 (d, *J* = 9.1, 2H, 2×CH), 7.77 (d, *J* = 8.5, 2H, 2×CH), 7.92 (d, *J* = 9.1,

2H, 2×CH), 7.93 (d, *J* = 8.5, 2H, 2×CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ_C 12.2, 13.7, 15.1, 21.4, 22.9, 24.5, 26.0, 27.0, 27.3, 27.6, 28.3, 29.7, 30.6, 31.2, 32.1, 33.1, 33.7, 43.3, 45.2, 47.1, 47.4, 112.6, 115.5, 119.1, 122.4, 125.1, 132.5, 134.2, 145.2, 155.4, 165.2, 165.6 ppm. MS cacld for $C_{190}H_{337}N_{46}$ $[M+H]^+$: 3266.01; found 3266.04. Elemental analysis calcd. for $C_{190}H_{336}N_{46}$: C 69.89; H 10.37; N 19.73; found C 69.80 H 10.08; N 19.60.

Synthesis of dendron **2**:

Dendron **2** (0.25 g, 40.2%) was obtained from the reaction of **C_8G_3Cl** (0.6 g, 0.2 mmol) with 3,3'-Iminodipropionitrile (0.074 g, 0.6 mmol) in a similar manner. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.86-0.90 (m, 48H, 16×CH_3), 1.28 (s, br., 168H, 84×CH_2), 1.59 (s, br., 32H, 16×CH_2), 3.46 (s, br., 32H, 16×CH_2), 3.79+3.83 (2s, 48H, 24×CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ_C 12.3, 13.6, 15.1, 21.4, 22.9, 24.5, 26.0, 27.0, 27.3, 27.6, 28.4, 29.7, 30.6, 31.3, 32.1, 33.1, 33.7, 41.6, 43.3, 45.2, 47.1, 47.4,118.8, 165.2, 165.6 ppm. MS cacld for $C_{179}H_{329}N_{44}$ $[M+H]^+$: 3097.81; found 3097.93. Elemental analysis calcd. for $C_{179}H_{328}N_{44}$: C 69.42; H 10.68; N 19.90; found C 69.35 H 10.46; N 19.69.

Figure S1. MALDI-TOF mass spectrometer characterization of dendrons **1** and **2**.

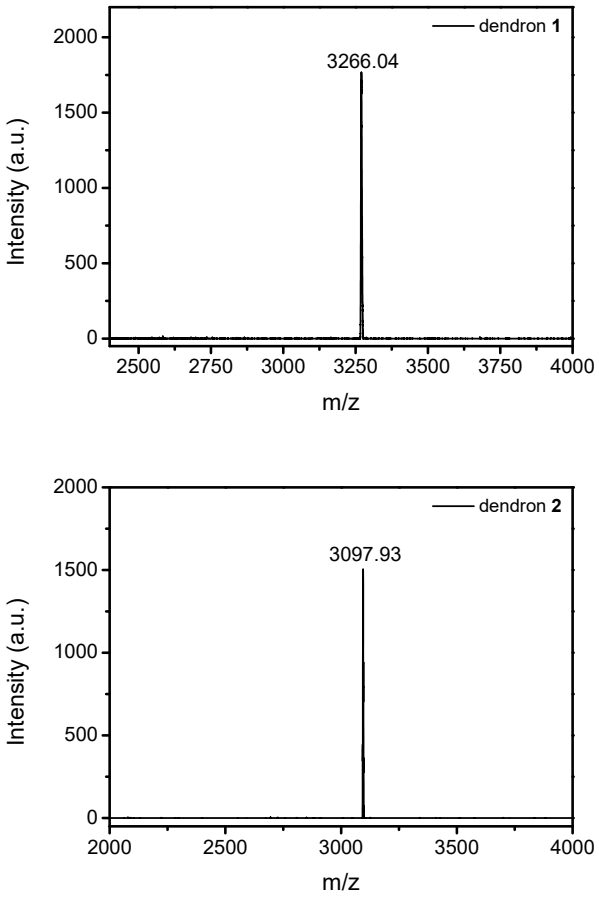


Figure S2. Thermo-gravimetric analysis of dendron **2** between 40 and 850°C under nitrogen at the heating rate of 10 °C/min.

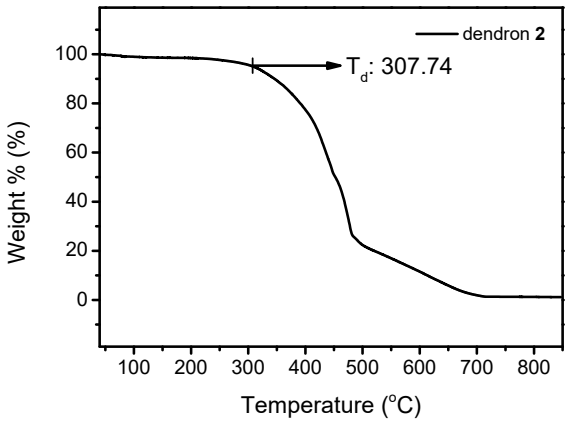


Figure S3. The BET isotherms of dendron **2** at 195K.

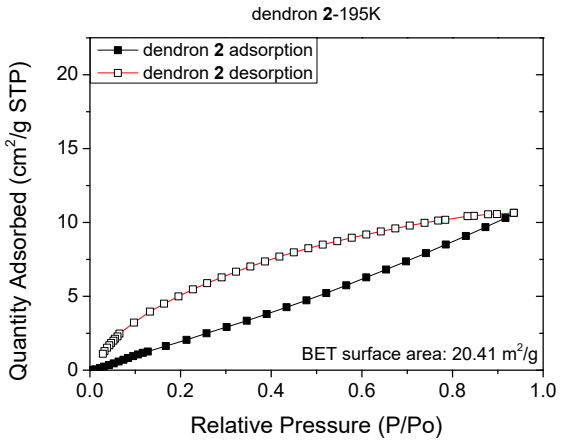
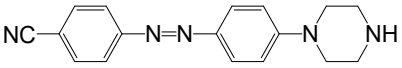


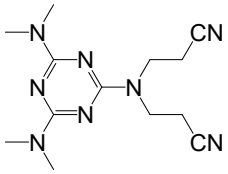
Table 1. Computational detail

The geometric optimizations and frequencies of core **A** and **B** were calculated by density functional theory (DFT) at the B3LYP/6-31G** level with Gaussian 09 Program.

Core **A**: 

Dipole moment: 8.7154 Debye

Symbol	X	Y	Z	Symbol	X	Y	Z
N	7.154378	0.196598	0.014803	C	-7.68035	-0.11732	-0.02409
C	6.311411	1.203783	-0.62601	N	-8.83895	-0.22779	-0.03705
C	4.888485	1.303319	-0.05107	H	7.362542	0.48648	0.969458
N	4.24868	-0.0124	-0.03652	H	6.239995	0.952115	-1.69157
C	5.061503	-1.03419	0.638129	H	6.79966	2.181262	-0.55228
C	6.472261	-1.09688	0.040294	H	4.30334	1.977428	-0.68108
C	2.857446	-0.10623	-0.00513	H	4.924859	1.74035	0.964156
C	2.212514	-1.35766	-0.15184	H	4.580236	-2.00848	0.554
C	0.831979	-1.44938	-0.162	H	5.131713	-0.79963	1.716217
C	0.024642	-0.30709	-0.02942	H	6.407111	-1.46474	-0.99152
C	0.653365	0.942455	0.120533	H	7.077885	-1.81161	0.607559
C	2.033378	1.040284	0.135731	H	2.797543	-2.2583	-0.2951
N	-1.35938	-0.52159	-0.05482	H	0.342725	-2.41022	-0.2872
N	-2.07361	0.519916	0.050719	H	0.035944	1.825271	0.241242
C	-3.4667	0.27318	0.02324	H	2.480107	2.01492	0.287563
C	-4.28382	1.406028	0.153499	H	-3.80546	2.37324	0.265205
C	-5.66739	1.286039	0.139384	H	-6.2993	2.161697	0.24056
C	-6.25434	0.017935	-0.00789	H	-5.89757	-2.09735	-0.25411
C	-5.43586	-1.12211	-0.14009	H	-3.41231	-1.86142	-0.22511
C	-4.05634	-0.9962	-0.12458				

Core **B**: 

Dipole moment: 7.8452 Debye

Symbol	X	Y	Z	Symbol	X	Y	Z
N	1.414032	-0.70563	-0.30218	C	-2.10437	-0.63659	-0.24363
C	1.663863	-2.0774	-0.7173	N	-0.85832	-1.1455	-0.36904
C	2.537536	0.189875	-0.05582	N	-1.5529	2.732102	0.610662
C	1.551209	-3.10406	0.435005	N	-3.15286	-1.48545	-0.45595
C	2.544175	-2.89134	1.489353	C	-0.47329	3.667043	0.88007
N	3.338005	-2.70117	2.315168	C	-2.89652	3.262636	0.76407
C	2.847055	1.073801	-1.28942	C	-2.96253	-2.87035	-0.84775
C	3.978167	1.972988	-1.05869	C	-4.53362	-1.05303	-0.32705
N	4.876116	2.680327	-0.85552	H	-0.56759	4.071076	1.896164
H	0.937052	-2.36048	-1.48101	H	0.482503	3.159628	0.783553
H	2.662846	-2.12543	-1.15917	H	-0.5098	4.508499	0.175999
H	2.304963	0.83082	0.794976	H	-3.0783	3.560128	1.805446
H	3.409246	-0.41244	0.207478	H	-3.02394	4.149707	0.130896
H	0.546804	-3.03469	0.863426	H	-3.62134	2.506062	0.476111
H	1.674279	-4.11795	0.035839	H	-1.90091	-3.07506	-0.95615
H	3.066781	0.44783	-2.16198	H	-3.38717	-3.54604	-0.0934
H	1.958392	1.669134	-1.52079	H	-3.46883	-3.06861	-1.80165
C	0.121489	-0.24988	-0.17201	H	-5.049	-1.10955	-1.29528
N	-0.03434	1.04459	0.136495	H	-5.06662	-1.7024	0.379037
C	-1.32182	1.432102	0.269845	H	-4.56016	-0.0285	0.033759
N	-2.38934	0.635513	0.081317				