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SUPPORTING INFORMATION

Encapsulation of Functional Moieties within Branched Star Polymers: Effect of Chain Length and Solvent on Site Isolation

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General Methods: Hydroxy-terminated and coumarin-terminated star polymers **1-3** as well as tetrakis(3,5-bis(2',2'-dihydroxymethylpropionyloxy)phenyl)porphyrin were synthesized as described previously.[1] Coumarin-3-carboxylic acid chloride was prepared prior to use from coumarin 3-carboxylic acid using oxalyl chloride and catalytic amounts of DMF in CH_2Cl_2. ε-Caprolactone (99%) was distilled over CaH_2. Tin(II) 2-ethylhexanoate (Aldrich) as well as 1-pyrenemethanol were used as received. ^{1}H NMR spectra were recorded on a Bruker AMX 300 (300 MHz) spectrometer with TMS as internal standard. The number average molecular weights of the polymers **1-3**, **7**, and **8** were calculated from the ratio of the CH_2O methylene proton signals (δ = 4.06 ppm) and the CH_2OH methylene proton signals (δ = 3.65 ppm) in the ^{1}H NMR spectra. PGSE NMR experiments were carried out on a Bruker DRX 500 (500 MHz) spectrometer equipped with a microprocessor-controlled gradient unit and a 5 mm multinuclear probe. A BPP-LED pulse sequence[2] (Bruker's pulse program "ledbpgs2s") with a gradient pulse width δ = 3 ms and a delay between the gradient pulses Δ = 100 ms was used. The gradient strength g was calibrated using the diffusion coefficient of HDO in D_2O as a reference.[3] Measurements were performed at 298±1 K in $CDCl_3$ and CD_3CN, respectively (~ 0.1 mM polymer concentrations). Linear fitting ($R > 0.99$) according to the Stejskal-Tanner equation:[4] $\ln(I/I_0) = g^2\gamma^2\delta^2(\Delta-\delta/3)D$ using the individual polymer peak areas of the FT-NMR spectra gave the diffusion coefficients D, from which the hydrodynamic radii R_H were derived using the Stokes-Einstein equation: $R_H = (k_BT)/(6\pi\eta D)$, with $\eta_{298K}(CHCl_3)$ = 0.542 mPas and $\eta_{298K}(CH_3CN)$ = 0.345 mPas. GPC measurements were performed on a Waters 150CV plus GPC system equipped with a differential refractive index detector and a M486 UV detector (254 nm detection

wavelength) using THF as the mobile phase at 45 °C and a flow rate of 1 mL/min. The samples were separated through four 5 μm PL Gel columns (Polymer Laboratories) with porosities of 100 Å, 500 Å, 1000 Å and mixed C. The columns were calibrated with 18 narrow polydispersity polystyrene samples. For the light scattering measurements, a system consisting of a Waters M590 solvent delivery system equipped with an OPTILAB DSP interferometric refractometer, a DAWN® DSP laser photometer (488 nm laser wavelength) with 488 ±1 nm UV filters on detectors 7, 9, and 11, dn/dc, and Wyatt's Astra software was used. Separation was achieved in THF or $CHCl_3$ on a set of two Polymer Standard SVD linear columns (8 x 300 mm, 5 μm) at 45 °C and 1.0 ml/min flow rate. MALDI-TOF mass spectra were measured on a Perseptive Biosystems Voyager-DE spectrometer in delayed extraction mode and an acceleration voltage of 20 keV. Samples were prepared using a 1:20 ratio of analyte (5 mg/mL in THF) to matrix solution (*trans*-indoleacrylic acid, 10 mg/mL in THF). Absorption spectra were recorded in chloroform or acetonitrile on a Cary 50 UV-Visible Spectrophotometer. Fluorescence spectra were measured of degassed solutions (1cm cells, $OD_{max} < 0.1$) using an ISA/SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. The samples **3a-e** and **4** were excited at 350 nm, slit widths were set to 2 nm bandpass for excitation and 5 nm bandpass for emission. Correction for variations in lamp intensity over time and wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. The quantum yields for energy transfer were calculated from the ratio of the integrated, for absorbance corrected emission spectra of **3a-e** and model compound **4**. To determine the I_1:I_3 ratio, pyrene core stars **7a-d** and **8a-d** were excited at 345 nm, and slit widths were set to 0.5 nm for both excitation and emission.

Preparation of Coumarin-labeled Porphyrin Core Dendrimer 3e: Tetrakis(3,5-bis(2',2'-dihydroxymethylpropionyloxy)phenyl)porphyrin was dissolved (25 mg, 0.015 mmol) in 0.3 mL of pyridine. 4-Dimethylaminopyridine (DMAP, 1 mg, 0.007 mmol) and coumarin-3-carboxylic acid chloride (75 mg, 0.36 mmol) dissolved in 0.5 mL CH_2Cl_2

were added, and it was stirred at room temperature overnight. After evaporation of the solvent, the crude product was purified by flash chromatography (silica gel, 5 % MeOH in CH_2Cl_2) to give **3e** as a brownish powder in 83 % yield. **3e**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 8.88 (broad s, 8 H, porph *β*-H), 8.43 (broad s, 16 H, cou =CH-), 7.91 (broad s, 8 H, porph Ar-*o,o'*-H), 7.83 (s, 4 H, Ar-*p*-H), 7.33-7.26 (m, 32 H, cou Ar-H), 6.92-6.96 (m, 32 H, cou Ar-H), 4.78 (d, ^2J (H,H) = 12 Hz, 32 H, CH_2O), 1.66 (s, 24 H, CH_3), -3.44 (broad s, 2 H, NH); MALDI-TOF MS (*trans*-3-indoleacrylic acid matrix): *m/z* = 4424 (calcd for $C_{244}H_{158}N_4O_{80}^+$ 4426); Anal. C: 66.40, H: 3.65, N: 1.42 (calcd C: 66.22, H: 3.60, N: 1.27); UV/vis ($CHCl_3$) λ_{max} (ε) 295 nm (456000), 335 nm (267000), 420 nm (519000), 513 nm (22300), 546 nm (7700), 589 nm (6500), 644 nm (3200).

Preparation of Model Compound 4: Model compound **4** was prepared from known 1,1,1-tris(4-hydroxyphenyl)ethane-core star polymer,[5] which was dissolved (1 equiv.) in 60 equiv. pyridine and dry CH_2Cl_2. 1 Equiv. DMAP and 50 equiv. coumarin-3-carboxylic acid chloride dissolved in CH_2Cl_2 were added, and it was stirred at room temperature overnight. After evaporation of the solvent, the crude product was dissolved in the minimum amount of THF and precipitated into cold methanol. Extensive washing with methanol and drying under vacuum gave polymer **4** as a white powder in quantitative yield. **4**: $MW_{(NMR)}$ = 14,900, $PD_{(GPC)}$ = 1.11; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.54 (broad s, 6 H, cou =CH-), 7.66-7.63 (m, 12 H, cou Ar-H), 7.38-7.32 (m, 12 H, cou Ar-H), 7.11-6.94 (m, 12 H, Ar-H), 4.36 (t, ^3J (H,H) = 6 Hz, 12 H, CH_2O_2C-cou), 4.06 (t, ^3J (H,H) = 6 Hz, poly, CH_2O), 2.34 (t, ^3J (H,H) = 6 Hz, poly, CH_2CO), 1.71-1.60 (m, poly, CH_2CH_2), 1.43-1.34 (m, poly, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 173.43, 173.40, 163.01, 156.50, 155.08, 148.46, 134.21, 129.43, 124.70, 118.22, 117.79, 116.66, 65.57, 64.00, 46.63, 33.99, 33.75, 28.22, 28.13, 25.40, 25.36, 24.45, 24.34; UV/vis ($CHCl_3$) λ_{max} 294 nm, 335 nm; λ_{emi} 418 nm.

General Procedure for Preparation of Pyrene Core Initiators 5 and 6:[1] 1 Equiv. of the respective alcohol was dissolved in the minimum amount of dry THF, 1.2 equiv. of isopropylidene-2,2-bis(methoxy)propionic acid[6] per hydroxyl group and 0.2 equiv. of 4-dimethylaminopyridinium tosylate (DPTS) per hydroxyl group were added. Then, a ~ 1.5 M solution of 1.2 equiv. 1,3-diisopropylcarbodiimide per hydroxyl group in CH_2Cl_2 was added and it was stirred overnight. The reaction mixture was filtered through a glass

filter, the residue rinsed with a small amount of CH_2Cl_2, and the filtrate evaporated *in vacuo*. Flash chromatography (silica gel, gradient from 100 % hexanes to 30 % ethyl acetate in hexanes) gave the acetonide-protected intermediate products as slightly yellow viscous oils that slowly crystallized. The respective acetonides were dissolved in the minimum amount of THF, some methanol and 2 M H_2SO_4 (~ 1 ml per 0.1 mmol of acetonide group) added. After complete deprotection as judged by TLC, excess ammonia in methanol (1:1) was added. The solvent was removed *in vacuo*, the resulting residue dissolved in THF, filtered, and evaporated to give the free alcohols as white powders.

5: This was prepared as above from **5(acetonide)** (98 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.27-7.99 (m, 9 H, Ar-H), 5.89 (s, 2 H, $ArCH_2O$), 3.92 (dd, ^2J (H,H) = 12 Hz, ^3J (H,H) = 6 Hz, 2 H, CH_2O), 3.71 (dd, ^2J (H,H) = 12 Hz, ^3J (H,H) = 6 Hz, 2 H, CH_2O), 2.86 (t, ^3J (H,H) = 6 Hz, 2H, OH), 1.03 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 175.8, 131.8, 131.2, 130.6, 129.5, 128.3, 128.3, 127.9, 127.7, 127.3, 126.1, 125.6, 125.5, 124.9, 124.6, 124.6, 122.6, 68.5, 65.6, 49.4, 17.1; Anal. C: 75.68, H: 5.66 (calcd C: 75.84, H: 5.79); UV/vis ($CHCl_3$) λ_{max} (ε) 267 nm (24500), 278 nm (44200), 315 nm (11700), 329 nm (27600), 345 nm (40500). **5(acetonide)**: This was prepared as above from 1-Pyrenemethanol and isopropylidene-2,2-bis(methoxy)propionic acid (91 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.26-7.99 (m, 9 H, Ar-H), 5.89 (s, 2 H, $ArCH_2O$), 4.22 (d, ^2J (H,H) = 12 Hz, 2 H, CH_2O), 3.64 (d, ^2J (H,H) = 12 Hz, 2 H, CH_2O), 1.41 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 174.2, 131.7, 131.2, 130.7, 129.4, 128.7, 128.1, 127.8, 127.6, 127.3, 126.1, 125.5, 125.4, 124.9, 124.6, 124.5, 122.9, 98.1, 66.0, 65.3, 42.1, 24.7, 22.6, 18.6; Anal. C: 77.43, H: 6.31 (calcd C: 77.30, H: 6.23).

6: This was prepared as above from **6(acetonide)$_2$** (99 %). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, TMS): δ 8.35-8.08 (m, 9 H, Ar-H), 5.87 (s, 2 H, $ArCH_2O$), 4.64 (t, ^2J (H,H) = 5 Hz, 4 H, OH), 4.18 (dd, ^2J (H,H) = 12 Hz, ^3J (H,H) = 11 Hz, 4 H, CH_2O), 3.46 (dd, ^2J (H,H) = 11 Hz, ^3J (H,H) = 5 Hz, 4 H, CH_2O), 3.41 (dd, ^2J (H,H) = 11 Hz, ^3J (H,H) = 5 Hz, 4 H, CH_2O), 1.22 (s, 3 H, CH_3), 0.97 (s, 6 H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): 174.07, 172.33, 131.11, 130.66, 130.17, 128.86, 128.84, 128.04, 127.67, 127.60, 127.26, 126.36, 125.55, 125.48, 124.64, 123.94, 123.73, 122.97, 64.95, 64.91, 63.69, 50.25, 46.50, 17.18, 16.63; Anal. C: 66.38, H: 6.41 (calcd C: 66.20, H: 6.25); UV/vis ($CHCl_3$)

λ_{max} (ε) 267 nm (24600), 278 nm (44800), 315 nm (11800), 329 nm (28400), 345 nm (41600). **6(acetonide)$_2$**: This was prepared as above from **5** and isopropylidene-2,2-bis(methoxy)propionic acid (85 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.31-8.01 (m, 9 H, Ar-H), 5.90 (s, 2 H, $ArCH_2O$), 4.32 (dd, ^2J (H,H) = 17Hz, ^2J (H,H) = 12 Hz, 4 H, CH_2O), 3.98 (ddd, ^2J (H,H) = 17Hz, ^2J (H,H) = 12 Hz, ^3J (H,H) = 2 Hz, 4 H, CH_2O), 3.44 (d, ^2J (H,H) = 12 Hz, ^3J (H,H) = 2 Hz, 4 H, CH_2O), 1.32 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 173.44, 172.48, 131.88, 131.14, 130.65, 129.59, 128.38, 128.31, 127.93, 127.90, 127.27, 125.56, 125.52, 124.89, 124.61, 124.52, 122.68, 97.97, 65.81, 65.74, 65.50, 65.32, 47.01, 41.88, 24.87, 22.09, 18.26, 17.67; Anal. C: 69.55, H: 7.00 (calcd C: 69.07, H: 6.71).

General Procedure for Preparation of Pyrene Core Star Polymers 7 and 8: A procedure similar to the one reported by Trollsås, Hedrick, and coworkers was used.[5,7,8] The carefully dried initiators **5** and **6** were dissolved in ε-caprolactone and the temperature raised to 105 °C before a catalytic amount of Tin(II) 2-ethylhexanoate was added. The molar initiator/monomer ratio was determined as the product of the degree of polymerization and the number of initiating sites. The molar amount of the catalyst was ~ 1/200. The reaction mixture was heated for 16 h, diluted with THF, and precipitated into cold methanol to give white powders in almost quantitative yields. **7**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.31-8.04 (m, 9 H, Ar-H), 5.89 (s, 2 H, $ArCH_2O$), 4.06 (t, ^3J (H,H) = 6 Hz, poly, CH_2O), 3.95 (t, ^3J (H,H) = 6 Hz, 4 H, CH_2OCO), 3.65 (t, ^3J (H,H) = 6 Hz, 4 H, CH_2O), 2.34 (t, ^3J (H,H) = 6 Hz, poly, CH_2CO), 1.71-1.60 (m, poly, CH_2CH_2), 1.43-1.33 (m, poly, CH_2), 1.24 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 173.59, 173.45, 173.40, 131.69, 131.02, 130.47, 129.48, 128.39, 128.16, 128.10, 127.83, 127.20, 126.08, 125.52, 125.44, 124.69, 124.42, 124.40, 122.72, 64.00, 63.91, 62.38, 46.37, 34.09, 33.97, 33.41, 32.19, 28.20, 28.04, 25.38, 25.18, 24.43, 17.63; UV/vis ($CHCl_3$) λ_{max} (rel. intensity) 267 nm (0.56), 287 nm (1.00), 315 nm (0.27), 329 nm (0.63), 345 nm (0.93). **8**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.30-8.05 (m, 9 H, Ar-H), 5.89 (s, 2 H, $ArCH_2O$), 4.06 (t, ^3J (H,H) = 6 Hz, poly, CH_2O), 3.64 (t, ^3J (H,H) = 6 Hz, 8 H, CH_2O), 2.31 (t, ^3J (H,H) = 6 Hz, poly, CH_2CO), 1.71-1.60 (m, poly, CH_2CH_2), 1.44-1.33 (m, poly, CH_2), 1.24 (s, 3 H, CH_3), 1.04 (s, 6 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 173.53, 173.33, 172.56, 171.82, 131.76, 130.99, 130.46, 129.43, 128.31, 128.10, 127.87,

127.85, 127.18, 126.09, 125.56, 125.46, 124.69, 124.53, 124.39, 122.51, 64.71, 64.10, 63.95, 62.23, 46.73, 46.15, 34.08, 33.94, 33.55, 32.19, 28.33, 28.18, 25.37, 25.21, 24.58, 24.42, 24.22, 17.43, 17.36; UV/vis ($CHCl_3$) λ_{max} (rel. intensity) 267 nm (0.55), 287 nm (1.00), 315 nm (0.27), 329 nm (0.62), 345 nm (0.93).

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