Supporting Information

Controlled Synthesis of Conjugated Polymers in Dendritic

Mesoporous Silica Nanoparticles

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Materials and Methods Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. 2-bromo-3-hexylthiophene was purified by vacuum distillation at 120 °C before polymerization. N,N-dimethylacetamide (DMAc) and diisopropylethylamine (DIPEA) were distilled over calcium hydride before use.

Methods

¹H NMR (600 MHz) spectra were recorded in chloroform-d (CDCl₃) on a Bruker ASCEND 600 NMR spectrometer. High-resolution transmission electron microscopic (HR-TEM) images were obtained on a JEM-2100 microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Scanning transmission electron microscopic (STEM) images were obtained on a Talos F200X TEM at an acceleration voltage of 200 kV. Fluorescence spectra of conjugated polymers were obtained on Lumina (Thermo fisher, USA) and UV-vis spectra were collected by an Evolution 201 UV spectrophotometer (Thermo fisher, USA) at 25 °C. The number-averaged molecular weight (M_n) and the polydispersity index (PDI) of conjugated polymers were determined on a WATERS 1515 equipped with a series of PS gel columns, using THF as an eluent at 40 °C with a PS calibration. The palladium contents in the catalysts or in the polymeric products were analyzed by ICP-AES on a Thermo Elemental IRIS 1000 instrument. Mass spectrometric experiments (MALDI-TOF) of conjugated polymers were performed on a Mass spectrometer 4800 plus MALDI-TOF/TOF MS Analyzer (AB Sciex, USA) equipped with a Nd:YAG laser emitting at 355 nm, and operated at an accelerating voltage of 20 kV in reflection mode. 4000 series Explorer and DATA Explorer (AB Sciex, USA) were used for data acquisition and processing. The extraction delay time was set to 450 ns. All mass spectra were collected by averaging the signals of 500 individual laser shots. The possibility coefficients chosen for simulated populations of each polymer chain in Figure 2c were: from P_1 to P_9 [1, 0.98, 0.93, 0.84, 0.7, 0.37, 0.22, 0.12, 0.08], and P_x were set to 0 when $x > 9^1$. The high solution P3HT mass spectra were simulated by using pyMacroMS² (Figure S6).

Synthesis of Pd@DMSNs catalysts

Preparation of DMSNs

According to the reported literature³, a mixture of cetyl-trimethylammonium tosylate (CTATos, 1.92 g), triethanolamine (0.347 g) and deionized water (100 ml) was stirred at 80 °C for 1 h. After the surfactant was completely dissolved, tetraethyl-orthosilicate (TEOS, 14.68 ml) was quickly added into the mixture, then stirred vigorously at 80 °C for another 2 h. The products were

filtered, washed three times with deionized water, and dried overnight in an oven at 80 °C under vacuum. In order to functionalize DMSNs with amino groups, the surfactant was removed by calcination at 550 °C for 6 h in a continuous air flow.

Preparation of DMSNs-NH₂

In a 100 ml round-bottom flask, a mixture of DMSNs (2.0 g), 3-aminopropyltriethoxysilane (APTES, 6.67 ml), and toluene (25 ml) was refluxed for 48 h. The mixture was filtered, washed with acetone and chloroform for three times respectively, and dried overnight in an oven at 60 °C under vacuum to yield the final product.

Preparation of Pd@DMSNs

DMSNs-NH₂ (100 mg) was dispersed in deionized water (10 ml) and the mixture was sonicated for 15 min, then stirred vigorously at room temperature for 10 min. Then, H₂PdCl₄ solution (0.6 ml, 10 mM in H₂O) was added dropwise and further sonicated for 15 min, followed by stirring for 2 h. Freshly prepared NaBH₄ solution (1 ml, 1 M in H₂O) was added dropwise to the mixture and further stirred for 2 h. The product was collected by centrifugation, washed three times with water and ethanol respectively, and dried overnight at 80 °C under vacuum.

General procedure for the CSGP of conjugated polymers in Pd@DMSNs.



A mixture of 2-bromo-3-hexylthiophene (199.5 μ l, 1.0 mmol), Pd@DMSNs (5 mg, 0.033 % Pd), pivalic acid (102 mg, 1.0 mmol), K₂CO₃ (415 mg, 3.0 mmol) and N,N-dimethylacetamide (DMAc, 2 ml) was added to a 10 ml sealed tube. After three freeze-pump-thaw cycles, the tube was sealed under nitrogen atmosphere and stirred at 120 °C for 120 h. After cooled to room temperature, the mixture was washed with THF (20 ml × 3). Then the THF solution was concentrated by evaporating and later added dropwise into stirred methanol (80 ml). The precipitate was rinsed with methanol for three times and dried under vacuum at room temperature overnight to obtain P3HT (129 mg, 78 %, denoted as **P1**). When a higher Pd loading (0.33%) was applied, the polymerization was complete in 15 h to give P3HT in 87% yield with similar molecular weight and PDI value.

Other conjugated polymers (**P2-P10**) were synthesized following a similar procedure that was briefly described below.



P2¹: 9,9-Dioctyl-2,7-dibromofluorene (126.4 mg, 0.23 mmol), 3,4-ethylenedioxythiophene (24.6 μ l, 0.23 mmol), Pd@DMSNs (5 mg, 0.072 % Pd), pivalic acid (23.5 mg, 0.23 mmol), KOAc (136 mg, 1.38 mmol) and DMAc (2 ml) were used during polymerization. The polymerization was carried out at 120 °C for 120 h to yield the product (88 mg, 73 %).



P3: 1,4-Diiodo-2,5-bis(hexyloxy)benzene^{4,5} (106.0 mg, 0.2 mmol), 3,4ethylenedioxythiophene (21.4 μ l, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 % Pd), pivalic acid (20.4 mg, 0.2 mmol), K₂CO₃ (165.6 mg, 1.2 mmol) and DMAc (2 ml) were used during polymerization. The polymerization was carried out at 100 °C for 120 h to yield the product (72 mg, 76 %).



P4: 2,7-Dibromo-9,9'-spiro-bifluorene (23.8 mg, 0.05 mmol), 4,7-bis(3,4dimethoxythiophen-2-yl) benzothiadiazole⁶ (21.7 mg, 0.05 mmol), Pd@DMSNs (10 mg, 0.66 % Pd), pivalic acid (5.1 mg, 0.05 mmol), K₂CO₃ (41.4 mg, 0.3 mmol) and DMAc (1 ml) were used during polymerization. The polymerization was carried out at 120 °C for 10 h and reprecipitated into ethyl acetate to yield the product (32 mg, 86%).



P5: 1,4-Diiodo-2,5-bis(2-ethylhexyloxy)benzene^{7,8} (117.3 mg, 0.2 mmol), 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (66.0 mg, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 %

Pd), K₂CO₃ (165.6 mg, 1.2 mmol) and DMAc (2 ml) were used during polymerization. The polymerization was carried out at 100 °C for 120 h to yield the product (52 mg, 63 %).



P6: 9,9-Dioctyl-2,7-dibromofluorene (109.7 mg, 0.2 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (128.5 mg, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 % Pd), K₂CO₃ (165.6 mg, 1,2 mmol) and DMAc (2 ml) were used during polymerization. The polymerization was carried out at 120 °C for 120 h to yield the product (116 mg, 75 %).



P7: 1,4-Diiodo-2,5-bis(hexyloxy)benzene (159.1 mg, 0.3 mmol), 2,1,3-Benzothiadiazole-4, 7-bis(boronic acid pinacol ester) (116.4 mg, 0.3 mmol), Pd@DMSNs (50 mg, 0.55 % Pd), K₂CO₃ (248.4 mg, 1.8 mmol) and DMAc (2 ml) were used during polymerization. The polymerization was carried out at 100 °C for 24 h to yield the product (71 mg, 56 %).



P8: 1,4-diethynylbenzene (25.2 mg, 0.2 mmol), 9,9-dioctyl-2,7-dibromofluorene (109.7 mg, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 % Pd), DIPEA (0.21 ml, 1.2 mmol) and DMAc (1 ml) were used during polymerization. The polymerization was carried out at 80 °C for 120 h to yield the product (59 mg, 58 %).



P9: 1,4-Diethynylbenzene (25.2 mg, 0.2 mmol), 1,4-diiodobenzene (66.0 mg, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 % Pd), DIPEA (0.21 ml, 1.2 mmol) and DMAc (1 ml) were used during polymerization. The polymerization was carried out at 60 °C for 120 h to yield the product (26 mg, 67 %).



P10: 2,5-bis(trimethylstannyl)thiophene (82.0 mg, 0.2 mmol), 2,5-dibromo-hexylthiophene (42.9 μ l, 0.2 mmol), Pd@DMSNs (5 mg, 0.082 % Pd), and DMAc (1 ml) were used during polymerization. The polymerization was carried out at 120 °C for 120 h to yield the product (38 mg, 77 %).

General procedure for the convensional SGP of conjugated polymers

The polymerizations were conducted with $Pd(PPh_3)_2Cl_2(10 \text{ mg})$ as the homogeneous catalyst. The procedures of classical SGP are similar with CSGP as mentioned above. The reaction time of classical SGP of P1, P2, P3, P4, P5, P6, P7, P8, P9 and P10 were set as 1.5 h, 2 h, 3 h, 3 h, 3 h, 1 h, 0.5 h, 1.5 h, 1 h and 0.5 h, respectively. It should be noted that the reaction times of the classical SGPs have also be prolonged to 24 h (or even longer) according to literature procedures. However, the formation of large amounts of precipitate made the fair comparison between classical SGP and CSGP impossible. Since the Flory's "equal reactivity" principle only applies where monomer, oligomers and all the polymer segments are well soluble in reaction mixture, the formation of any inhomogeneous species (like high polymers) would make the polymerization unpredicable and difficult to reproduce. Therefore, the reaction time for each classical SGP was set right before significant formation of precipitate.

Procedure for the Recycling and Reusing Study of Pd@DMSNs Catalysts

The polymerization was carried out under the same reaction conditions as described above for **P1** with 0.33% Pd loading and 15 h of polymerization time. After each polymerization, the catalysts were washed with THF (20 ml × 6) and water (20 ml × 3), dried overnight at 80 °C under vacuum and then subjected for the next cycle. The catalysts were reused for 3 more cycles with no obvious deterioration on the catalytic activity or control over the molecular weight of the products.



Figure S1. TEM images of Pd@DMSNs.



Figure S2. STEM images of Pd@DMSNs.



Figure S3. N₂ physisorption isotherms of the DMSNs (a) and their corresponding pore size distribution curve calculated by the BJH method (b).



Figure S4. Particle size distribution of Pd in Pd@DMSNs as measured with TEM.



Figure S5. Optical (left) and fluorescence (right) images ($\lambda_{ex} = 365 \text{ nm}$) of conjugated mesopolymer powders. (a, b) P2, (c, d) P3, (e, f) P4, (g, h) P5, (i, j) P6, (k, l) P7, (m, n) P8, (o, p) P9, (q, r) P10.



Figure S6. UV-Vis absorption spectra (a, 1 μ g/ml) and fluorescence emission spectra of conjugated polymers in THF solutions (b, 1 μ g/ml, $\lambda_{ex} = 365$ nm, except for P5, P6, P8, and P9, $\lambda_{ex}=330$ nm). Optical images (c) and fluorescence images (d) of the conjugated polymer solutions in THF (2 mg/ml, $\lambda_{ex}=365$ nm).



Figure S7. SEM images of drop-casted P2 thin-film.

Experiment P1

Processing parameters

mzRar	nge	mzOffset	ppmDev	resolution	minRelAbu	ndance
[500, 3000]		0.0	100	1500	0.0)1
	endg	proupPairs	monomers	adduction	charge	
	HH		3HT	+	1	
HBr		HBr				
BrBr						

Matching overview



Experimental vs. calculated spectrum



Identified species

Polymer co	omposition		Matched peaks					
				Most abundant	m/z	m/z	Δ	
Monomers	Endgroups	Formula & ion	Amount	isotope	(exp+offset)	(calc)	(ppm)	
[5]	HH	H72C50S5	0.04	832.4232	832.4283	832.4232	6.10	
					833.4273	833.4263	1.21	
[5]	HBr	H71Br1C50S5	0.13	912.3323	910.3452	910.3337	12.62	
					911.3445	911.3368	8.49	
					912.3453	912.3323	14.25	
					913.3541	913.3348	21.14	
					914.3324	914.3319	0.50	
[6]	HH	H86C60S6	0.16	998.5048	998.5175	998.5048	12.64	
					999.5135	999.5079	5.57	
					1000.5157	1000.5056	10.13	

Polymer co	omposition				Mate	ched peaks	
				Most abundant	m/z	m/z	Δ
Monomers	Endgroups	Formula & ion	Amount	isotope	(exp+offset)	(calc)	(ppm)
701					1001.5287	1001.5059	22.82
[6]	HBr	H85Br1C60S6	0.53	1078.4142	1076.4325	1076.4153	15.93
					1077.4272	1077.4184	8.18
					1078.4261	1078.4142	11.03
					1079.4299	1079.4164	12.55
					1080.4220	1080.4140	7.38
					1081.4144	1081.4144	0.06
[7]	HH	H100C70S7	0.23	1164.5865	1164.5938	1164.5865	6.27
					1165.5959	1165.5896	5.46
					1166.5958	1166.5876	7.07
					1167.6074	1167.5880	16.61
					1168.5864	1168.5866	0.18
[7]	HBr	H99Br1C70S7	0.83	1244.4962	1242.5046	1242.4970	6.18
					1243.5060	1243.5001	4.73
					1244.5087	1244.4962	10.03
					1245.5111	1245.4982	10.37
					1246.5082	1246.4963	9.56
					1247.5127	1247.4965	13.00
					1248.5022	1248.4951	5.67
					1249.5132	1249.4943	15.09
[8]	HH	H114C80S8	0.29	1330.6681	1330.6707	1330.6681	1.94
					1331.6742	1331.6712	2.24
					1332.6755	1332.6697	4.40
					1333.6791	1333.6699	6.86
					1334.6730	1334.6687	3.21
					1335.6719	1335.6678	3.05
[8]	HBr	H113Br1C80S8	1.00	1410.5782	1408.5840	1408.5786	3.83
					1409.5918	1409.5817	7.15
					1410.5873	1410.5782	6.45
					1411.5859	1411.5799	4.26
					1412.5864	1412.5784	5.70
					1413.5824	1413.5784	2.84
					1414.5867	1414.5771	6.75
[8]	BrBr	Br2C80H112S8	0.04	1488.4881	1488.5142	1488.4881	17.53
[9]	HH	H128C90S9	0.27	1497.7528	1496.7572	1496.7497	5.01
					1497.7592	1497.7528	4.23
					1498.7493	1498.7516	1.56
					1499.7559	1499.7518	2.70
					1500.7556	1500.7510	3.10

Polymer co	omposition				Mate	ched peaks	
				Most abundant	m/z	m/z	Δ
Monomers	Endgroups	Formula & ion	Amount	isotope	(exp+offset)	(calc)	(ppm)
[9]	HBr	H12/Br1C90S9	0.95	1576.6601	15/4.6683	1574.6602	5.16
					15/5.66/1	1575.6633	2.40
					15/6.6/32	1576.6601	8.30
					15//.66//	15/7.6617	3.84
					15/8.6698	1578.6604	5.93
					15/9.6694	1579.6603	5.79
54.01					1580.6681	1580.6597	5.29
[10]	HH	H142C100S10	0.30	1663.8344	1662.8290	1662.8313	1.41
					1663.8304	1663.8344	2.41
					1664.8318	1664.8335	1.02
					1665.8373	1665.8337	2.17
					1666.8295	1666.8330	2.09
[10]	HBr	H141Br1C100S10	0.82	1742.7421	1740.7421	1740.7418	0.13
					1741.7451	1741.7450	0.09
					1742.7483	1742.7421	3.58
					1743.7482	1743.7434	2.72
					1744.7472	1744.7424	2.75
					1745.7482	1745.7424	3.33
					1746.7474	1746.7417	3.26
					1747.7140	1747.7408	15.36
[11]	HH	H156C110S11	0.26	1830.9153	1828.9241	1828.9129	6.09
					1829.9172	1829.9161	0.64
					1830.9155	1830.9153	0.10
					1831.9198	1831.9157	2.26
					1832.8969	1832.9149	9.85
[11]	HBr	H155Br1C110S11	0.65	1908.8240	1906.8262	1906.8235	1.43
					1907.8369	1907.8266	5.42
					1908.8267	1908.8240	1.40
					1909.8301	1909.8252	2.53
					1910.8292	1910.8243	2.56
					1911.8214	1911.8244	1.54
					1912.8345	1912.8235	5.76
					1913.8247	1913.8228	1.02
[12]	НН	H170C120S12	0.20	1996.9972	1994.9910	1994.9946	1.80
					1995.9851	1995.9977	6.30
					1996.9932	1996.9972	2.01
					1997.9816	1997.9975	7.97
					1998.9807	1998.9969	8.10
					1999.9750	1999.9965	10.75

Polymer co	omposition				Mate	ched peaks	
				Most abundant	m/z	m/z	Δ
Monomers	Endgroups	Formula & ion	Amount	isotope	(exp+offset)	(calc)	(ppm)
[12]	HBr	H169Br1C120S12	0.48	2075.9070	2072.8987	2072.9051	3.08
					2073.9080	2073.9082	0.12
					2074.8987	2074.9059	3.47
					2075.9043	2075.9070	1.31
					2076.9082	2076.9063	0.93
					2077.8984	2077.9062	3.75
					2078.8931	2078.9054	5.95
54.01			0.40		2079.9077	2079.9050	1.28
[13]	HH	H184C130S13	0.12	2163.0790	2161.0637	2161.0762	5.77
					2162.0894	2162.0793	4.64
					2163.0547	2163.0790	11.24
					2164.0664	2164.0793	5.97
					2165.0823	2165.0788	1.60
[13]	HBr	H183Br1C130S13	0.36	2241.9888	2238.9778	2238.9867	3.98
					2239.9785	2239.9898	5.05
					2240.9746	2240.9878	5.87
					2241.9924	2241.9888	1.62
					2242.9612	2242.9882	12.03
					2243.9768	2243.9882	5.08
					2244.9751	2244.9874	5.46
[14]	HH	H198C140S14	0.10	2329.1608	2327.1587	2327.1578	0.38
					2328.1543	2328.1609	2.85
					2329.1577	2329.1608	1.32
					2330.1194	2330.1611	17.92
					2331.1479	2331.1607	5.47
[14]	HBr	H197Br1C140S14	0.22	2408.0706	2405.0471	2405.0683	8.81
					2406.0391	2406.0714	13.46
					2407.0542	2407.0696	6.42
					2408.0652	2408.0706	2.24
					2409.0540	2409.0700	6.68
					2410.0383	2410.0701	13.16
					2411.0845	2411.0694	6.24
[14]	BrBr	Br2C140H196S14	0.33	2486.9794	2493.2212	2492.9764	98.20
					2495.2048	2494.9744	92.35
[15]	HH	H212C150S15	0.09	2495.2426	2493.2212	2493.2394	7.31
					2495.2048	2495.2426	15.12
					2496.2466	2496.2429	1.47
					2497.2354	2497.2427	2.94
					2498.1882	2498.2424	21.67

Polymer c	omposition				Mat	ched peaks	
				Most abundant	m/z	m/z	Δ
Monomers	Endgroups	Formula & ion	Amount	isotope	(exp+offset)	(calc)	(ppm)
[15]	HBr	H211Br1C150S15	0.18	2574.1523	2571.1582	2571.1499	3.21
					2572.1497	2572.1531	1.33
					2573.1443	2573.1515	2.80
					2574.1479	2574.1523	1.71
					2575.1477	2575.1520	1.66
					2576.1365	2576.1519	6.00
					2577.1323	2577.1514	7.41
					2578.1204	2578.1510	11.89
[15]	BrBr	Br2C150H210S15	0.30	2653.0613	2659.2910	2659.0579	87.66
					2660.2988	2660.0584	90.37
[16]	HH	H226C160S16	0.07	2661.3243	2659.2910	2659.3210	11.29
					2660.2988	2660.3242	9.53
					2662.3328	2662.3247	3.02
					2663.3323	2663.3246	2.90
[16]	HBr	H225Br1C160S16	0.13	2741.2338	2738.1787	2738.2347	20.44
					2739.2129	2739.2333	7.47
					2740.2422	2740.2341	2.95
					2741.2629	2741.2338	10.62
					2742.2495	2742.2338	5.74
					2743.2075	2743.2333	9.40
[16]	BrBr	Br2C160H224S16	0.02	2820.1434	2825.3704	2825.1405	81.37
[17]	HH	H240C170S17	0.06	2828.4065	2825.3704	2825.4027	11.43
[17]	HBr	H239Br1C170S17	0.10	2907.3157	2905.3066	2905.3152	2.94
					2906.3086	2906.3159	2.51
					2907.3000	2907.3157	5.37
					2908.3237	2908.3156	2.79
					2909.2859	2909.3154	10.13

Isobaric species

No isobaric macromolecules in the simulation...



Figure S9. ¹H NMR spectrum of P1 in CDCl₃



Figure S10. ¹H NMR spectrum of P2 in CDCl₃.



Figure S11. ¹H NMR spectrum of P3 in CDCl₃.



Figure S12. ¹H NMR spectrum of P4 in CDCl₃.



Figure S13. ¹H NMR spectrum of P5 in CDCl₃.



Figure S14. ¹H NMR spectrum of P6 in CDCl₃.



Figure S15. ¹H NMR spectrum of P7 in CDCl₃.



Figure S16. ¹H NMR spectrum of P8 in CDCl₃.



Figure S17. ¹H NMR spectrum of P9 in CDCl₃.



Figure S18. ¹H NMR spectrum of P10 in CDCl₃.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2089	2871	1939	3974	5249	1.374156	1.384277	1.828400

Figure S19. GPC curve of P1.



Broad Unknown Relative Chromatogram

Figure S20. GPC curve of P2.



			Broau	UNKNOW	in Relati	vereak	Table		
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2716	3345	2760	<mark>414</mark> 5	5100	1.231567	1.239237	1.524729

Figure S21. GPC curve of P3.



Figure S22. GPC curve of P4.

Broad Unknown Relative Chromatogram



			вгоао	UNKNOW	/n Relati	vereak	Table		
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4692	6064	5003	8141	10961	1.292464	1.342533	1.807463

Figure S23. GPC curve of P5.



Broad Unknown Relative Chromatogram

Figure S24. GPC curve of P6.



	Bload Olikilowi Relative Feak Table											
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Dalton\$)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw			
1		2973	4305	2786	6687	9788	1.448291	1.553297	2.273642			

Figure S25. GPC curve of P7.



Figure S26. GPC curve of P8.



			Dioau	UIIKIIUV	III INCIALI	verean	Table		
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Dalton\$)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2628	3567	2707	5162	7675	1.357062	1.447086	2.151688

Figure S27. GPC curve of P9.



Figure S28. GPC curve of P10.

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