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Preparation and Optical Investigation of Monodisperse Oligo(9,9-dioctylfluorene)s Containing One Fluorenone Unit**

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Abstract: A set of monodisperse oligo(9,9-dioctylfuorene)s, each containing only one fluorenone unit, was synthesized by using iterative Suzuki cross-coupling and iododesilylation reactions. Their optical properties were also investigated.

Keywords: conjugation · energy transfer · fluorenone · oligomers · polyfluorenes

Introduction

Polyfluorenes are a class of promising blue-light-emitting polymers, which exhibit extremely high solution and solid-state quantum yields.[1] However, in practical applications, polyfluorenes exhibited poor color stability. A low-energy green emission band is generated during operation or annealing in air. In the earlier literature, the origin of this low-energy green emission was attributed to the aggregation or excimer formation in the bulky materials.[2] Recent studies have proposed that the origin of the green emission band is rather from fluorenone defects than aggregation or formation of excimers.[3] However, little is known regarding to their structure–property relationship.

Monodisperse, π-conjugated oligomers have gained increasing scientific attention in recent years, because they can be used to better elucidate the structure–property relationship than the corresponding polymers.[4] Here we designed and synthesized a set of monodisperse oligofluorenes with only one fluorenone unit in the center of the oligomers, and also investigated their optical properties. It should be mentioned that Wegner, Geng, and Miller have recently reported the synthesis, characterization, and optical properties of monodisperse fluorene oligomers free of ketonic defects.[5]

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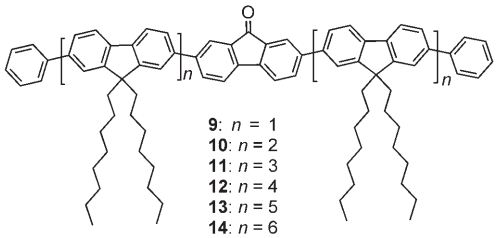
[**] Editorial note: Please also see the following paper, which is on a similar subject.

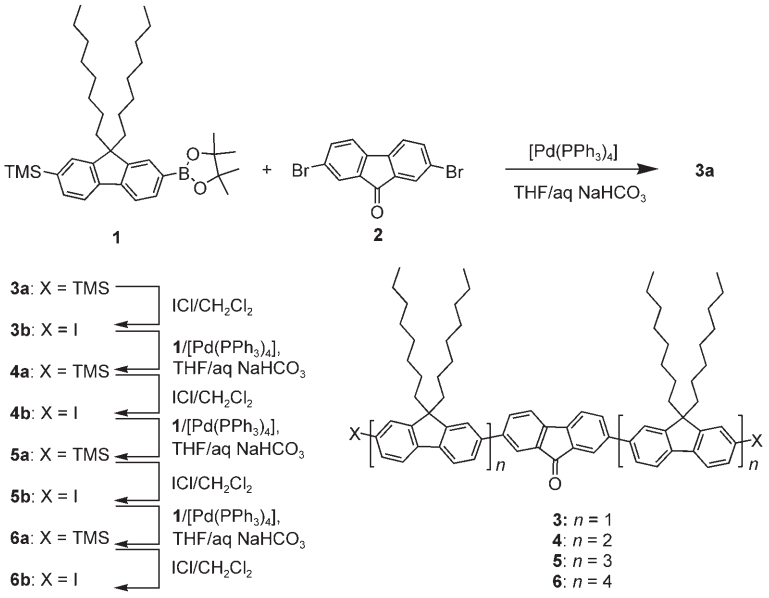
Results and Discussion

Repetitive strategies are normally required for the synthesis of structurally defined and monodisperse oligomers. As defined by Moore, the growth processes can be divided into three categories, that is, simple repetitive synthesis, orthogonal repetitive synthesis, and divergent/convergent processes.[6] Considering the large number of steps required in the synthesis and purification of longer oligomers, it is desirable to reduce the number of synthetic steps to simplify their preparation and to improve the overall yield of the final product. This may be achieved in a double stage divergent/convergent growth approach based on the large building blocks synthesized by either divergent or convergent methods. The synthetic route leading from compounds **1**–**8** to the formation of monodisperse oligomers **9**–**14** is illustrated in Schemes 1–3.



9: $n = 1$
10: $n = 2$
11: $n = 3$
12: $n = 4$
13: $n = 5$
14: $n = 6$

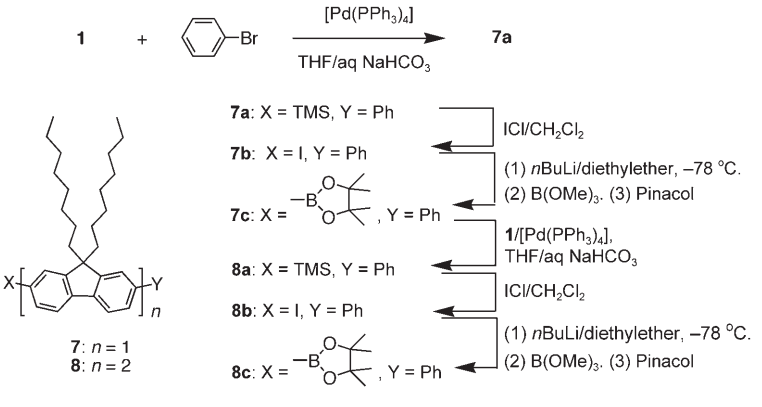
Scheme 1 depicts the synthesis of oligomers **3**–**6**, carrying either trimethylsilyl (TMS) or iodo groups at the two termini. The chemistry used in the synthesis was iododesilylation and Suzuki cross-coupling reactions developed by Schlüter et al. to synthesize the monodisperse oligophenylene rods and macrocycles.[7] Starting from TMS-masked 7-trimethylsilyl-9,9-dioctylfluorene-2-boronic pinacol ester (**1**),[4a] cross-



Scheme 1.

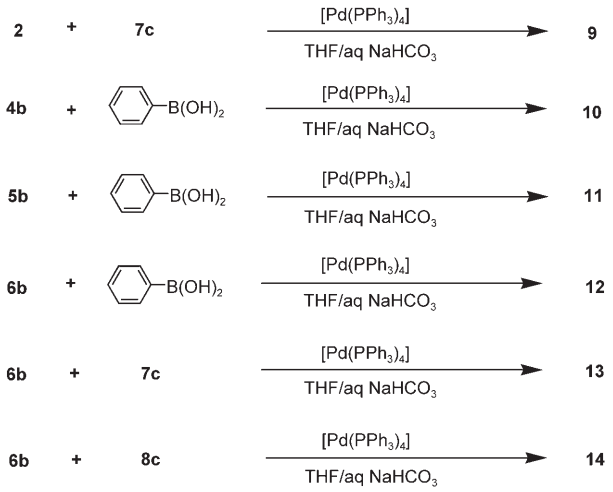
coupling of **1** and 2,7-dibromofluorenone (**2**)[8] under standard Suzuki–Miyaura cross-coupling conditions afforded di-TMS 3-mer **3a** in a yield of 95%. Iododesilylation of **3a** with iodine monochloride in CH_2Cl_2 at 0°C gave the corresponding diiodide **3b** in a 97% yield. Reaction of **3b** with **1** gave the subsequent 5-mer **4a** in a 89% yield after purification by flash chromatography. Subsequent iodination led to diiodide **4b** in a yield of 91%. Repeating the above reaction sequence, 7-mers **5a** and **5b** and 9-mers **6a** and **6b** were obtained in good to excellent yields (83–98%) after purification by simple flash chromatography.

The synthesis of building blocks **7c** and **8c** are outlined in Scheme 2. Starting from compound **1**, coupling with bromobenzene afforded **7a** in a 95% yield. Conversion of **7a** into **7b** was accomplished in 98% yield. Subsequent halo-lithium exchange and quenching with trimethyl borate gave the corresponding boronic acid, the conversion of which into the cyclic boronic ester was achieved by refluxing with pinacol in CH_2Cl_2. Compound **7c** was obtained as a colorless oil in a 42% yield. Repeating the above reaction sequence, **8a**, **8b**, and **8c** were obtained in yields of 91, 98, and 63%, respectively.



Scheme 2.

Scheme 3 shows the synthesis of the target longer oligomers **9–14**. Reaction of **2** and **7c** under standard Suzuki cross-coupling conditions afforded 3-mer **9** in a 61% yield. Coupling **4b** with benzeneboronic acid gave 5-mer **10** in a 50% yield. Coupling **5b** with benzeneboronic acid afforded 7-mer **11** in an 82% yield after purification by simple flash chromatography on silica gel column. Coupling of **6b** with benzeneboronic acid, **7c**, and **8c** gave 9-mer **12**, 11-mer **13**, and 13-mer **14** in yields of 48, 56, and 27%, respectively. The purification of **12–14** was accomplished by combination of flash chromatography and preparative SEC (size elution chromatography). The purity of **9–14** was checked by gel permeation chromatography (GPC) with THF as an eluent. As shown in Figure 1, all the peaks are symmetrical and monomodal with a polydispersity index of 1.01–1.04.



Scheme 3.

Optical properties of fluorenone and monodisperse oligomers **9–14** were investigated with UV-absorption and florescence spectroscopy (Figure 2 and Table 1). In toluene, fluorenone displayed a strong absorption band below 350 nm and a weak peak centered at around 400 nm. All the oligomers exhibited an intensive broad absorption band in the range of 350–400 nm. The absorption maximum of the oligomers is red-shifted with increasing the

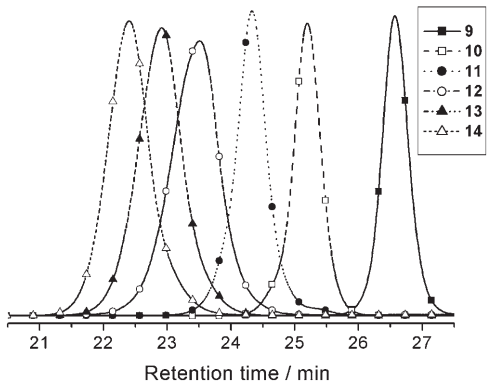


Figure 1. GPC elution traces of **9**–**14** with THF as an eluent.

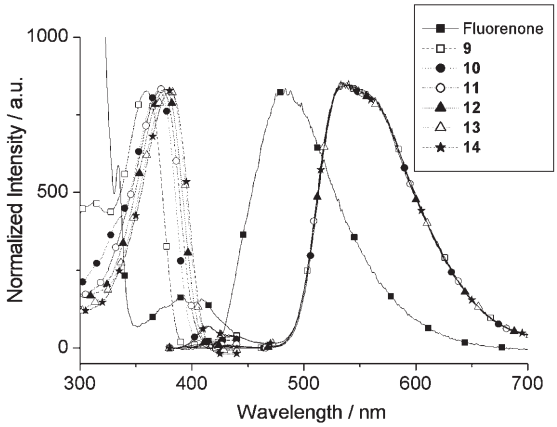


Figure 2. UV-visible absorption and photoluminescent spectra of oligomers **9**–**14** in toluene.

Table 1. Summary of the absorption and emission spectra (solution and film) as well as the fluorescence quantum yields (in toluene) of fluorenone and the fluorenone-containing oligomers.

	UV [nm]		FL [nm]		
	solution	film	solution	film	Φ_F
fluorenone			483	509	0.01
9	359	363	535	557	0.19
10	370	374	535	553	0.20
11	373	374	535	554	0.20
12	376	382	535	554	0.19
13	379	385	535	554	0.21
14	380	389	535	554	0.21

conjugation length. Fluorenone displayed a blue-green emission peak at round 483 nm. Compared with fluorenone, the emission wavelength of the oligomers was red-shifted. All the oligomers **9**–**14** showed almost fully superimposed emission spectra with an intense green to orange emission band peaked at around 535 nm. This phenomenon indicates that the emission wavelength is independent of the length of the conjugated oligomers. The emission state of the oligomers is only related to the fluorene units adjacent to the central fluorenone unit. The experimental results we obtained agree quite well with the theoretical prediction that the emissive state is strongly confined to the fluorenone unit.[9] Fluorenone-containing oligomers **9**–**14** exhibited a large Stokes shift of up to about 160 nm. This number is much larger than that of the fluorene oligomers. Compared with the corresponding fluorene oligomers, the introduction of an acceptor group (fluorenone) in the oligomers' main chain gives rise to intramolecular charge-transfer effect, which is characterized by the larger Stokes shift and the red-shifted structureless emission.[10] For the two longest oligomers **13** and **14** (about 10–12 nm in length) the weak blue emission residues from the fluorene segments were observed.

Solid films on quartz plates used for UV-visible absorption and fluorescence characterization were prepared by spin coating with 1% toluene solution at 1500 rpm. The absorption and emission spectra of the spin-coated films (**9**–**14**) are shown in Figure 3. In film fluorenone exhibited a

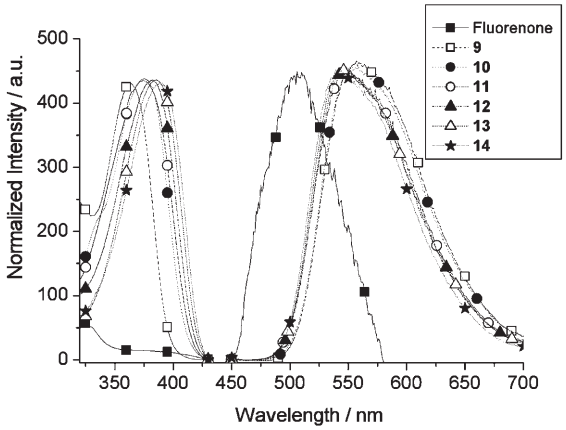


Figure 3. UV-visible absorption and photoluminescent spectra of oligomers **9**–**14** in films.

red-shifted weak emission peak at around 509 nm. The red-shift and low intensity of fluorenone emission in film are probably due to the formation of the aggregation and self-quenching their fluorescence. Compared with their emission spectra in solution, their film emission spectra were slightly red-shifted by about 8–10 nm. All polymer films (**9**–**14**) displayed a structureless green-orange band that peaked at around 544 nm. In their film emission spectra no blue emission residue was detected. Slight blue-shift of the emissive peaks (about 3 nm) was observed with increasing the fluorene segments from one to six on each side of the oligomers. The quantum yields (Φ_F) of oligomers **9**–**14** in dilute toluene was measured to be around 0.19–0.21 in comparison to 9,10-diphenylanthracene (in cyclohexane, $\Phi_F = 0.9$).[11] Due to the intramolecular charge transfer effects in the fluorenone-containing oligomers, this number is much lower than that of the fluorene oligomers.

The thermal properties of the oligomers were investigated by using differential scanning calorimetry (DSC). The DSC traces of the second heating run are shown in Figure 4. All oligomers displayed a glass transition and a crystal melting peak. The results are summarized in Table 2. The glass transitions and the crystal melting peaks could be easily identified as the temperature increased, but the transition temper-

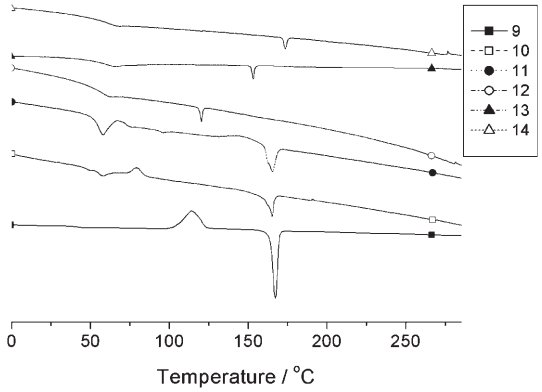


Figure 4. DSC traces of oligomers **9–14** (second heating at 10 °C min^{-1}).

Table 2. Summary of the glass transition temperatures (T_g), the melting temperatures (T_m), and the enthalpy of melting of the fluorenone-containing oligomers.

	T_g [°C]	T_m [°C]	ΔH_m [J g^{-1}]
9	44	167	43.9
10	52	163	5.3
11	54	162	3.1
12	55	120	0.56
13	59	153	0.6
14	63	173	0.65

ature from nematic to isotropic was hard to follow due to the small transition enthalpy. As shown in Table 2, the glass transition temperature increased as the backbone chain length increased. Oligomers **9** and **10** showed exothermic crystallization peaks at around 114 and 79 °C, respectively. This peak was not observed for the longer oligomers (**11–14**). With the increase of the chain length, the melting temperature first decreased and then increased. The detailed investigation of the in-situ and in real time crystallization behaviors by using hot-stage AFM are undergoing and will be reported elsewhere.

Conclusion

In conclusion, we have synthesized a set of monodisperse fluorene oligomers (with up to 12 fluorene units) containing only one fluorenone unit in the center of the molecules by a double stage divergent/convergent growth approach. Optical studies revealed that the oligomers have large Stokes shifts that absorb in ultraviolet region and emit in green-orange region. The emission wavelength is independent of the conjugation length, that is, increasing the conjugation length does not change their emission spectra. All oligomers exhibit relatively low quantum efficient yield.

Experimental Section

All chemicals were purchased from Acros and used without further purification. Solvents were dried according to standard procedures. All reactions were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-300 and Avance-400 NMR spectrometers with $CDCl_3$ as a solvent. UV/Vis absorption spectra were recorded on a Shimadzu UV-1601PC. Fluorescence spectra were recorded on a Varian-FLR025. Elemental analysis was carried out on a Carlo Erba model 1106 elemental analyzer. The molecular weights were determined by using gel permeation chromatography (Waters 410) against polystyrene standards with THF as an eluent. Differential scanning calorimetry was measured on a Mettler DSC 822e with a heating and cooling rate of 10 °C min^{-1}.

Compound 3a: A mixture of **1** (1.47 g, 2.5 mmol), **2** (0.39 g, 1.0 mmol), THF (20 mL), water (10 mL), and $NaHCO_3$ (0.35 g, 4 mmol) was carefully degassed before and after [Pd(PPh$_3$)$_4$] (50 mg, 0.04 mmol) was added. The mixture was stirred and refluxed for 4 days. CH_2Cl_2 was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×30 mL), and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. Chromatography on silica gel eluting with CH_2Cl_2/hexane (1:5, v/v) afforded **3a** (1.05 g, 95 %) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 2H), 7.85–7.83 (d, J = 7.6 Hz, 2H), 7.80–7.78 (d, J = 7.6 Hz, 2H), 7.73–7.71 (d, J = 7.2 Hz, 2H), 7.66–7.64 (d, J = 8.0 Hz, 4H), 7.61 (s, 2H), 7.53–7.51 (d, J = 8.0 Hz, 2H), 7.49 (s, 2H), 2.04–2.00 (t, J = 8.0 Hz, 8H), 1.21–1.07 (br, 40H), 0.82–0.79 (t, J = 6.8 Hz, 12H), 0.69–0.68 (br, 8H), 0.33 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 151.9, 150.2, 142.9, 142.7, 141.2, 139.4, 138.7, 135.3, 133.4, 131.9, 127.6, 125.6, 123.1, 121.1, 120.7, 120.2, 119.1, 55.2, 40.2, 31.8, 30.0, 29.9, 29.2, 29.1, 29.1, 23.8, 22.6, 14.0, −0.9 ppm; elemental analysis calcd (%) for $C_{77}H_{104}OSi_2$: C 83.94, H 9.51; found: C 83.75, H 9.66.

Compound 3b: A solution of ICl (3 mL, 3 mmol) in CH_2Cl_2 was added dropwise to a solution of **3a** (1.05 g, 0.95 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. Then a larger excess of aqueous $NaHSO_3$ solution was added to destroy the unreacted ICl. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×30 mL), and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2 to afford **3b** (1.11 g, 97 %) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 2H), 7.84–7.81 (d, J = 10.2 Hz, 2H), 7.77–7.74 (d, J = 7.8 Hz, 2H), 7.69 (s, 2H), 7.69–7.61 (br, 6H), 7.58 (s, 2H), 7.49–7.47 (d, J = 7.5 Hz, 2H), 2.07–1.87 (t, J = 7.5 Hz, 8H), 1.33–1.07 (br, 40H), 0.83–0.79 (t, J = 6.3 Hz, 12H), 0.64 ppm (br, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.6, 155.0, 152.6, 144.6, 144.0, 141.7, 141.7, 140.7, 137.5, 136.8, 134.9, 133.7, 127.4, 124.6, 123.1, 122.5, 122.3, 121.8, 94.4, 57.1, 41.8, 33.3, 31.4, 31.2, 30.7, 25.3, 24.1, 15.6 ppm; elemental analysis calcd (%) for $C_{71}H_{86}I_2O$: C 70.52, H 7.71; found: C 70.33, H 7.39.

Compound 4a: The general procedure for synthesis of **3a** was followed. Compound **3b** (1.10 g, 0.91 mmol), **1** (1.34 g, 2.3 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.5 g, 6 mmol), and [Pd(PPh$_3$)$_4$] (45 mg, 0.04 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/hexane (1:5, v/v) to afford **4a** (1.52 g, 89 %) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (s, 2H), 7.87–7.78 (br, 8H), 7.74–7.65 (br, 16H), 7.53–7.50 (d, J = 8.1 Hz, 4H), 2.13–2.07 (br, 16H), 1.25–1.11 (br, 80H), 0.84–0.77 (br, 40H), 0.33 ppm (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 151.8, 151.7, 150.1, 142.9, 142.6, 140.8, 140.7, 140.4, 138.9, 133.3, 131.7, 127.5, 126.1, 125.9, 125.6, 123.0, 121.4, 121.0, 120.7, 120.0, 120.0, 119.9, 118.9, 55.3, 55.0, 40.3, 40.0, 31.7, 29.9, 29.8, 29.1, 23.7, 22.5, 14.0, −1.0 ppm; elemental analysis calcd (%) for $C_{135}H_{184}OSi_2$: C 86.29, H 9.87; found: C 86.08, H 9.97.

Compound 4b: The general procedure for synthesis of **3b** was followed. ICl (2 mL, 2 mmol), **4a** (1.52 g, 0.81 mmol), and CH_2Cl_2 (10 mL) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to afford **4b** (1.47 g, 91 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 2H), 7.88–7.82 (br, 6H), 7.78–7.75 (d, J = 10.4 Hz, 2H), 7.70–7.61 (br, 18H), 7.51–7.49 (d, J = 10.4 Hz, 2H), 2.10–2.00 (br, 16H), 1.27–1.11 (br, 80H), 0.85–0.74 ppm (br, 40H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 153.4, 151.9, 151.8, 150.9, 142.6, 140.8, 140.5, 139.8, 138.5, 135.9, 135.2, 133.3, 132.1, 126.2, 125.7, 123.0, 121.4, 121.3, 121.0, 120.7, 120.2, 120.1, 120.00, 92.4, 55.4, 40.4, 40.2, 31.7,

29.9, 29.9, 29.7, 29.1, 23.8, 23.7, 22.5, 22.5, 14.0, 14.0 ppm; elemental analysis calcd (%) for $C_{129}H_{166}I_2O$: C 78.00, H 8.42; found: C 77.96, H 8.50.

Compound 5a: The general procedure for synthesis of **3a** was followed. Compound **4b** (1.24 g, 0.62 mmol), **1** (0.92 g, 1.6 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.30 g, 4 mmol), and $[Pd(PPh_3)_4]$ (50 mg, 0.04 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/hexane (1:4, v/v) to give **5a** (1.37 g, 83%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.08$ (s, 2H), 7.86–7.79 (br, 12H), 7.72–7.67 (br, 24H), 7.54–7.52 (br, 4H), 2.13–2.05 (br, 24H), 1.14 (br, 120H), 0.82 (br, 60H), 0.34 ppm (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.0$, 151.8, 151.7, 150.2, 143.0, 141.4, 140.9, 140.6, 140.4, 140.3, 140.1, 140.0, 127.7, 126.2, 126.0, 123.1, 121.5, 121.1, 120.8, 120.2, 120.1, 120.0, 119.0, 55.5, 55.3, 55.1, 40.4, 40.1, 31.8, 30.0, 29.9, 29.2, 23.9, 23.8, 22.6, 14.0, −0.8 ppm; elemental analysis calcd (%) for $C_{193}H_{264}OSi_2$: C 87.27, H 10.02; found: C 87.47, H 10.00.

Compound 5b: The general procedure for synthesis of **3b** was followed. ICl (2 mL, 2 mmol), **5a** (1.37 g, 0.52 mmol), and CH_2Cl_2 (10 mL) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to give **5b** (1.37 g, 96%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (s, 2H), 7.85–7.82 (br, 10H), 7.77–7.61 (br, 28H), 7.51–7.48 (d, $J = 7.5$ Hz, 2H), 2.11–2.03 (br, 24H), 1.13 (br, 120H), 0.82–0.81 ppm (br, 60H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 194.1, 153.4, 151.9, 151.8, 150.9, 142.9, 142.6, 141.1, 140.7, 140.4, 139.2, 138.5, 135.8, 135.3, 133.3, 132.1, 126.1, 123.0, 121.4, 121.3, 121.0, 120.7, 120.1,119.9, 92.4, 55.4, 55.3, 40.4, 40.3, 40.2, 31.7, 30.0, 29.9, 29.2, 23.8, 23.7, 22.5, 14.0 ppm; elemental analysis calcd (%) for $C_{187}H_{246}I_2O$: C 81.27, H 8.97; found: C 81.08, H 9.13.

Compound 6a: The general procedure for synthesis of **3a** was followed. Compound **5b** (0.93 g, 0.34 mmol), **1** (0.49 g, 0.84 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.3 g, 3 mmol), and $[Pd(PPh_3)_4]$ (30 mg, 0.026 mmol) were used. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) to afford **6a** (1.02 g, 88%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.08$ (s, 2H), 7.88–7.79 (br, 16H), 7.75–7.68 (br, 32H), 7.54–7.51 (d, $J = 7.8$ Hz, 4H), 2.12–2.02 (br, 32H), 1.14 (br, 160H), 0.83–0.79 (br, 80H), 0.34 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.2$, 152.0, 151.8, 151.8, 151.7, 150.2, 141.4, 140.8, 140.6, 140.6, 140.5, 140.1, 140.0, 135.3, 133.4, 127.7, 126.2, 126.0, 123.1, 121.5, 120.8, 120.2, 120.0, 119.0, 55.5, 55.4, 55.3, 55.1, 40.4, 40.2, 31.8, 30.0, 30.0, 29.9, 29.2, 29.2, 29.1, 23.9, 23.8, 22.6, 14.1, −0.8 ppm; elemental analysis calcd (%) for $C_{251}H_{344}OSi_2$: C 87.80, H 10.10; found: C 87.33, H 9.97.

Compound 6b: The general procedure for synthesis of **3b** was followed. ICl (0.5 mL, 0.5 mmol), **6a** (0.64 g, 0.19 mmol), and CH_2Cl_2 (10 mL) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to give **6b** (0.64 g, 98%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.08$ (s, 2H), 7.86–7.75 (br, 14H), 7.72–7.62 (br, 36H), 7.51–7.48 (d, $J = 7.8$ Hz, 2H), 2.12–2.01 (br, 32H), 1.14 (br, 160H), 0.85–0.79 ppm (br, 80H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 194.2, 153.5, 152.0, 151.8, 150.9, 142.7, 141.2, 140.9, 140.8, 140.5, 140.3, 140.0, 139.8, 139.3, 138.6, 135.9, 135.3, 133.4, 126.2, 123.1, 121.5, 121.1, 120.8, 120.0, 92.5, 55.5, 55.4, 40.4, 40.3, 31.8, 31.1, 30.3, 30.0, 29.6, 29.2, 23.9, 23.8, 22.6, 14.1 ppm; elemental analysis calcd (%) for $C_{245}H_{326}I_2O$: C 83.10, H 9.28; found: C 83.46, H 9.38.

Compound 7a: The general procedure for synthesis of **3a** was followed. Bromobenzene (2.60 g, 16.6 mmol), **1** (7.48 g, 12.7 mmol), THF (70 mL), water (30 mL), $NaHCO_3$ (3.0 g, 36 mmol), and $[Pd(PPh_3)_4]$ (300 mg, 0.26 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with hexane to give **7a** (6.5 g, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$–7.75 (d, $J = 8.1$ Hz, 1H), 7.71–7.66 (br, 3H), 7.58–7.55 (d, $J = 8.1$ Hz, 2H), 7.51–7.45 (br, 4H), 7.38–7.33 (t, $J = 7.2$ Hz, 1H), 2.02–1.97 (t, $J = 8.1$ Hz, 4H), 1.21–1.06 (br, 20), 0.83–0.79 (t, $J = 6.6$ Hz, 6H), 0.71–0.69 (br, 4H), 0.32 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.6$, 150.2, 141.8, 141.4, 140.4, 140.2, 139.0, 131.8, 128.8, 127.6, 127.2, 127.1, 125.9, 121.6, 120.0, 119.0, 55.1, 40.4, 40.2, 31.8, 30.0, 29.9, 29.2, 29.1, 23.8, 22.6, 14.1, −0.8 ppm; elemental analysis calcd (%) for $C_{38}H_{54}Si$: C 84.69, H 10.10; found: C 84.58, H 9.98.

Compound 7b: The general procedure for synthesis of **3b** was followed. ICl (15 mL, 15 mmol), **7a** (5.38 g, 10 mmol), and CH_2Cl_2 (30 mL) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to give **7b** (5.78 g, yield 98%) as a slight pink solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$–7.71 (d, $J = 4.8$ Hz, 1H), 7.67–7.65 (m, 4H), 7.59–7.56 (d, $J = 7.2$ Hz, 1H), 7.53 (s, 1H), 7.49–7.45 (t, $J = 7.2$ Hz, 3H), 7.39–7.35 (t, $J = 7.2$ Hz, 1H), 2.03–1.90 (m, 4H), 1.23–1.06 (m, 20H), 0.83–8.00 (t, $J = 6.8$ Hz, 6H), 0.67–0.66 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 153.4$, 150.8, 141.5, 140.7, 140.4, 139.3, 135.9, 132.1, 128.8, 127.2, 127.2, 126.1, 121.4, 120.0, 92.5, 55.4, 40.2, 31.8, 29.9, 29.1, 23.7, 22.6, 14.0 ppm; elemental analysis calcd (%) for $C_{35}H_{45}I$: C 70.93, H 7.65; found: C 70.95, H 7.76.

Compound 7c: *n*BuLi (1.5 mL, 4.3 mmol) was added to a solution of **7b** (2.1 g, 3.5 mmol) in diethyl ether (40 mL) at −78 °C under nitrogen. The solution was kept at −78 °C for 0.5 h, and then $B(OCH_3)_3$ (1 mL, 9 mmol) added at this temperature. The reaction was stirred over night and warmed gradually to room temperature. Aqueous hydrochloric acid (2.0 mL) was added, the organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 30 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/ether (1:1, v/v) to afford the crude boronic acid as colorless oil.

A mixture of the boronic acid prepared above, pinacol (1.0 g, 8.5 mmol), and dry CH_2Cl_2 (20 mL) was refluxed for 10 h. Removal of the solvent, the crude product was purified by chromatography on silica gel eluting with ethyl acetate/hexane (1:14, v/v) to afford **7c** (0.9 g, 42%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.85$–7.80 (t, $J = 7.5$ Hz, 1H), 7.78 (s, 2H), 7.74–7.72 (d, $J = 7.5$ Hz, 1H), 7.69–7.67 (d, $J = 7.2$ Hz, 2H), 7.60–7.57 (d, $J = 8.7$ Hz, 2H), 7.50–7.45 (t, $J = 7.5$ Hz, 2H), 7.39–7.34 (t, $J = 7.5$ Hz, 1H), 2.06–2.00 (m, 4H), 1.41 (s, 12H), 1.26–1.05 (m, 20H), 0.83–0.79 (m, 6H), 0.66–0.65 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.6$, 148.7, 142.3, 140.3, 139.1, 138.8, 132.4, 127.4, 127.3, 125.8, 125.7, 124.5, 120.2, 118.9, 117.6, 82.3, 53.8, 38.8, 30.4, 28.5, 27.8, 23.5, 22.3, 21.1, 12.6 ppm; elemental analysis calcd (%) for $C_{41}H_{57}BO_2$: C 83.08, H 9.69; found: C 82.85, H 9.72.

Compound 8a: The general procedure for synthesis of **3a** was followed. Compound **7b** (2.92 g, 4.9 mmol), **1** (3.04 g, 5.2 mmol), THF (50 mL), water (20 mL), $NaHCO_3$ (1.8 g, 21 mmol), and $[Pd(PPh_3)_4]$ (121 mg, 0.1 mmol) were used. The crude product was purified by chromatography on silica gel eluting with hexane to give **8a** (4.2 g, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.85$–7.82 (d, $J = 8.0$ Hz, 3H), 7.78–7.68 (m, 7H), 7.66–7.63 (m, 2H), 7.57–7.50 (m, 4H), 7.42–7.35 (t, $J = 7.6$ Hz, 1H), 2.14–2.06 (m, 8H), 1.24–1.14 (m, 40H), 0.87–0.82 (m, 20H), 0.38 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.8$, 151.8, 151.7, 150.2, 141.8, 140.7, 140.6, 140.3, 140.1, 140.0, 131.9, 128.8, 127.7, 127.2, 126.2, 126.1, 126.1, 121.6, 121.5, 121.5, 120.0, 119.1, 55.3, 55.2, 40.5, 40.2, 31.8, 30.1, 30.0, 29.3, 29.2, 29.2, 29.2, 23.9, 23.9, 22.6, 14.1, −0.8 ppm; elemental analysis calcd (%) for $C_{38}H_{54}Si$: C 86.76, H 10.21; found: C 86.50, H 10.21.

Compound 8b: The general procedure for synthesis of **3b** was followed. ICl (10 mL, 10 mmol), **8a** (4.0 g, 4.3 mmol), and CH_2Cl_2 (10 mL) were used. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to afford **8b** (4.15 g, 98%) as a pink oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$–7.74 (m, 3H), 7.70–7.67 (m, 5H), 7.63–7.59 (m, 5H), 7.50–7.46 (m, 3H), 7.39–7.35 ppm (t, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 153.5$, 151.8, 151.7, 150.9, 141.7, 140.5, 140.3, 140.1, 140.0, 139.3, 135.9, 132.1, 128.8, 127.2, 127.1, 126.3, 126.2, 126.1, 121.6, 121.4, 121.4, 120.0, 120.0, 92.4, 55.5, 55.3, 40.4, 40.2, 31.8, 30.0, 29.9, 29.2, 23.9, 23.8, 22.6, 22.6, 14.1, 14.0 ppm; elemental analysis calcd (%) for $C_{64}H_{85}I$: C 78.34, H 8.73; found: C 78.59, H 8.81.

Compound 8c: The general procedure for synthesis of **7c** was followed. **8b** (1.2 g, 1.2 mmol), diethyl ether (30 mL), *n*BuLi (0.5 mL, 1.4 mmol), and $B(OCH_3)_3$ (0.9 mL, 8 mmol) were used to prepare the boronic acid. The crude boronic acid was purified by chromatography on silica gel eluting with CH_2Cl_2/ether (1:1, v/v) to afford the boronic acid as colorless oil. Pinacol (0.30 g, 2.5 mmol) and CH_2Cl_2 (20 mL) were used to prepare the corresponding boronic ester **8c**. Compound **8c** was obtained as a colorless oil (0.76 g, 63%) by chromatography on silica gel eluting with ethyl acetate/hexane (1:14, v/v). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.87$–7.75 (m, 6H), 7.72–7.60 (m, 8H), 7.52–7.47 (t, $J = 7.2$ Hz, 2H), 7.40–7.35

(t, $J=7.2$ Hz, 1H), 2.10–2.06 (m, 8H), 1.42 (s, 12H), 1.26–1.11 (m, 40H), 0.82–0.71 ppm (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=150.7$, 150.3, 142.4, 139.6, 139.1, 138.7, 138.6, 132.4, 127.5, 127.3, 125.8, 125.7, 124.7, 124.6, 120.2, 120.1, 118.9, 118.5, 117.6, 82.3, 53.9, 53.8, 39.0, 38.8, 30.4, 28.6, 27.8, 23.5, 22.4, 22.3, 21.2, 12.6 ppm;elemental analysis calcd (%) for $C_{41}H_{57}BO_2$: C 85.67, H 9.96; found: C 85.55, H 9.72.

Compound 9: The general procedure for synthesis of **3a** was followed. Compound **2** (16 mg, 0.047 mmol), **7c** (72 mg, 0.12 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.1 g, 1 mmol), and $[Pd(PPh_3)_4]$ (3 mg, 0.003 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/hexane (1:4, v/v) to afford **9** (32 mg, 61%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.06$ (s, 2H), 7.86–7.80 (m, 6H), 7.71–7.60 (m, 14H), 7.51–7.48 (t, $J=7.5$ Hz, 4H), 7.40–7.36 (t, $J=7.2$ Hz, 2H), 2.10–2.06 (br, 8H), 1.18–1.09 (br, 40H), 0.82–0.73 ppm (br, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=194.2$, 151.9, 151.7, 142.9, 142.6, 141.6, 140.8, 140.3, 139.8, 138.5, 135.2, 133.4, 128.8, 127.2, 127.2, 126.1, 125.7, 123.1, 121.6, 121.0, 120.7, 120.2, 120.1, 55.4, 40.4, 31.7, 30.0, 29.2, 23.8, 22.6, 14.0 ppm; elemental analysis calcd (%) for $C_{83}H_{96}O$: C 89.84, H 8.72; found: C 89.63, H 8.91.

Compound 10: The general procedure for synthesis of **3a** was followed. Compound **4b** (32 mg, 0.016 mmol), benzeneboronic acid (6 mg, 0.05 mmol), THF (10 mL), water (5 mL), $NaHCO_3$ (0.02 g, 0.2 mmol), and $[Pd(PPh_3)_4]$ (2 mg, 0.002 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/hexane (1:4, v/v) to afford **10** (15 mg, 50%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.06$ (s, 2H), 7.85–7.80 (m, 10H), 7.79–7.60 (m, 22H), 7.49 (t, $J=7.6$ Hz, 4H), 7.39–7.37 (t, $J=8.0$ Hz, 2H), 2.10–2.06 (br, 16H), 1.20–1.10 (br, 80H), 0.81–0.78 ppm (br, 40H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=196.8$, 152.0, 151.8, 151.7, 143.0, 142.6, 140.7, 140.4, 140.0, 135.3, 133.4, 128.8, 127.2, 127.1, 126.1, 126.0, 125.7, 121.6, 121.4, 121.1, 120.8, 120.1, 120.1, 120.0, 107.6, 55.4, 55.3, 45.3, 42.8, 40.4, 31.8, 30.0, 29.5, 29.3, 29.2, 23.8, 22.6, 14.0 ppm; elemental analysis calcd (%) for $C_{141}H_{176}O$: C 89.75, H 9.40; found: C 89.44, H 9.52.

Compound 11: The general procedure for synthesis of **3a** was followed. Compound **5b** (138 mg, 0.05 mmol), benzene boronic acid (15 mg, 0.125 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.1 g, 1 mmol), and $[Pd(PPh_3)_4]$ (4 mg, 0.003 mmol) were used. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) to afford **11** (109 mg, 82%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.07$ (s, 2H), 7.88–7.80 (br, 14H), 7.71–7.60 (br, 30H), 7.52–7.47 (t, $J=7.5$ Hz, 4H), 7.43–7.35 (m, 2H), 2.11–2.10 (br, 24H), 1.26–1.13 (br, 120H), 0.83–0.78 ppm (br, 60H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 194.1, 152.0, 151.8, 151.7, 140.8, 140.5, 140.4, 140.1, 140.0, 139.9, 139.7, 135.3, 128.7, 127.2, 126.1, 126.0, 125.7, 123.1, 121.6, 121.5, 121.1, 120.7, 120.1, 119.9, 96.1, 55.4, 55.3, 40.4, 31.7, 30.0, 29.2, 23.8, 22.6, 14.0 ppm; elemental analysis calcd (%) for $C_{199}H_{256}O$: C 89.71, H 9.69; found: C 88.94, H 9.70.

Compound 12: The general procedure for synthesis of **3a** was followed. Compound **6b** (124 mg, 0.035 mmol), benzene boronic acid (13 mg, 0.11 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.1 g, 1 mmol), and $[Pd(PPh_3)_4]$ (4 mg, 0.003 mmol) were used. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) and preparative size elution chromatography (SEC) on Bio-Beads S-X eluting with THF to afford **12** (48 mg, 56%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.07$ (s, 2H), 7.92–7.80 (m, 18H), 7.70–7.59 (m, 38H), 7.51–7.39 (t, $J=7.5$ Hz, 4H), 7.37–7.31 (m, 2H), 2.10 (br, 32H), 1.13–0.98 (br, 160H), 0.82–0.78 ppm (br, 80H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.1$, 170.7, 163.5, 156.9, 151.9, 151.7, 151.6, 141.6, 140.7, 140.4, 140.3, 140.0, 139.9, 135.2, 133.3, 128.6, 127.1, 126.0, 125.9, 125.6, 122.9, 121.5, 121.4, 121.0, 120.7, 120.0, 119.9, 119.8, 94.1, 55.3, 55.2, 40.3, 40.1, 31.7, 31.5, 29.9, 29.8, 29.1, 23.8, 23.5, 22.7, 22.6, 22.5, 13.9 ppm; elemental analysis calcd (%) for $C_{257}H_{336}O$: C 89.69, H 9.84; found: C 88.97, H 10.05.

Compound 13: The general procedure for synthesis of **3a** was followed. Compound **6b** (95 mg, 0.027 mmol), **7c** (60 mg, 0.1 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.1 g, 1.0 mmol), and $[Pd(PPh_3)_4]$ (5 mg, 0.004 mmol) were used. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) and preparative size elution chromatography (SEC) on Bio-Beads S-X eluting with THF to afford **11** (54 mg, 48%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.08$ (s, 2H), 7.86–7.80 (m, 22H), 7.71–7.60 (m, 46H), 7.52–7.47 (t, $J=$ 7.4 Hz, 4H), 7.37 (m, 2H), 2.12 (br, 40H), 1.14 (br, 200H), 0.83–0.79 ppm (br, 100H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=194.1$, 152.0, 151.8, 143.0, 142.7, 141.7, 140.8, 140.5, 140.0, 139.7, 139.1, 138.5, 135.3, 133.4, 128.7, 127.2, 126.1, 125.7, 123.1, 121.5, 121.1, 120.7, 119.9, 96.1, 55.4, 55.3, 40.4, 31.7, 30.0, 29,2, 28.8, 23.9, 22.6, 14.0 ppm; elemental analysis calcd (%) for $C_{315}H_{416}O$: C 89.68, H 9.94; found: C 88.94, H 10.11.

Compound 14: The general procedure for synthesis of **3a** was followed. Compound **6b** (93 mg, 0.026 mmol), **8c** (80 mg, 0.082 mmol), THF (20 mL), water (10 mL), $NaHCO_3$ (0.1 g, 1 mmol), and $[Pd(PPh_3)_4]$ (5 mg, 0.004 mmol) were used. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) and preparative size elution chromatography (SEC) on Bio-Beads S-X eluting with THF to afford **12** (36 mg, 27%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.07$ (s, 2H), 7.93–7.76 (m, 26H), 7.71–7.56 (m, 54H), 7.49–7.44 (t, $J=7.5$ Hz, 4H), 7.43–7.34 (m, 2H), 2.22–2.12 (br, 48H), 1.13 (br, 240H), 0.83–0.71 ppm (br, 120H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 196.4, 175.2, 152.0, 151.8, 151.7, 140.9, 140.8, 140.5, 140.0, 139.8, 138.6, 135.3, 128.8, 127.2, 126.2, 126.1, 125.8, 123.1, 121.6, 121.5, 121.1, 120.8, 120.2, 120.1, 120.0, 96.1, 55.5, 55.4, 40.4, 31.8, 30.0, 29.5, 29.4, 29.2, 24.1, 23.9, 22.6, 22.5, 14.1 ppm; elemental analysis calcd (%) for $C_{373}H_{496}O$: C 89.67, H 10.01; found: C 88.80, H 9.95.

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