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Synthesis of Shape-Persistent Macrocycles by a One-Pot Suzuki–Miyaura Cross-Coupling Reaction

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Dedicated to Professor Jiacong Shen on the occasion of his 80th birthday

Shape-persistent macrocycles have attracted considerable interest as molecular components in the fields of supramolecular chemistry and materials science due to their unique molecular structures and properties.[1–2] These rigid molecular rings with a nanoscale sized hole in the center may be tailored with specific chemical constitutions, geometrical shapes, peripheral functional groups, and so on. Recent advances in the preparation, supramolecular self-assembling, and practical applications of shape-persistent macrocycles have verified this class of molecules as promising building blocks for supramolecular chemistry and nanodevice fabrication. Intense efforts have been devoted to the synthesis of shape-persistent macrocycles, and they have been well summarized in several excellent reviews.[3] The most successful methods used in the synthesis of shape-persistent macrocycles include the following approaches: 1) intramolecular ring closure of α,ω-difunctionalized oligomer strategy and the one-pot intermolecular coupling and intramolecular cyclization method; 2) the template strategy; 3) thermodynamically controlled synthetic strategies.[3] Based on these elegant synthetic strategies, a large number of shape-persistent macrocycles with well-defined shapes and sizes have been prepared and reported.[1]

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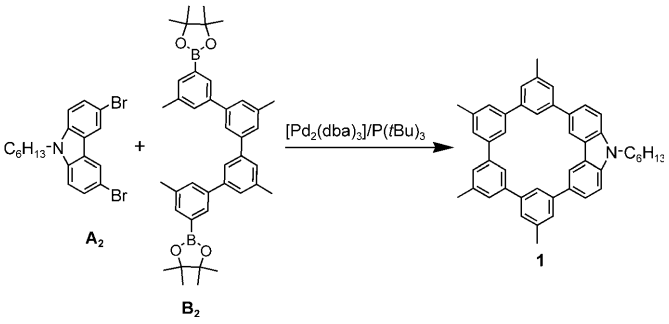
Recently, Sherburn and Sinclair found that Suzuki–Miyaura coupling of diiodoaryls and arylboronic acid in a feed ratio of 10:1 afforded the product of double coupling in good yields.[4] Hu and Dong demonstrated that the use of $[Pd_2(dba)_3]$ and tBu_3P as the catalyst precursor for Suzuki–Miyaura cross-coupling of dibromobenzenes with arylboronic acid (1 equiv) afforded exclusively diaryl-substituted benzenes.[5] Scherf et al. reported the cross-coupling of 2,7-dibromofluorene with arylboronic acid (1 equiv) formed preferentially the diaryl-substituted fluorenes.[6] Yokozawa et al. reported chain-growth Suzuki–Miyaura polymerization of an AB-type monomer, bromoarylboronic acid, using $[PdBr\{P(tBu)_3\}(Ph)]$ as an arylpalladium halide catalyst.[7] Kiriy et al. have successfully grafted polyfluorene onto a functionalized surface by catalyst-transfer chain-growth Suzuki–Miyaura polycondensation of 7-bromo-9,9-bis(2-ethyl-hexyl)-9H-fluoren-2-ylboric using $[Pd(tBu_3P)_2]$ as the catalyst precursor.[8] Very recently, Yokozawa et al. have demonstrated that catalyst-transfer Suzuki–Miyaura polycondensation can be used to prepare even diblock conjugated polymers with a narrow molecular weight distribution.[9] We have recently demonstrated that the catalyst-transfer Suzuki–Miyaura cross-coupling (CTSMCC) reaction can be used to prepare hyperbranched polymers with a branching degree of 100%.[10] We think the unique catalyst-transfer behavior can be used to prepare shape-persistent macrocycles. Herein, we report the application of the CTSMCC reaction in the preparation of shape-persistent macrocycles. To the best of our knowledge, this is the first example of the synthesis of macrocycles by the CTSMCC reaction. Four macrocycles were selected as targeted macrocycles to verify our idea.

Due to the competition of linear polymerization, a one-pot reaction usually affords macrocycles in very low yield. Therefore, the synthesis of shape-persistent macrocycles normally requires pseudo high dilution.[1h,11] The reactants are usually added to the reaction vessel by a syringe pump over

several days.[3e,12] Schlüter et al. have first reported the syntheses of many kinds of phenylene-based shape-persistent macrocycles by the Suzuki–Miyaura cross-coupling reaction.[11] They have demonstrated that yields of cyclization dropped from 68–85% for iodotelechelics to 18% for bromotelechelics for a one precursor route. For the two precursor route, cyclization yields for iodotelechelics are in the range of 30 to 50%, whereas for cyclization of bromotelechelics the yield is only around 13%.[10] Herein, we will demonstrate that shape-persistent macrocycles and even more complicated bimacrocycles can be easily synthesized in relatively high yield in a one-pot reaction using two and three precursor routes. One-pot technique has many clear advantages over the pseudo high dilution one in many aspects, such as the ease of preparing macrocycles on a larger scale, shorter reaction times, a simpler reaction setup. In addition, the synthesis of macrocycles by the one precursor route is more time consuming than that of the two precursor one.

As shown in Scheme 1, macrocycle **1** is synthesized by a one-pot CTSMCC of two precursors. Coupling of 3,6-dibromocarbazole $\mathbf{A_2}$ and diboronic pinacol ester monomer $\mathbf{B_2}$



Scheme 1. Synthesis of macrocycle **1** by catalyst-transfer Suzuki–Miyaura coupling reaction.

was carried out in a biphasic mixture of THF and aqueous $NaHCO_3$ with $[Pd_2(dba)_3]$ and $P(t\mathrm{Bu})_3$ as catalyst precursors. The catalyst Pd^0 loads varied from 0.5 to 10 mol%. The reaction mixture was stirred at reflux under a nitrogen atmosphere for 5 days. Macrocycle **1** can be easily purified by chromatography on a silica gel column or by preparative gel permeation chromatography (GPC). The structure of carbazole-containing macrocycle **1** is characterized unambiguously by ^1H and ^{13}C NMR spectroscopy, element analysis, and MALDI-TOF mass spectroscopy. The coupling reaction conditions were screened by varying the amount of catalyst and the concentration of monomers. The crude coupling products were characterized by GPC analysis to estimate the yields of macrocycle **1**. The concentrations of monomers, the amounts of catalyst, and the yields of macrocycle **1** are listed in Table 1. Under the conditions tested, the yields of macrocycle **1** by the one-pot CTSMCC reaction are in the range of 37 to 67%. The yields are comparable with the synthesis of macrocycles from a one precursor route using the high-dilution technique.[3e,11] For a control experiment, the use of a traditional catalyst precursor, $[Pd(PPh_3)_4]$, for the coupling reaction was also performed. The results are also summarized in Table 1. Under the exact same conditions, the use of $[Pd(PPh_3)_4]$ only afforded the desired macrocycle **1** in a yield of 16% (Table 1, entry 6). The GPC elution curves of the crude products of macrocycle **1** synthesized by using $[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$ or $[Pd(PPh_3)_4]$ as catalyst precursors are shown in Figure 1a. Clearly, for the catalyst-transfer reaction the higher-molecular-weight side products are significantly smaller than those of the normal Suzuki–Miyaura reaction. The reason for the high yield cyclization of two precursors to form macrocycle **1** is that when bulky $P(t\mathrm{Bu})_3$ is used as a ligand, the palladium catalyst will transfer from one bromide to another one through the carbazole unit and the two coupling reactions will happen successively.[5–10] The concentration of reactive species is determined by that of the catalyst not the reactants. Therefore, for the synthesis of macrocycles, the CTSMCC reaction is intrinsically of a pseudo-high-dilution nature.

Table 1. Synthesis of macrocycle **1**.[a]

Entry	Concentration [mM]	Catalyst precursor	Pd^0 [mmol%]	Yield [%]
1	1.25	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	0.5	55
2	1.25	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	1.0	56
3	1.25	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	2.0	56
4	1.25	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	5.0	65
5	1.25	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	10.0	67
6	1.25	$[Pd(PPh_3)_4]$	2.0	16
7	2.50	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	5.0	54
8	5.00	$[Pd_2(dba)_3]/P(t\mathrm{Bu})_3$	5.0	37

[a] Reaction conditions: mixture of $\mathbf{A_2}$, $\mathbf{B_2}$, $[Pd_2(dba)_3]\cdot CHCl_3$, and $P(t\mathrm{Bu})_3$, aqueous $NaHCO_3$, and THF; reflux; 5 days under N_2.

As shown in Scheme 2, the CTSMCC reaction was also utilized for the synthesis of larger macrocycle **2**. The synthesis and characterization of precursor $\mathbf{D_2}$ are described in the Supporting Information. The CTSMCC of diboronic esters ($\mathbf{D_2}$) and 2,7-dibromo-9,9-dioctylfluoene ($\mathbf{C_2}$) with $[Pd_2(dba)_3]$ and $P(t\mathrm{Bu})_3$ as catalyst precursors afforded macrocycle **2** in a yield of 42%. For the control experiment, the use of $[Pd(PPh_3)_4]$ as the catalyst precursor the coupling reaction afforded macrocycle **2** in a yield of 9%. The yield of macrocycle **2** cannot be estimated by the GPC elution curves of the crude product, since the macrocycle and some linear oligomers eluted simultaneously. Nevertheless, pure macrocycle **2** can be obtained by silica gel column chromatography. Macrocycle **2** is fully characterized by ^1H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectroscopy.

It is also possible to synthesize more complicated shape-persistent macrocyclic structures by using the CTSMCC reaction. As a demonstration of its potential use, we have successfully prepared dodecylene spacer linked bimacrocycle **3** and spiro-bridged bimacrocycles **4** using the CTSMCC reaction, as shown in Scheme 3. The synthesis of bimacrocycles **3** and **4** involves three precursors, that is, four coupling reac-

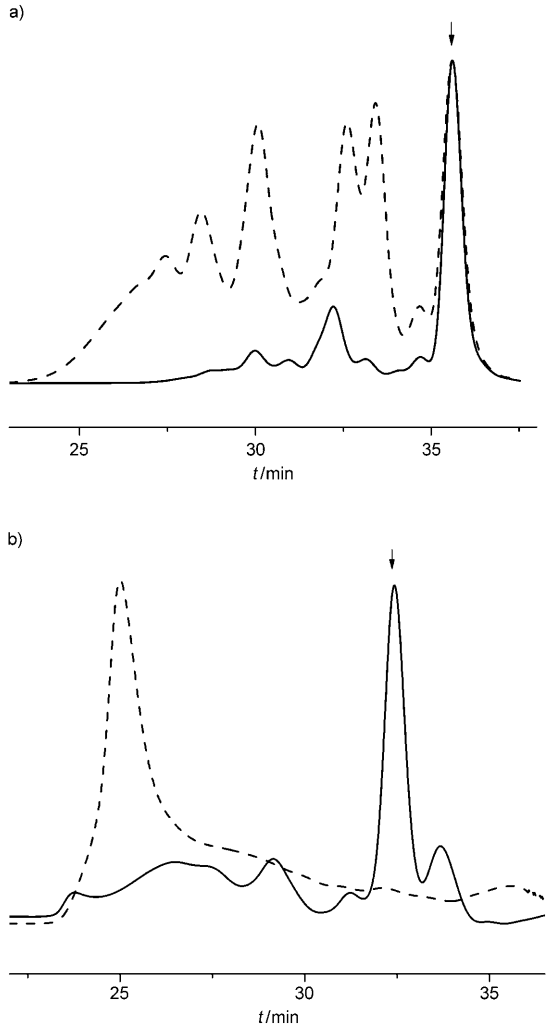
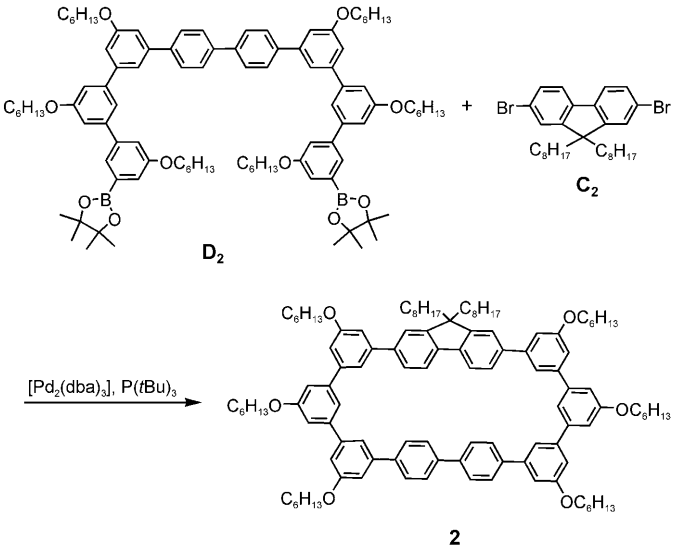


Figure 1. a) The GPC curves of crude product of macrocycle **1** catalyzed by 1.0% $[Pd_2(dba)_3]$+4.0% $P(tBu)_3$ (——) and 2.0% $[Pd(PPh_3)_4]$ (-----). b) The GPC curves of crude product of macrocycle **3** catalyzed by 1.0% $[Pd_2(dba)_3]$+4.0% $P(tBu)_3$ (——) and 2.0% $[Pd(PPh_3)_4]$ (-----). The sharp peaks marked with arrows represent target macrocycles.

tions. The reaction of diboronic ester $\mathbf{B_2}$ and tetrabromide $\mathbf{A_4}$ under the CTSMCC reaction conditions using $[Pd_2(dba)_3]/P(tBu)_3$ as catalyst precursors afforded bimacrocycle **3** in a yield of 40%; whereas the coupling of $\mathbf{B_2}$ and $\mathbf{A_4}$ under similar conditions using $[Pd(PPh_3)_4]$ as the catalyst precursor only afforded a trace amount of **3**, which cannot be separated. The GPC elution curves of crude macrocycle **3** synthesized by using $[Pd_2(dba)_3]/P(tBu)_3$ and $[P(PPh_3)_4]$ as catalyst precursors are shown in Figure 1b. It is noticeable that the formation of undesired oligomer side products is markedly suppressed under the CTSMCC reaction conditions. Similarly, three-dimensional spiro-bridged shape-persistent bimacrocycle **4** was also prepared by the CTSMCC reaction. The coupling of tetraboronic ester $\mathbf{D_4}$ and dibromide $\mathbf{C_2}$ under similar conditions afforded the desired spiro-bridged bimacrocycle **4** in a yield of 21%, which was purified by preparative TLC on silica gel plates. For the control experiment, the use of $[Pd(PPh_3)_4]$ as the catalyst precursor



Scheme 2. Synthesis of macrocycle **2** by catalyst-transfer Suzuki–Miyaura coupling reaction.

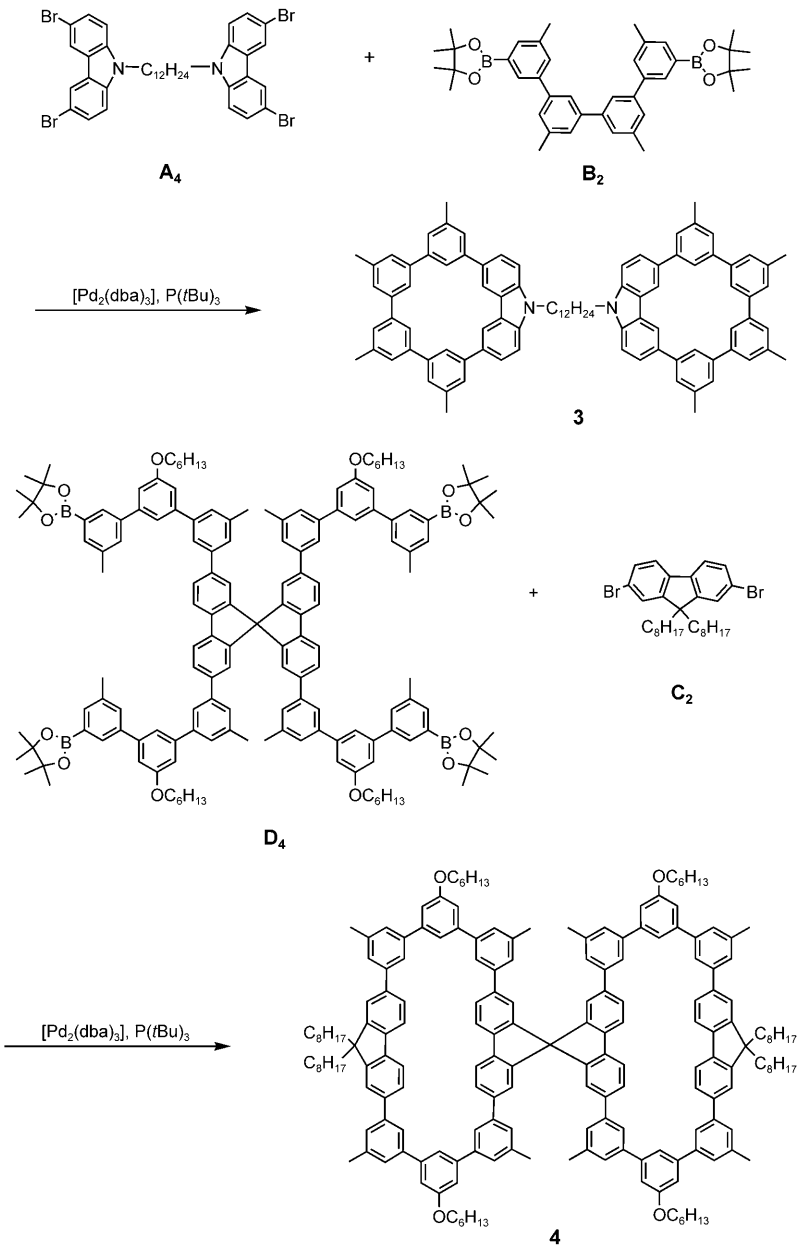
led to no desired product being separated. The structures of bimacrocycles **3** and **4** were also confirmed by MALDI-TOF mass spectroscopy, as shown in Figure 2, and ^1H and ^{13}C NMR spectroscopy. The molecular ion of bimacrocycle **3** is at *m*/*z* 1216.7 (calcd: 1216.7). The MALDI-TOF mass spectrum of bimacrocycle **4** has two signals at *m*/*z* 2516.0 (calcd: 2515.6 [M^+]) and 2539.1 (calcd: 2538.6 [M^++Na]).

In conclusion, shape-persistent macrocyclic structures were successfully synthesized in yields of 21 to 67% by a one-pot CTSMCC reaction. The reaction was carried out with $[Pd_2(dba)_3]$ as the zero-valent palladium source and P-(tBu)$_3$ as the bulky ligand. In comparison, the control experiment using traditional conditions with $[Pd(PPh_3)_4]$ as the catalyst precursor only afforded the desired macrocycles in yields of about 0 to 16%. Our results have clearly demonstrated that the CTSMCC reaction can be a very useful method for the synthesis of shape-persistent macrocycles, the synthetic routes of which are usually tedious.

Experimental Section

General procedure for four macrocycles: Arylbromide and arylboronic ester were carefully dissolved in neat THF, then water and $NaHCO_3$ were added to the solution. After carefully degassing the mixture, $[Pd_2(dba)_3]\cdot CHCl_3$ and $P(tBu)_3$ or $[Pd(PPh_3)_4]$ were added. The mixture was stirred and heated at reflux under nitrogen for five days. After cooling, water was added, the mixture was extracted with CH_2Cl_2 (×3), and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by preparative GPC and then silica gel column chromatography; for macrocycle **4**, it was purified by preparative TLC.

GPC analysis: After the reactions were cooled, a 1.0 mL aliquot of the reaction mixture was dried over anhydrous Na_2SO_4 and filtered through a membrane (polytetrafluoroethylene (PTFE), 0.2 μm pore size), then the samples were subject to GPC analysis using THF as an eluent. All of



Scheme 3. Synthesis of bimacrocycles **3** and **4**.

the GPC measurements were carried out under conditions as identical as possible.

Synthesis and characterization of macrocycle 1: A mixture of $\mathbf{B_2}$ (92.1 mg, 0.15 mmol), 3,6-dibromo-9-hexyl-9H-carbazole (61.4 mg, 0.15 mmol), $NaHCO_3$ (1.0 g, 0.012 mol), H_2O (10 mL), and THF (120 mL) was carefully degassed before $[Pd(PPh_3)_4]$ or $[Pd_2(dba)_3]\cdot CHCl_3$ and $P(t\mathrm{Bu})_3$ was added. The mixture was stirred and heated at reflux for 5 days under nitrogen. Water and CH_2Cl_2 were added and then the organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography on silica gel using hexane/CH_2Cl_2 (5:2, v/v) as the eluent to afford macrocycle **1** as a colorless solid (for $Pd_2(dba)_3$ and $P(t\mathrm{Bu})_3$, yield: 61 mg, 67%; for $Pd(PPh_3)_4$, yield: 15 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 2H), 8.17 (s, 2H), 8.09 (s, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.62 (s, 4H), 7.58 (s, 2H), 7.52 (s, 2H), 7.39 (d, J = 8.3 Hz, 2H), 4.26 (t, J = 7.1 Hz, 2H), 2.57 (s, 6H), 2.53 (s, 6H), 1.97–1.93 (m, 2H), 1.35 (br s, 6H), 0.89 ppm (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 141.6, 141.5, 140.1, 139.8, 138.8, 138.7, 133.1, 127.5, 127.2, 126.0, 125.1, 124.6, 124.1, 123.7, 122.3, 122.1, 109.5, 43.9, 31.6, 29.3, 27.0, 22.6, 22.0, 21.8, 14.0; MALDI-TOF MS: m/z: 609.6 [M^+]; HRMS (ESI$^+$): m/z: calcd for $C_{46}H_{43}N$: 609.33955; found: 609.33854; elemental analysis calcd (%) for $C_{46}H_{43}N$: C 90.60, H 7.11, N 2.30; Found: C 90.24, H 7.15, N 2.41.

Synthesis and characterization of macrocycle 2: A mixture of $\mathbf{D_2}$ (146.3 mg, 0.1 mmol), 2,7-dibromo-9,9-dioctyl-9H-fluorene (54.8 mg, 0.1 mmol), $NaHCO_3$ (1.0 g, 0.012 mol), H_2O (10 mL), and THF (100 mL) was carefully degassed before $[Pd(PPh_3)_4]$ (2.3 mg, 2 μmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (1.0 mg, 1 μmol) and $P(t\mathrm{Bu})_3$ (0.81 mg, 4 μmol) was added. The mixture was stirred and heated at reflux for 5 days under nitrogen. Water and CH_2Cl_2 were added and then the organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was first purified by preparative GPC and then by column chromatography on silica gel using hexane/CH_2Cl_2 (5:2, v/v) as the eluent to afford macrocycle **2** as a colorless solid (for $[Pd_2(dba)_3]\cdot CHCl_3$ and $P(t\mathrm{Bu})_3$, yield: 67.1 mg, 42%; for $[Pd(PPh_3)_4]$, yield: 14.4 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.74 (m, 10H), 7.68–7.60 (m, 8H), 7.53 (s, 2H), 7.23–7.16 (m, 12H), 4.20–4.06 (m, 12H), 2.12 (t, J = 6.0 Hz, 4H), 1.98–1.76 (m, 12H), 1.63–1.46 (m, 12H), 1.46–1.32 (m, 24H), 1.29–1.18 (m, 4H), 1.08–0.82 (m, 38H), 0.62 ppm (t, J = 5.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 160.0, 159.9, 151.5, 143.8, 143.2, 143.0, 142.4, 142.1, 140.3, 140.2, 140.1, 139.8, 127.6, 127.5, 127.4, 126.9, 121.4, 120.1, 119.4, 118.7, 118.6, 113.0, 112.7, 112.5, 112.1, 111.9, 111.7, 68.4, 68.3, 68.2, 55.8, 40.5, 31.7, 31.6, 30.0, 29.4, 29.1, 25.8, 25.6, 23.9, 22.6, 22.5, 14.1, 13.9, 1.0 ppm; MALDI-TOF MS: m/z: 1598.2 [M^+]; elemental analysis calcd (%) for $C_{113}H_{144}O_6$: C 84.91, H 9.08; found: C 84.93, H 8.91.

Synthesis and characterization of bimacrocycle 3: A mixture of $\mathbf{B_2}$ (92.1 mg, 0.15 mmol), compound $\mathbf{A_4}$ (61.2 mg, 0.075 mmol), $NaHCO_3$ (1.0 g, 0.012 mol), H_2O (10 mL), and THF (120 mL) was carefully degassed before $[Pd(PPh_3)_4]$ (3.5 mg, 3 μmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (1.5 mg, 1.5 μmol) and $P(t\mathrm{Bu})_3$ (1.22 mg, 6 μmol) was added. The mixture was stirred and heated at reflux for 5 days under nitrogen. Water and CH_2Cl_2 were added and then the organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was first purified by preparative GPC and then by column chromatography on silica gel using hexane/CH_2Cl_2 (5:2, v/v) as the eluent to afford macrocycle **3** as a colorless solid (for $[Pd_2(dba)_3]\cdot CHCl_3$ and $P(t\mathrm{Bu})_3$, yield: 36.5 mg, 40%; for $[Pd(PPh_3)_4]$, yield: 4.5 mg, 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 4H), 8.15 (s, 4H), 8.07 (s, 4H), 7.67 (d, J = 8.3 Hz, 4H), 7.60 (s, 8H), 7.56 (s, 4H), 7.51 (s, 4H), 7.37 (d, J = 8.4 Hz, 4H), 4.24 (t, J = 6.9 Hz, 4H), 2.55 (s, 12H), 2.51 (s, 12H), 1.92 (m, 4H), 1.35 (br s, 12H), 0.86 ppm (t, J = 4.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 141.6, 141.5, 140.1, 139.7, 138.8,

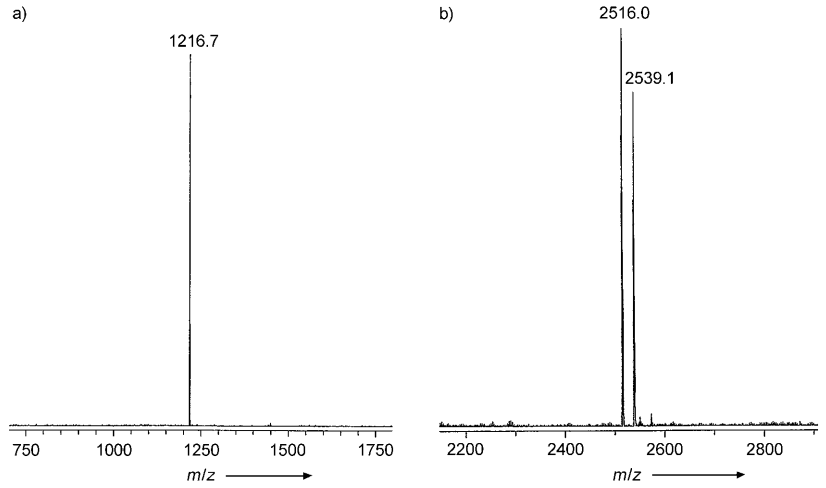


Figure 2. MALDI-TOF mass spectra of bimacrocycles **3** (a) and **4** (b).

138.7, 133.0, 127.5, 127.2, 126.0, 125.1, 124.6, 124.1, 123.6, 122.3, 122.0, 109.5, 43.9, 31.6, 29.3, 27.2, 22.7, 22.0, 21.8, 14.1 ppm; MALDI-TOF MS: m/z: 1216.7 [M^+]; elemental analysis calcd (%) for $C_{92}H_{84}N_2$: C 90.75, H 6.95, N 2.30; found: C 90.37, H 7.15, N 2.39.

Synthesis and characterization of spiro-bridged bimacrocycle 4: A mixture of **D_4** (224.6 mg, 0.1 mmol), 2,7-dibromo-9,9-dioctyl-9H-fluorene (109.6 mg, 0.2 mmol), $NaHCO_3$ (1.0 g, 0.012 mol), H_2O (10 mL), and THF (100 mL) was carefully degassed before [$Pd(PPh_3)_4$] (4.6 mg, 4 μmol) or [$Pd_2(dba)_3$]·$CHCl_3$ (2.0 mg, 2 μmol) and P(tBu)$_3$ (1.7 mg, 8 μmol) was added. The mixture was stirred and heated at reflux for 5 days under nitrogen. Water and CH_2Cl_2 were added and then the organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by preparative TLC using hexane/CH_2Cl_2 (5:2, v/v) as the eluent to afford macrocycle **4** as a colorless solid (for [$Pd_2(dba)_3$]·$CHCl_3$ and P(tBu)$_3$, yield: 52.8 mg, 21%; for [$Pd(PPh_3)_4$], trace mount of product). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.0 Hz, 4H), 7.82 (d, J = 8.1 Hz, 4H), 7.72 (d, J = 7.8 Hz, 4H), 7.60–7.52 (m, 20H), 7.48 (s, 4H), 7.25 (s, 4H), 7.17 (m, 8H), 7.14 (s, 4H), 6.98 (s, 4H), 4.04 (t, J = 6.4 Hz, 8H), 2.53 (s, 12H), 2.33 (s, 12H), 1.94 (t, J = 6.0 Hz, 8H), 1.79 (m, 8H), 1.46 (m, 8H), 1.36–1.26 (m, 24H), 0.89–0.55 ppm (m, 64H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 152.0, 149.8, 144.2, 142.5, 142.2, 142.1, 141.0, 140.9, 140.5, 140.3, 140.2, 139.9, 138.9, 138.3, 127.6, 126.9, 126.7, 126.2, 125.6, 125.4, 125.2, 122.6, 122.4, 122.4, 120.5, 119.9, 119.3, 112.8, 112.0, 68.2, 54.8, 40.3, 31.6, 31.4, 29.8, 29.7, 29.3, 28.8, 28.7, 25.7, 23.7, 22.6, 22.4, 21.8, 21.4, 14.0, 13.9 ppm; MALDI-TOF MS: m/z: 2516.0 [M^+].

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