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Synthesis of the functionalized cavitands with inwardly directed dialkylsilyl groups and phosphorous lone pairs

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ABSTRACT

Cavitands endowed with dialkylsilyl groups are described, involving the ^{1}H NMR spectra of nearby δ 0 areas. The differences of chemical shifts between in- and outwardly directed alkyls toward the cavity disclosed that introverted alkyls were put under strong π surroundings. The findings have been amplified to the synthesis of novel phosphorous ligands.

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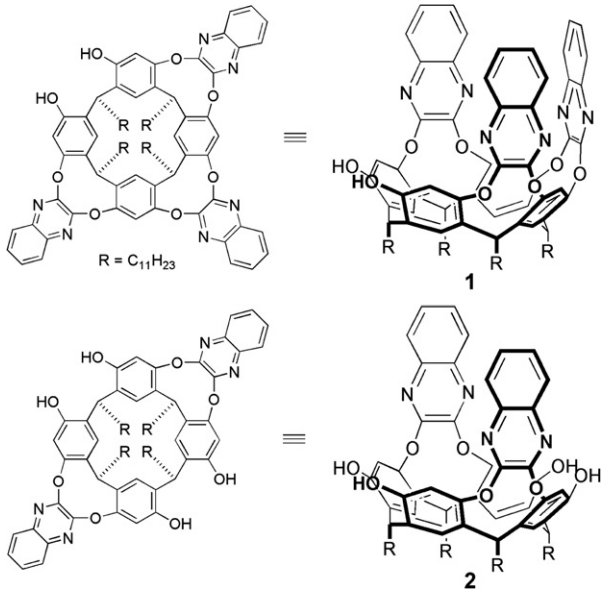
Natural supramolecular systems consolidate the inwardly directed functions. Binding site of enzymes, polypeptides, and RNA strands can fold around a substrate, and in the folded state the functionality converges on the substrate.[1,2] The introverted functionalities in biological macromolecules play quintessential roles in catalysis.[3]

In a similar vein, synthetic approach to the chemical space with introverted functionality has been pioneered,[4–6] particularly by Rebek and co-workers.[7] They use the deepened cavitand derived from Högberg's resorcinarene scaffold and 4 aromatic exteriors. The functional substituent is up in the interior room, like a fishing line, toward the tapered end. Indeed, there are many parallels between the synthetic and natural systems: the introverted functionality can recognize guests,[8] accelerate[9] and catalyze reactions,[10] and stabilize reactive intermediates.[11,12] However, the organization of functional substituents is underrepresented in supramolecular chemistry, due to the synthetic difficulty in functionalizing concave surfaces.[13]

Herein, we report the functionalized cavitands with dialkylsilyl groups which were derived from tri- or diquinoxaline-spanned cavitands **1** and **2** (Scheme 1). The dialkyls on silicon atom were discriminated between in- and outwardly directed towards the cavity. It revealed that the magnetically shielded environment caused by the cavitand shifts inwardly directed alkyl protons to strongly upfield in the ^{1}H NMR spectra. Additionally, we have synthesized the phosphorus-induced cavitand (Scheme 2).

The tri- and diquinoxaline-spanned cavitands on the basis of Högberg's resorcinarene,[14] **1** and **2**, were prepared according to the literature.[15] Then, the silylation of **1** in toluene was performed with dichlorodimethylsilane in the presence of triethylamine.[16]



Scheme 1. Tri- and diquinoxaline-spanned resorcin[4]arenes, **1** and **2**.

After the reaction at ambient temperature for 2 h, the starting material **1** was completely disappeared in TLC monitoring. The desired product **3** purified by column chromatography was obtained in 77% yield.[17] This condition was also effective to the reactions with dichlorodiethylsilane and dichlorodipropylsilane, providing 70% of **4** and 67% of **5**, respectively. Next, the silylation of **2** in toluene was carried out with dichlorodimethylsilane at 75 °C. After the reaction for 1.5 h, the tetraol **2** was totally consumed in TLC analyzing, providing **6** in 81% (Scheme 3). This condition also

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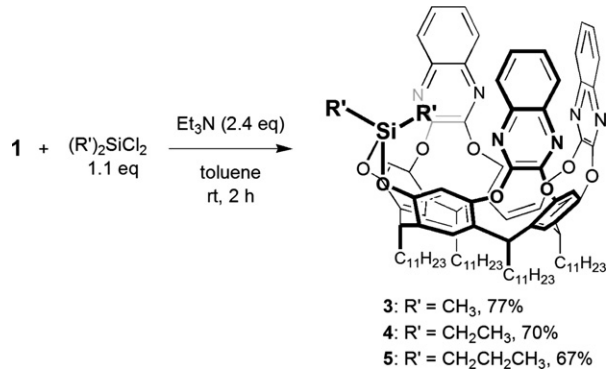
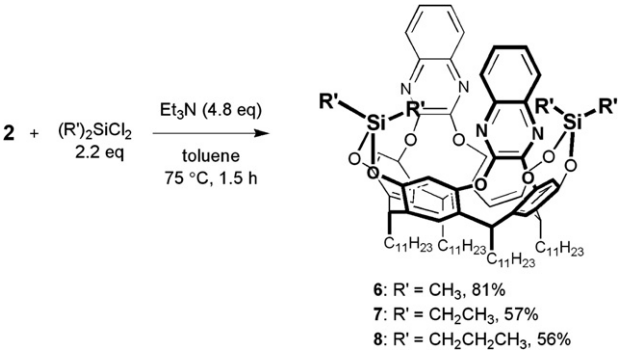


Scheme 2. Synthesis of **3**, **4**, and **5**.



Scheme 3. Synthesis of **6**, **7**, and **8**.

worked well in the reactions with dichlorodiethylsilane and dichlorodipropylsilane, providing 57% of **7** and 56% of **8**, respectively.

The ^{1}H NMR spectra of **3** at 298 K were recorded in several deuterated solvents; $CDCl_3$, CD_2Cl_2, acetone-d_6, benzene-d_6, and toluene-d_8. The CH-methine protons, which are located directly below the quinoxaline units in **3**, were situated at mid-field region; δ 5.73, 5.65 in $CDCl_3$, δ 5.70, 5.61 in CD_2Cl_2, δ 5.77, 5.67 in acetone-d_6, δ 6.22, 6.12 in benzene-d_6, and δ 6.16, 6.07 in toluene-d_8. These values indicate that the vase conformation was ensured in each deuterated solvents.[4c,15a]

On the other hand, upfield portions of ^{1}H NMR spectra in nearby δ 0 area showed two kinds of singlet peaks; one is corresponding to the methyl protons situated inwardly toward the cavity and the other outwardly.[18] The results are shown in Figure 1; **3** in (a) $CDCl_3$, (b) CD_2Cl_2, (c) acetone-d_6, (d) benzene-d_6, (e) toluene-d_8. The in- and outside methyls on the silicon atom in (a) $CDCl_3$ appeared at δ −0.59 and 0.48, respectively. The chemical shift change ($\Delta\delta$ value) between them was 1.07. In the spectrum (b) CD_2Cl_2, singlet methyl peaks were situated at δ −0.77 and 0.46, which gave $\Delta\delta$ value 1.23. These values denote that the inside methyl group was put under the obviously sharp π-environment based on cavitand space. In the spectrum (c), acetone-d_6 also afforded upfield shift of the inside methyl protons from δ 0.43 to δ −0.85, giving $\Delta\delta$ value 1.28. In the spectra (d), benzene-d_6 afforded larger $\Delta\delta$ values than $CDCl_3$, CD_2Cl_2, and acetone-d_6. The outwardly directed methyl located in δ 0.21 and the inward one did in δ −1.19, along with $\Delta\delta$ value 1.40. Note that in the spectrum (e), toluene-d_8 clearly emphasized the $\Delta\delta$ values 1.60 which was calculated from δ −1.41 of the inside methyl protons and δ 0.19 of the outside ones. Thus, $\Delta\delta$ values of the methyl groups of **3** were strongly affected with the solvents.

The solvent effects seen in Figure 1 are in agreement with the vase-kite switching systems as studied by Diederich and co-workers,[19] in which a class of quinoxaline-spanned cavitands is apt to form the vase in aromatic solvents as compared with chlorinated solvents. The vase-kite switching in **3** would average the chemical shift values of inside methyl protons, which brings the $\Delta\delta$ values in appearance.[4c,20] The large $\Delta\delta$ values in Figure 1, therefore, imply

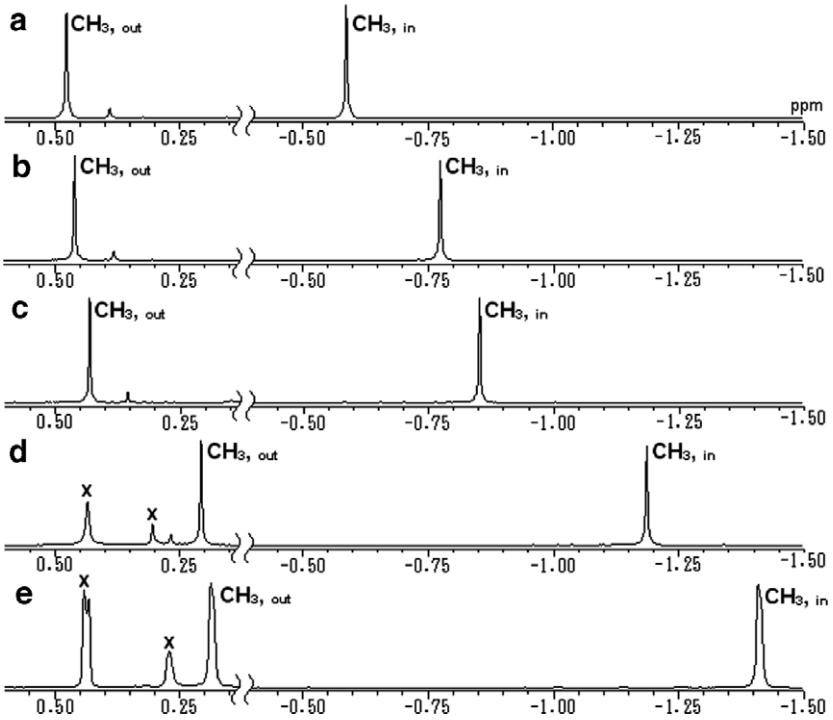


Figure 1. Upfield portions of ^{1}H NMR spectra of 3 (400 MHz, 298 K) in the solvents: (a) $CDCl_3$; (b) CD_2Cl_2; (c) acetone-d_6; (d) benzene-d_6; (e) toluene-d_8. The peaks labeled with CH_3, in and CH_3, out correspond to in- and outwardly directed methyl protons toward the cavity, respectively.

that the inside methyl protons frequently stay at the cavity of the vase conformation. Accordingly, the solvent-dependent spectra in Figure 1 suggest that the cavitand **3** prefers the vase form in toluene-d_8 and benzene-d_6 rather than in acetone-d_6, CD_2Cl_2, and $CDCl_3$. Actually, the chemical shifts of CH-methine protons in **3** with toluene-d_8 gave relatively large δ 6.16: this supports that the vase form is predominant.[4]

The nearby δ 0 areas of **4** and **5** in toluene-d_8 are represented in Figure 2, which also gave the upfield shifts of inside alkyl protons. In (b) **4**, the CH_2 of ethyl group was situated at δ −1.04 inside, and at δ 0.75 outside, providing $\Delta\delta$ 1.79. The CH_3 of ethyl group was situated at δ 0.066 inside, and at δ 1.14 outside, which yielded $\Delta\delta$ 1.07. In (e) **5**, the each proton of SiCH_2-, -CH_2-, and -CH_3 were positioned inside at δ −0.77, 0.71, 0.081, and outside at δ 0.79, 1.67, 1.06, giving $\Delta\delta$ 1.56, 0.96, 0.98, respectively. The maximum $\Delta\delta$ values in **4** and **5** were led by the protons of CH_2 groups that are directly connected to the silicon atom.

Figure 3 shows the nearby δ 0 areas of **6**, **7**, and **8** in toluene-d_8. The spectrum of (a) **6** showed two singlet peaks of methyl protons with $\Delta\delta$ 1.48; one is at δ −1.25 and the other is at δ 0.23. The former corresponds to inwardly directed methyl protons to the cavity of **6**, and the latter is for outwardly directed ones. The ethyl groups of (b) **7** inside the cavity shifted upfield to the quartet peak δ −0.93 for CH_2, and the triplet peak δ 0.19 for CH_3. The corresponding outside protons were seen at δ 0.80 for CH_2, and δ 1.18 for CH_3, so the $\Delta\delta$ values of CH_2 and CH_3 were 1.73 and 0.99, respectively. In the case of (c) **8**, the inward protons of SiCH_2–, –CH_2–, and –CH_3 were positioned at δ −0.69, 0.84, 0.30, and the outward at δ 0.84, 1.72, 1.09, giving $\Delta\delta$ 1.54, 0.88, 0.79, respectively.

The $\Delta\delta$ values of **3**, **4**, **5**, **6**, **7**, and **8** in toluene-d_8 are summarized in Figure 4. The protons of CH_2 or CH_3 groups directly bonded with silicon atoms were endowed with relatively large values; the maximum 1.79 in **4**, and the minimum 1.54 in **8**. Other protons of methylene and methyl groups always furnished the $\Delta\delta$ values in 1.0 or thereabout. This would be attributed to the free rotation of inwardly directed Si–CH_2 bond in ethyl and propyl groups. The CH_3 group of inside ethyl (**4**, **7**) and the CH_3CH_2 group of inside propyl (**5**, **8**) can come out from the strong area of magnetically shielded environments; hence, the chemical shifts were averaged at about 1.0. Whatever the cause, the position of protons in CH_2 group bonded to silicon atoms was sufficiently covered by the anisotropic effect of the cavity.

In this context, we have explored the fundamental finding applicable to the supramolecular catalyst center; the novel phosphorous ligands **9** and **10** in Scheme 4.[21,22] The reactions of **1** or **2** with tris(dimethylamino)phosphine proceeded in the presence of triethylamine to yield the products with 57% and 43%, respectively. The unambiguous ^{1}H NMR spectra in $CDCl_3$ revealed that the products were single isomer in 97% selectivity. On the ^{1}H NMR spectrum in the reaction of **1**, the doublet peak of the protons for the dimethylamino group predominantly emerged at δ 2.78 (d, $^4J_{PH}$ = 11 Hz). The minor peak sparingly appeared at δ 2.58 (d, $^4J_{PH}$ = 11 Hz). The spectrum in the reaction of **2** also recorded a main peak at δ 2.85 (d, $^4J_{PH}$ = 11 Hz), and a minor peak at δ 2.59 (d, $^4J_{PH}$ = 11 Hz). Our desired conformations of **9** and **10** are illustrated in Scheme 4: phosphorus moieties are axially oriented to the resorcinarene skeleton with inwardly directed P lone pairs to the cavity. However, the major peaks have not been identified as

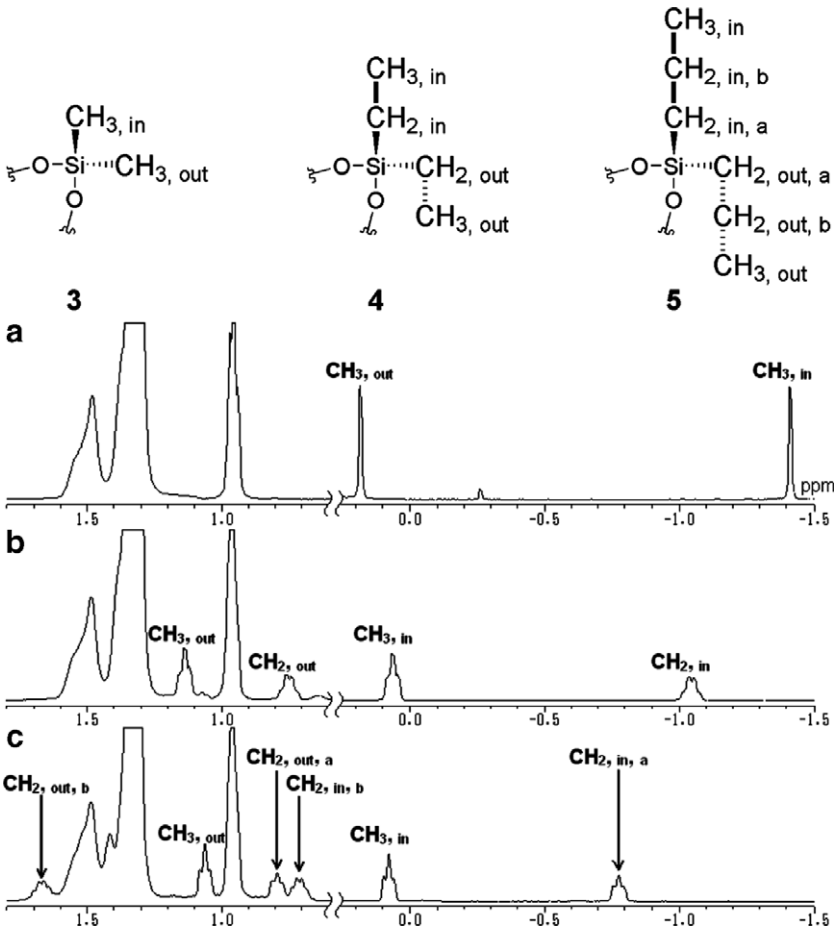


Figure 2. Upfield portions of ^{1}H NMR spectra (400 MHz, 298 K, toluene-d_8) of (a) 3, (b) 4, and (c) 5. The peaks of alkyl protons on the silyl groups are labeled with letters, respectively.

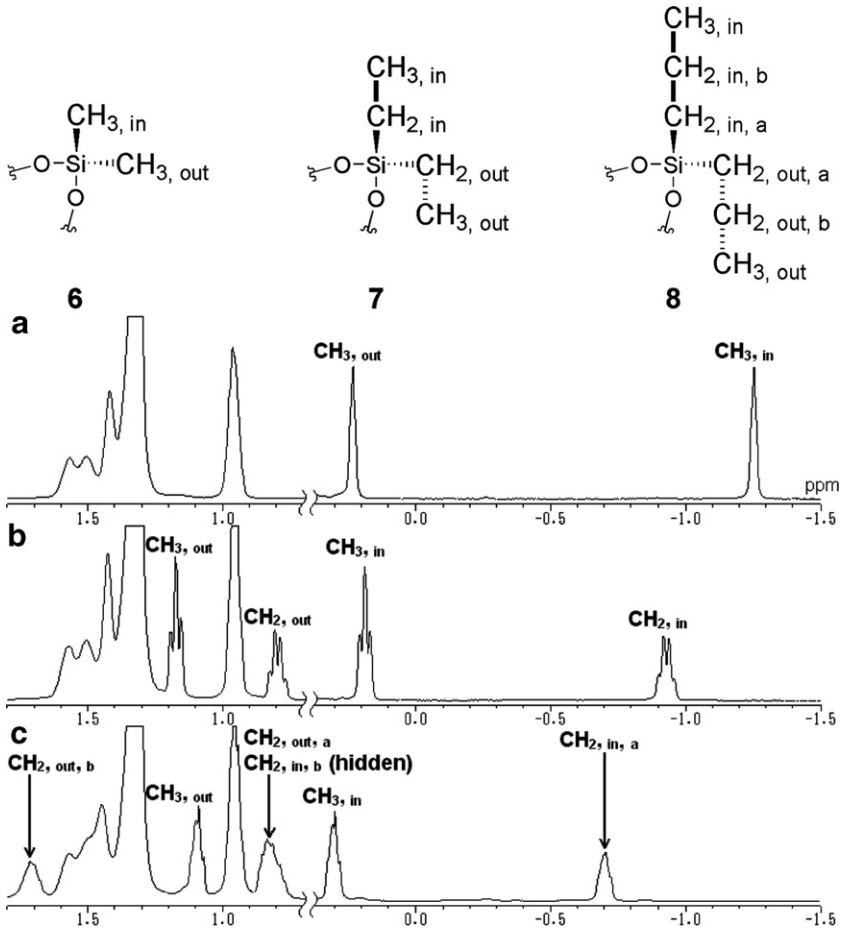


Figure 3. Upfield portions of ^{1}H NMR spectra (400 MHz, 298 K, toluene-d_8) of (a) 6, (b) 7, and (c) 8. The peaks of alkyl protons on the silyl groups are labeled with letters, respectively.

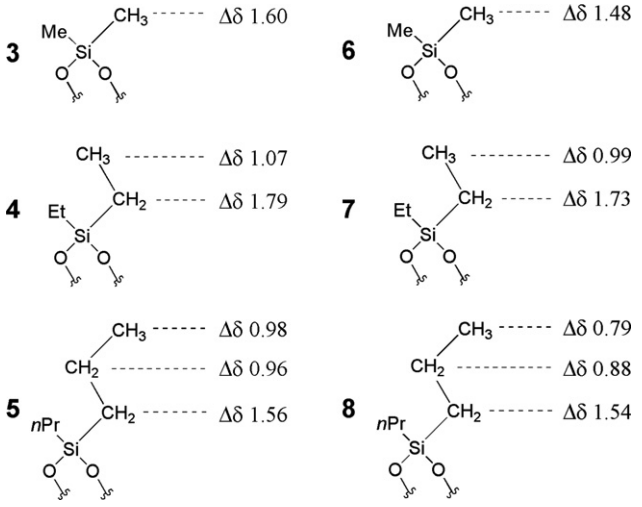
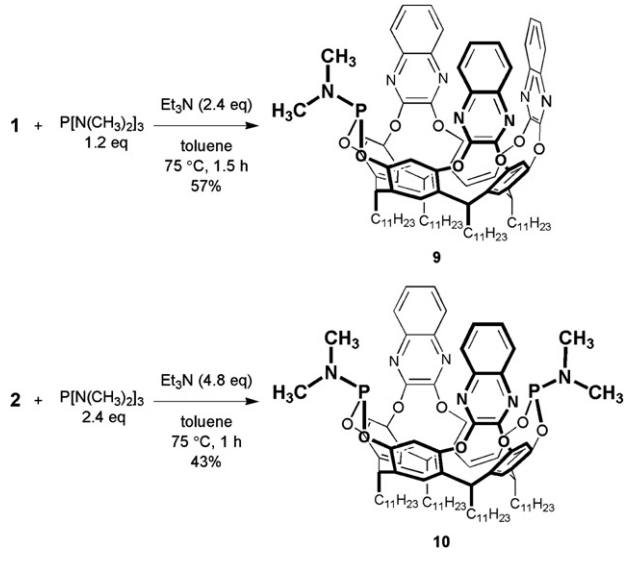


Figure 4. The differences of chemical shifts ($\Delta\delta$) in toluene-d_8 between in- and outwardly directed alkyl protons on silyl groups of 3, 4, 5, 6, 7, and 8.



Scheme 4. Synthesis of phosphorous ligands **9** and **10**.

desired conformers only by the above spectral data. Now, further investigation by obtaining the single crystals of **9** and **10** is in progress. It would be ideal if the P lone pairs would be clearly put in the anisotropic environments as **9** and **10** drawn in Scheme 4. Because such a position of the lone pairs was ensured to be strongly affected by the cavitand's anisotropy as shown in the study of silylated cavitands **3**–**8** in Figure 4. Thus, the 'folded P lone pairs' can offer the supramolecular environment with the specific cavity,[23] so the conceptual **9** and **10** would be expected to show the advantages of biocatalysis[24]: for example, chemo-, regio-, and sizeselective reactions under mild conditions. In addition, **9** and **10** can also

associate with unique coordination, so a variety of transition-metal catalyzed reactions can be envisaged.

In summary, we have reported a synthetic method to introduce dialkylsilyl groups into the quinoxaline-spanned resorcinarenes, along with a magnetically shielded environment caused by the cavitand space. Besides, the method enabled us to prepare the phosphorus-induced cavitands, although the orientations of phosphorus moieties were not determined. Work is now in progress to unveil the conformations of **9** and **10**.

Supplementary data

Supplementary materials associated with this article can be found in the online version, at doi:10.1016/j.tetlet.2008.05.103.

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17. *Representative experimental procedure for synthesis of* **3**: To the diol **1** (148 mg, 0.1 mmol) in a 20 mL Schlenk flask under an argon atmosphere were added toluene (2 mL), and Et_3N (24 mg, 0.24 mmol). After stirring for 10 min, $(CH_3)_2SiCl_2$ (14 mg, 0.11 mmol) was added, and the reaction was conducted for 2 h. The mixture was filtered, and washed with toluene, and then the filtrate was concentrated *in vacuo* to give crude products. Purification by short-plug column chromatography (CH_2Cl_2) afforded white solid materials, which were reprecipitated from MeOH to give **3** as white powders of 118 mg in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (2H, s), 7.89 (2H, d, J = 8.7 Hz), 7.85 (2H, dd, J = 3.7, 6.4 Hz), 7.65 (2H, d, J = 8.7 Hz), 7.54–7.50 (4H, m), 7.47–7,42 (2H, m), 7.30 (2H, s), 7.13 (2H, s), 7.11 (2H, s), 5.73 (1H, t, J = 8.2 Hz), 5.65 (2H, t, J = 8.2 Hz), 4.56 (1H, t, J = 8.2 Hz), 2.35–2.16 (8H, m), 1.52–1.22 (72H, m), 0.92–0.86 (12H, m), 0.47 (3H, s, outside $SiCH_3$), −0.59 (3H, s, inside $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 153.0, 152.8, 152.7, 152.5, 152.4, 150.4, 140.0, 139.9, 136.7, 136.1, 134.6, 132.6, 129.42, 129.35, 129.1, 128.0, 127.8, 124.0, 122.8, 118.8, 115.9, 35.3, 34.4, 34.1, 32.8, 32.6, 32.5, 32.2, 30.0, 29.6, 28.3, 28.2, 22.9, 14.4, −2.19 ($SiCH_3$), −4.40 ($SiCH_3$). ESI-MS m/z: 1575 (M^+). Anal. Calcd for $C_{98}H_{122}N_6O_8Si$: C, 76.42; H, 7.98; N, 5.46. Found: C, 76.15; H, 7.89; N, 5.42.
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21. *The spectral data for compound* **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 8.01 (d, J = 8.7 Hz, 2H), 7.72 (dd, J = 3.6, 7.3 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.58 (dd, J = 7.3, 7.3 Hz, 2H), 7.50 (dd, J = 7.3, 7.3 Hz, 2H), 7.39 (dd, J = 3.6, 7.3 Hz, 2H), 7.22 (s, 2H), 7.21 (s, 2H), 7.19 (s, 2H), 5.68 (t, J = 8.2 Hz, 2H), 5.68 (t, J = 8.2 Hz, 1H), 4.54 (t, J = 7.3 Hz, 1H), 2.78 (d, $^4J_{PH}$ = 11 Hz, 6H), 2.32 – 2.12 (m, 8H), 1.51-1.11 (m, 72H), 0.94 – 0.81 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 153.0, 152.9, 152.7, 152.5, 152.2, 149.5 (d, J_{CP} = 4.8 Hz), 139.92, 139.89, 139.8, 137.1, 136.3, 136.0, 134.4, 129.3, 129.0, 128.8, 128.03, 128.00, 127.9, 123.5, 122.5, 119.1, 117.3, 35.8, 35.2 (d, J_{CP} = 18.2 Hz), 34.3, 34.2, 33.0, 32.1, 31.7, 29.9, 29.6, 28.2, 28.1, 22.9, 14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 142.7. ESI-MS m/z: 1591 ($M+Cl^-$). Anal. Calcd. For $C_{98}H_{122}N_7O_8P$: C, 75.60; H, 7.90; N, 6.30. Found: C, 75.38; H, 7.86; N, 6.34.
22. The spectral data for compound **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 3.2, 6.4 Hz, 4H), 7.53 (dd, J = 3.2, 6.4 Hz, 4H), 7.31 (s, 4H), 7.21 (s, 4H), 5.69 (t, J = 8.2 Hz, 2H), 4.60 (t, J = 8.2 Hz, 2H), 2.85 (d, $^4J_{PH}$ = 11 Hz, 12H), 2.31–2.20 (m, 8H), 1.50–1.22 (m, 72H), 0.90 (t, J = 5.5 Hz, 6H), 0.89 (t, J = 5.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 152.2, 149.6 (d, J_{CP} = 2.9 Hz), 139.9, 137.1, 134.7, 129.3, 128.1, 122.7, 117.3, 35.8, 35.3 (d, J_{CP} = 18.2 Hz), 34.1, 32.1, 32.0, 31.7, 29.9, 29.6, 28.2, 22.9, 14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 142.4. ESI-MS m/z: 1538 ($M+Cl^-$). Anal. Calcd for $C_{92}H_{124}N_6O_8P_2$: C, 73.47; H, 8.31; N, 5.59. Found: C, 73.36; H, 8.36; N, 5.56.
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