Tetrahedron 69 (2013) 1516–1520

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A screw-shaped alignment of pyrene using *m*-calix[3]amide

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ARTICLE INFO

Article history:
Received 1 November 2012
Received in revised form 4 December 2012
Accepted 5 December 2012
Available online 12 December 2012

ABSTRACT

m-Calix[3]amide bearing three pyrenes (**1a**) was prepared by the condensation reaction of 3-nonylaminobenzoic acid derivative using Ph_3PCl_2. Pyrenyl groups were found to be aligned in the screw-like fashion by *m*-calix[3]amide as confirmed by the X-ray crystallography. Aromatic proton signals observed at the up-field region in the ^1H NMR spectrum at low temperature indicated that pyrenyl groups in **1a** are aligned in close proximity in THF solution. UV–vis absorption and fluorescence emission spectra did not show marked peak shift nor concentration fluorescence quenching compared with reference compounds implying no significant electronic interaction between pyrenyl groups. These results can be explained by the steric effect of the *m*-calix[3]amide platform. On the other hand, an excimer emission was observed for *m*-calix[3]amide having a flexible spacer between pyrene and *m*-calix[3]amide (**1b**).

1. Introduction

π-Conjugated molecules play a central role in organic optoelectronic materials. It is well known that not only the chemical structure but also the three dimensional alignment structure of π-conjugated molecules contributes largely to the performance of materials. Thus the programmable arrangement of π-conjugated molecules in space and the understanding of structure–properties relationship are of much importance. However, the three dimensional alignment structure is generally governed by the chemical structure of molecules, as represented by the herringbone packing of pentacene. One possible strategy to tune-up the alignment structure is the chemical modification at the periphery of π-conjugated molecules (Method 1). Kobayashi et al. succeeded in the cofacial packing of bis(methylthio)acenes by using S–S and S–π interactions.[1,2] Other groups also proposed the molecular design for the cofacial crystal packing of acene derivatives.[3,4] Another technique to control the alignment structure of π-conjugated molecules is the utilization of well-defined tethering unit (Method 2). Yoshizawa et al. recently reported a tubular macrocycle containing four anthracenes covalently connected by the *meta*-phenylene unit.[5] The covalent bond approach (Method 2) would be much reliable since the three dimensional alignment structure of π-conjugated molecules can be maintained both in the solid state and diluted solution. Pyrene having the high fluorescence quantum yield shows two characteristic luminescence behaviors,[6] namely a monomer emission observed in the diluted solution and an excimer emission derived from the associated dimer in the concentrated solution. The excimer emission can be also detected when pyrenes are forced into the confined space even in the diluted condition. Consequently, pyrene is a useful probe as the DNA fluorescence label to investigate their distance and chain conformation.[7] We will herein describe a novel alignment of three pyrenes using Method 2 and report optical properties of pyrene-carrying macrocycles in order to figure out the structure–properties relationship.

Cyclic *meta*-benzamide trimer (*m*-calix[3]amide) is efficiently synthesized by the condensation reaction of 3-alkylaminobenzoic acid derivatives due to the cis preference of the *N*-alkyl benzanilide skeleton.[8–13] *m*-Calix[3]amide has two conformers, in which the *syn* conformer has three benzene rings in the same orientation relative to the amide bond and the *anti* conformer has one benzene ring turning in other direction. The *syn* conformer prefers to the *anti* conformer both in the solid phase and solution. As a consequence, appended substituents on the benzene ring are positioned closely in the *syn* conformer of *m*-calix[3]amide. We have reported the synthesis and characterization of *m*-calix[3]amides bearing pyridine[14] and bithiophene[15] to reveal that *m*-calix[3]amide is suitable candidate for assembling functional groups in close proximity. In this paper, *m*-calix[3]amide was chosen as the platform to align pyrenes in the screw-like fashion. The synthesis of *m*-calix[3]amides having three pyrenes (**1a** and **1b**), *m*-calix[3]amide having one pyrene (**2**), and model compound (**3**) (Fig. 1) along with the

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0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.12.015

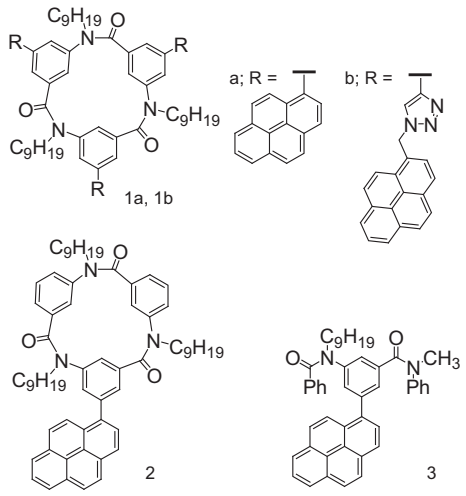


Fig. 1. Structure of *m*-calix[3]amides (**1a**, **1b**, and **2**) and model compound (**3**).

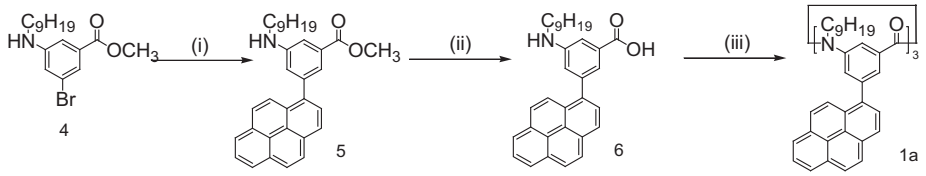
conformational characteristics of **1a** in solid and solution states and optical properties in solution will be described.

2. Results and discussion

Following to our previous report,[15] methyl 3-bromo-5-nonylaminobenzoate (**4**) was synthesized in three steps from 3-bromo-5-nitrobenzoic acid. *m*-Calix[3]amide bearing three pyrenes (**1a**) was synthesized from **4** as shown in Scheme 1. The synthetic route consists of the Suzuki–Miyaura cross coupling of **4** with pyrene-1-boronic acid, the hydrolysis of methyl ester by NaOH, and the cyclic oligomerization using Ph_3PCl_2 as the condensation reagent. Cyclic trimer **1a** was isolated by preparative GPC in 17% yield. The low yield of the product is likely due to the steric hindrance of the pyrenyl group. *m*-Calix[3]amide (**1b**) having a flexible spacer between pyrene and *m*-calix[3]amide was prepared for comparison and the synthetic route is shown in Scheme 2. Methyl 3-iodo-5-nonylaminobenzoate (**7**) was prepared from 3-iodo-5-nitrobenzoic acid. *m*-Calix[3]amide bearing three ethynyl groups (**10**) was obtained in three steps from **7** by the Sonogashira–Hagihara cross coupling with trimethylsilylacetylene, the concomitant de-silylation and ester hydrolysis by NaOH, and the cyclic oligomerization using $SiCl_4$. Finally, the Huisgen cycloaddition of **10** with 1-azidomethylpyrene in the presence of copper(I) iodide afforded **1b** in 70% yield. The cyclic oligomerization of 3-alkylaminobenzoic acid carrying the triazole ring with pyrene using Ph_3PCl_2 or $SiCl_4$ met with no success probably due to the basic character of the heterocycle.

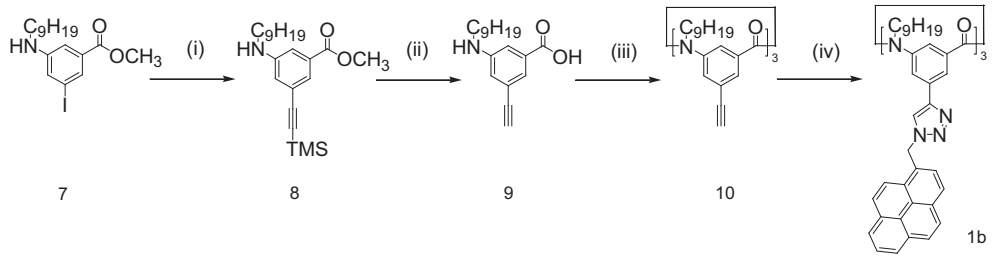
To investigate the optical properties of *m*-calix[3]amide in detail, *m*-calix[3]amide having one pyrene (**2**) and acyclic model compound (**3**) were prepared. The synthesis of **2** was carried out by the cyclic co-oligomerization of **6** and 3-nonylaminobenzoic acid using Ph_3PCl_2 as the condensation reagent, and the purification by preparative GPC afforded the desired compound **2** in 6% yield. On the other hand, **3** was prepared in three steps from **4**, which consists of the benzoylation of the *N*-nonylamino group, the ester–amide exchange of methyl ester, and the Suzuki–Miyaura cross coupling with pyrene-1-boronic acid. The detailed experimental procedures are described in the Supplementary data.

The alignment structure of three pyrenyl groups was determined by the single crystal X-ray crystallography using *m*-calix[3]amide bearing the ethyl substituent on the amide nitrogen (**1a**′) instead of **1a** (Fig. 2). **1a**′ adopts the *syn* conformation and three pyrenyl groups are arranged on the same side of the *m*-calix[3]amide skeleton. The tertiary amide bond has the nearly planer structure as judged by the dihedral angle Me–N–C–O to be 6.0° on average. The averaged dihedral angle formed between the benzene ring and the amide plane is 110.3°. Owing to the large steric hindrance induced by three pyrenyl groups, this value is larger than that observed for *m*-calix[3]amide bearing three phenyl groups (the corresponding dihedral angle is 100.0°).[12] The center-to-center distances between adjacent pyrenyl groups are approximately 6.2 Å and the dihedral angle between three pyrenyl groups is about 61°.



Scheme 1. Synthetic route to **1a**. Reagents and conditions: (i) pyrene-1-boronic acid, K_2CO_3, $Pd(PPh_3)_4$, THF, H_2O, reflux; (ii) NaOH, H_2O, THF, MeOH, 40 °C; (iii) Ph_3PCl_2, $(CHCl_2)_2$, reflux.

The close arrangement of three pyrenyl groups in **1a** was also evident in the ^1H NMR spectra (Fig. 3). At 293 K, the ^1H NMR spectrum showed broad signals and the position of aromatic proton signals was not much different from that of **6** (Supplementary data). When the spectrum was measured at 233 K, proton signals become sharp and several new signals were appeared due to the slow rotation around the carbon(benzene)–carbon(pyrene) bond relative to the NMR time scale. The doublet signal at 6.48 ppm can be assigned to the proton derived from the *anti* conformer.[16] Although the complete signal assignment is impossible, the proton signals observed at the up-field region (6.8–4.5 ppm) seem to be originated from pyrene protons, which are strongly shielded by the adjacent pyrenyl group. On the other hand, ^1H NMR spectra



Scheme 2. Synthetic route to **1b**. Reagents and conditions: (i) trimethylsilylacetylene, CuI, $Pd(PPh_3)_4$, Et_3N, 50 °C; (ii) NaOH, H_2O, THF, MeOH, rt; (iii) $SiCl_4$, pyridine, reflux; (iv) 1-azidomethylpyrene, CuI, DMF, 90 °C.

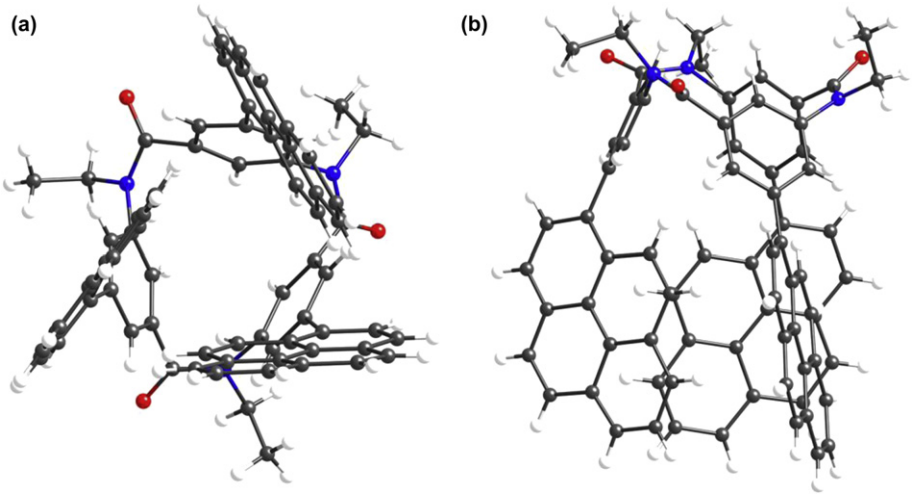


Fig. 2. Crystal structure of **1a**′ depicted as a ball and stick model. (a) Top view and (b) side view. Chloroform molecules are omitted for clarity. One of the pyrene group is disordered to two positions and the occupancies are refined (about 0.60 and 0.40). Disordered atoms of a pyrene rings, which have minor occupancy are omitted for clarity.

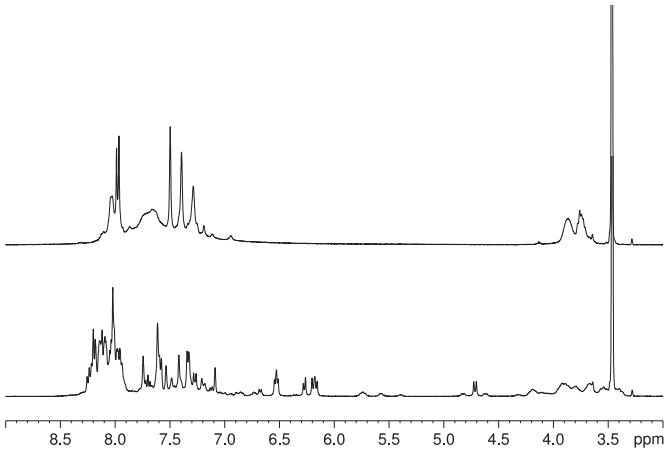


Fig. 3. ^{1}H NMR spectra of **1a** in THF-d_8 at 293 K (top) and 233 K (bottom).

of **2** and **3** showed no proton signals around the same region (Supplementary data). These results indicate that *m*-calix[3]amide is a suitable platform to realize the screw-like arrangement of three pyrenyl groups.

The UV–vis absorption and fluorescence emission spectra were measured in THF solution. Prior to the measurement, the solution was purged with nitrogen in order to avoid the fluorescence quenching by oxygen. The concentration of the solution are kept low ($<10^{-5}$ M) to prevent the intermolecular interaction. As shown in Fig. 4a, the absorption maximum wavelengths were similar between **1a**, **2**, and **3**, which indicates that they have comparable effective conjugation length. In our previous report,[15] the absorption maximum wavelength of *m*-calix[3]amide bearing three bithiophenes was blue-shifted by 9 nm from that of acyclic model compound to imply the intramolecular electronic interaction between bithiophenes. Hence three pyrenes included in **1a** have negligible interaction in the ground state. The absorption spectrum of **1b** showed the vibronic fine structure characteristic to pyrene (Fig. 4b). Fluorescence maximum wavelength of **1a** was red-shifted by 3–5 nm from those of **2** and **3**, and the tailing to the longer wavelength region was observed (Fig. 4c). The fluorescence emission from the associated state (excimer emission) was not observed from **1a**. These results indicate that three pyrenes in **1a** have very weak electronic interaction in the excited state because they cannot form the face-to-face stacked structure. In contrast, the fluorescence emission of **1b** appeared as a broad featureless band at the longer wavelength region (476 nm) having the quantum yield of 0.06. The flexible methylene spacer reduces the steric hindrance to permit the excimer emission. The fluorescence quantum yield of **3** was quite low (Φ_{fl}=0.04), which might be resulted from the twisted intramolecular charge transfer (TICT) by the rotation of the amide bonds.[17] On the other hand, the quantum yields of **1a** (Φ_{fl}=0.36) and **2** (Φ_{fl}=0.34) were high probably because the cyclic structure suppresses the rotation of the amide bond. It should be noted that the fluorescence quantum yield of **1a** and **2** are almost similar even though the chromophores are closely located in **1a**. This is also a consequence of the tilted alignment of three pyrenes in the *m*-calix[3]amide platform.

3. Conclusion

m-Calix[3]amides bearing three pyrenes (**1a** and **1b**), *m*-calix[3]amide having one pyrene (**2**), and model compound (**3**) were synthesized. The structure was investigated in the solid and solution states by the single crystal X-ray crystallography and ^{1}H NMR spectroscopy to find out that three pyrenyl groups in **1a** are arranged closely in space by the *m*-calix[3]amide platform. Optical properties in THF solution were investigated by UV–vis and fluorescence spectroscopy. The absorption and emission maximum wavelengths were similar between **1a**, **2**, and **3**. In contrast to **1b** having the flexible spacer between pyrene and *m*-calix[3]amide, **1a** showed monomer emission and no excimer emission was observed. **1a** had a high fluorescence quantum yield compared to **3** and the concentration quenching did not occur. These results indicate that *m*-calix[3]amide is an excellent platform to align conjugated molecules in close proximity and screw-like fashion. We believe that this new strategy for the programmable arrangement of π-conjugated molecules in space leads to the better understanding of structure–properties relationship of π-conjugated molecules.

4. Experimental section

4.1. Synthesis of 5

To a mixture of methyl 3-bromo-5-nonylaminobenzoate (**4**)[15] (0.70 g, 2.0 mmol) and pyrene-1-boronic acid (0.50 g, 2.0 mmol) in THF (20 mL) were added 2 M aq K_2CO_3 (8.0 mL) and $Pd(PPh_3)_4$

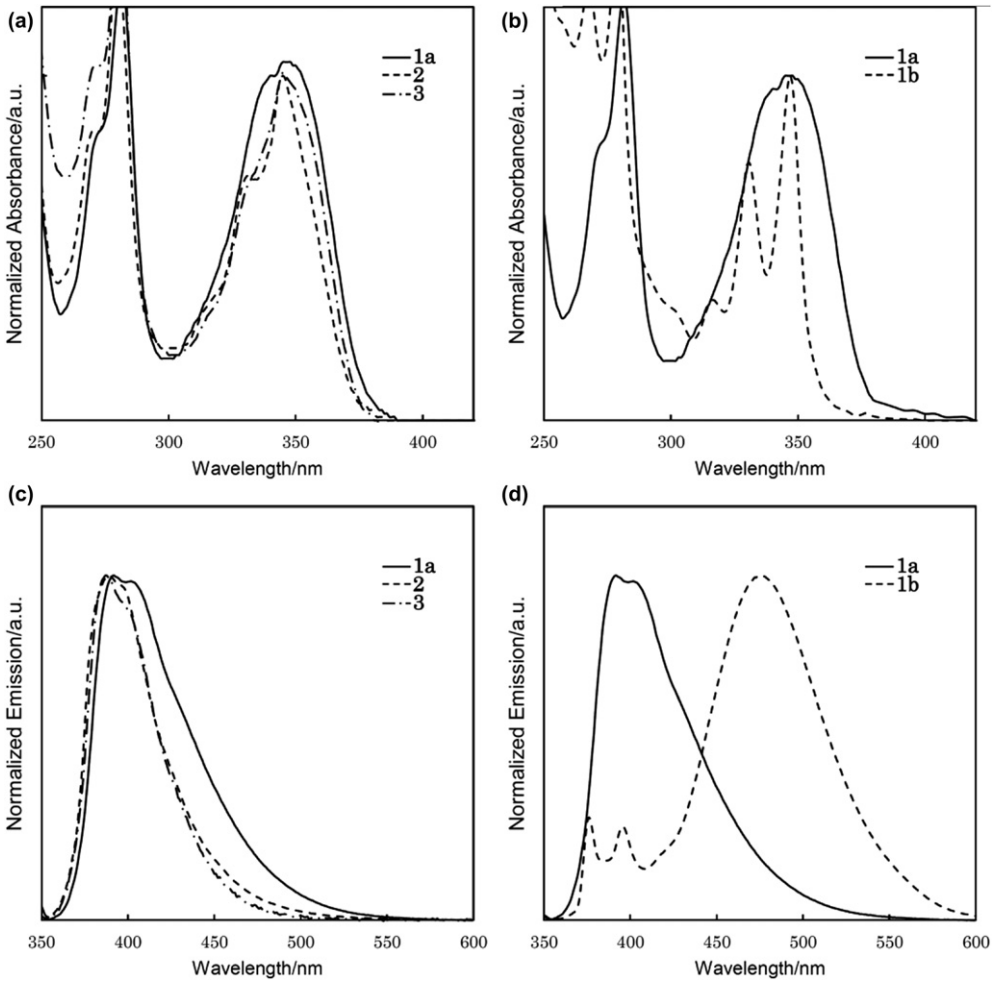


Fig. 4. Normalized absorption and emission spectra of **1a**, **1b**, **2**, and **3** in THF solution ($\lambda_{ex}=\lambda_{abs}$, room temperature).

(26 mg, 20 μmol), and the system was heated to reflux overnight. After an aqueous phase was extracted with DCM, the combined organic phase was washed with saturated aq Na_2CO_3. After drying over $MgSO_4$, solvents were removed by rotary evaporator. The crude product was purified by recrystallization from DCM/hexane to obtain yellow crystal in 0.55 g (57% yield). Mp 102–103 °C. ^{1}H NMR (δ, 200 MHz, ppm, $CDCl_3$) 8.47–7.91 (9H), 7.62 (s, 1H), 7.37 (s, 1H), 6.95 (s, 1H), 3.90 (s, 3H), 3.14 (t, J=7.0 Hz, 2H), 1.60 (m, 2H), 1.40–1.20 (12H), 0.87 (t, J=6.8 Hz, 3H). ^{13}C NMR (δ, 50 MHz, ppm, $CDCl_3$) 167.5, 148.5, 142.2, 137.3, 131.4, 131.1, 130.9, 130.6, 128.4, 127.5, 127.5, 127.4, 127.3, 127.3, 125.9, 125.2, 125.1, 124.8, 124.8, 124.5, 120.4, 119.2, 112.2, 52.0, 44.0, 31.8, 29.5, 29.4, 29.4, 29.2, 27.1, 22.6, 14.1. IR (ν, cm^{-1}) 3395, 2921, 2847, 1708, 1597, 1523, 1435, 1352, 1307, 1239, 1187, 1104, 987, 840, 772, 722. Anal. Calcd for $C_{33}H_{35}NO_2$: C, 82.98; H, 7.39; N, 2.93. Found: C, 81.89; H, 7.65; N, 2.85.

4.2. Synthesis of 6

To a solution of **5** (0.40 g, 0.84 mmol) in THF/MeOH (4 mL/4 mL) was added 2 M aq NaOH (4 mL), and the system was stirred for 10 h at 40 °C. The solution was acidified to pH 3–4 with 1 M aq HCl and the precipitate was collected to obtain yellow powder in 0.36 g (93% yield). ^{1}H NMR (δ, 200 MHz, ppm, $CDCl_3$) 7.56 (s, 1H), 7.30 (s, 1H), 6.94 (s, 1H), 3.14 (t, J=7.1 Hz, 2H), 3.06 (s, 1H), 1.63 (br m, 2H), 1.43–1.21 (12H), 0.89 (t, J=6.7 Hz, 3H). ^{13}C NMR (δ, 50 MHz, ppm, $CDCl_3$) 171.1, 147.7, 130.6, 123.3, 123.2, 121.1, 115.2, 83.1, 77.2, 44.4, 31.8, 29.5, 29.3, 29.2, 29.1, 27.0, 22.6, 14.0. IR (ν, cm^{-1}) 3734, 3628, 3422, 3275, 2925, 2850, 1682, 1597, 1506, 1429, 1344, 1305, 1270, 873, 773, 654.

4.3. Synthesis of 1a

To a solution of **6** (0.27 g, 0.74 mmol) in $(CHCl_2)_2$ (30.0 mL) was added Ph_3PCl_2 (0.87 mL, 2.6 mmol), and the mixture was heated to reflux for 12 h. After removal of $(CHCl_2)_2$, ethylacetate was added and washed with water. The organic phase was dried over $MgSO_4$ and solvents were removed by rotary evaporator. The crude product was purified by the preparative GPC ($CHCl_3$ as an eluent) to obtain white solid (72 mg, 17%). Mp>300 °C. ^{1}H NMR (δ, 600 MHz, ppm, $CDCl_3$) 8.40–6.81 (br m, 36H), 4.15–3.62 (br m, 6H), 1.84–1.60 (br s, 6H), 1.50–1.10 (br m, 36 H), 0.94–0.73 (br s, 9H). ^{13}C NMR (δ, 150 MHz, ppm, $CDCl_3$) 170.2, 142.7, 134.3, 131.0, 128.7, 128.3, 127.9, 127.8, 127.6, 127.1, 126.0, 125.3, 124.8, 31.8, 29.5, 29.4, 29.2, 27.8, 26.9, 22.6, 14.1. IR (ν, cm^{-1}) 2923, 2853, 1651, 1586, 1456, 843, 721. HR MALDI-TOF-MS calcd for $C_{96}H_{94}N_3O_3$ ($M+H^+$): 1336.7295. Found: 1336.8346.

4.4. Synthesis of 8

To a mixture of methyl 3-iodo-5-nonylaminobenzoate (**7**)[15] (0.40 g, 1.0 mmol), CuI (12 mg, 0.06 mmol), and $Pd(PPh_3)_4$ (34 mg, 0.03 mmol) in Et_3N (10 mL) was added trimethylsilylacetylene (0.28 mL, 2.0 mmol), and the system was heated to 50 °C for

6 h. After removal of solvents, DCM was added and washed with 1 M aq HCl. The organic phase was dried over $MgSO_4$ and solvents were removed by rotary evaporator. The crude product was purified by SiO_2 chromatography (DCM, R_f=0.7) followed by recrystallization from DCM/hexane to obtain yellow powder in 0.27 g (73% yield). Mp 112–113 °C. ^{1}H NMR (δ, 200 MHz, ppm, $CDCl_3$) 7.44 (s, 1H), 7.20 (s, 1H), 6.83 (s, 1H), 3.88 (s, 3H), 3.73 (s, 1H), 3.11 (t, J=7.4, 2H), 1.60 (br m, 2H), 1.41–1.23 (12H), 0.88 (t, J=6.7 Hz, 3H), 0.24 (s, 9H). ^{13}C NMR (δ, 50 MHz, ppm, $CDCl_3$) 166.8, 148.3, 131.0, 123.9, 121.8, 119.3, 113.9, 104.8, 93.9, 52.1, 43.8, 31.8, 29.5, 29.4, 29.3, 29.2, 27.0, 22.6, 14.1, −0.09. IR (ν, cm^{-1}) 3396, 2954, 2923, 2849, 2149, 1706, 1595, 1518, 1436, 1344, 1308, 1237, 1178, 1105, 996, 843, 771. Anal. Calcd for $C_{22}H_{35}NO_2Si$: C, 70.73; H, 9.44; N, 3.75. Found: C, 70.42; H, 9.57; N, 3.62.

4.5. Synthesis of 9

To a solution of **8** (0.20 g, 0.48 mmol) in THF/MeOH (2 mL/2 mL) was added 2 M aq NaOH (2 mL), and the system was stirred for 48 h at room temperature. The solution was acidified to pH 3–4 with 1 M aq HCl and the precipitate was collected to obtain white powder in 0.14 g (93% yield). Mp 112–113 °C. ^{1}H NMR (δ, 200 MHz, ppm, $CDCl_3$) 7.56 (s, 1H), 7.30 (s, 1H), 6.94 (s, 1H), 3.14 (t, J=7.1 Hz, 2H), 3.06 (s, 1H), 1.63 (br m, 2H), 1.43–1.21 (12H), 0.89 (t, J=6.7 Hz, 3H). ^{13}C NMR (δ, 50 MHz, ppm, $CDCl_3$) 171.1, 147.7, 130.6, 123.3, 123.2, 121.1, 115.2, 83.1, 77.2, 44.4, 31.8, 29.5, 29.3, 29.2, 29.1, 27.0, 22.6, 14.0. IR (ν, cm^{-1}) 3734, 3628, 3422, 3276, 2925, 2850, 1682, 1597, 1506, 1429, 1344, 1305, 1270, 873, 773, 654.

4.6. Synthesis of 10

To a solution of **9** (0.17 g, 0.60 mmol) in dry pyridine (4.0 mL) was added dropwise $SiCl_4$ (0.12 mL, 0.90 mmol) at 0 °C, and the mixture was heated to reflux for 12 h. After removal of pyridine, DCM was added and washed with 1 M aq HCl. The organic phase was dried over $MgSO_4$ and solvents were removed by rotary evaporator. The crude product was purified by the preparative GPC ($CHCl_3$ as an eluent) to obtain brown solid (16 mg, 10%). Mp>300 °C. ^{1}H NMR (δ, 600 MHz, ppm, $CDCl_3$) 7.62 (s, minor 3H×0.25), 7.35 (s, minor 3H×0.25), 7.15 (s, major 3H×0.75), 7.02 (s, major 3H×0.75), 6.84 (s, major 3H×0.75), 6.32 (s, minor 3H×0.25), 3.77 (m, major 3H×0.75 and minor 6H×0.25), 3.60 (m, major 3H×0.75), 3.12 (s, major and minor 3H), 1.60–1.48 (6H), 1.36–1.14 (36H), 0.88 (t, J=7.1 Hz, 9H). ^{13}C NMR (δ, 150 MHz, ppm, $CDCl_3$), 168.9, 142.3, 139.2, 133.0, 130.1, 127.1, 124.0, 81.1, 79.7, 50.1, 31.8, 29.5, 29.2, 29.1, 27.4, 26.7, 22.6, 14.1. IR (ν, cm^{-1}) 3734, 3306, 3235, 2924, 2853, 1648, 1581, 1433, 1389, 1328, 1261, 1127, 887, 802, 703, 652. HR MALDI-TOF-MS calcd for $C_{54}H_{70}N_3O_3$ ($M+H^+$): 808.5417. Found: 808.5050.

4.7. Synthesis of 1b

To a solution of **10** (16 mg, 0.02 mmol) and 1-azidomethylpyrene[18] (30 mg, 0.12 mmol) in DMF (2 mL) was added CuI (2.0 mg, 0.01 mmol), and the system was stirred for 6 h at 90 °C. After removal of solvents, DCM was added and washed with brine. The organic phase was dried over $MgSO_4$ and solvents were removed by rotary evaporator. The crude product was purified by SiO_2 chromatography (DCM then ethylacetate (R_f=0.9)) to obtain brown solid (23 mg, 70%). ^{1}H NMR (δ, 600 MHz, ppm, $CDCl_3$) 8.16–7.76 (24H×0.75, 27H×0.25), 7.71–7.66 (6H×0.25), 7.64 (s, 3H×0.75), 7.49 (s, 3H×0.25), 7.46 (3H×0.75), 7.19 (s, 3H×0.75), 7.13 (d, J=8.1 Hz, 3H×0.75), 6.69 (s, 3H×0.75), 6.23 (s, 3H×0.25), 5.85 (s, 6H×0.25), 5.55 (d, J=15.0 Hz, 3H×0.75), 5.38 (d, J=15.0 Hz, 3H×0.75), 3.77 (s, 3H×0.75), 3.67 (6H×0.25), 3.54(3H×0.75), 1.60–1.50 (6H), 1.30–1.05 (36H), 0.84 (t, J=7.3 Hz, 9H). ^{13}C NMR (δ, 150 MHz, ppm, $CDCl_3$) 169.5, 145.6, 142.9, 139.3, 131.4, 130.9, 130.3, 128.6, 128.3, 127.9, 127.2, 127.0, 126.7, 126.2, 126.0, 125.7, 125.6, 124.7, 124.4, 124.1, 121.5, 107.9, 67.6, 51.5, 49.6, 31.7, 29.7, 29.4, 29.2, 29.1, 27.5, 26.7, 23.9, 22.6, 14.1. IR (ν, cm^{-1}) 3868, 3044, 2922, 2851, 1651, 1590, 1453, 1391, 1304, 1185, 1129, 1044, 881, 845, 756, 706. HR MALDI-TOF-MS calcd for $C_{105}H_{102}N_{12}NaO_3$ ($M+Na^+$): 1602.8129. Found: 1602.8812.

Supplementary data

Experimental procedure, ^{1}H and ^{13}C NMR spectral data, and crystal data. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.12.015.

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