Synthesis of 9,10-Bis-ketoenamoanthryl and 9,10-Bis-isoxazolylanthryl Linked Biscalix[4]arenes: Atropisomers and Molecular Recognitions

Chia-Chen Tsaì, † I-Ting Ho, ‡ Jean-Ho Chu, † Li-Ching Shen, † Shou-Ling Huang, † and Wen-Sheng Chung*†

†Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, Republic of China
‡Instrumentation Center, National Taiwan University, Taipei, Taiwan 106, Republic of China

ABSTRACT: An efficient synthetic pathway for the synthesis of biscalix[4]arenes 5−10 using 1,3-dipolar cycloaddition reactions is reported. Biscalix[4]arene 10 is capable of forming a complex with methyl viologen because of favorable cation−π interactions and a proper cavity size to accommodate the guest. Moreover, biscalix[4]arenes 8a and 8b were found to be atropisomers at room temperature. These two conformers were unable to exchange at room temperature because of the restricted rotation of the C9−C11 or C10−C12 bonds of the β-amino-α,β-unsaturated ketones of anthracene.

INTRODUCTION

Biscalixarenes have been studied extensively in recent years because the structures usually contain interesting properties including allosteric effect, intramolecular oscillation, and conformational conversion. An internal cavity, formed naturally through the linkage of two calixarenes, can be used as a host not only for metal ions but also for neutral molecules. For example, Gutsche and co-workers reported that 5,5′-biscalix[5]arene can be used to selectively recognize fullerene over fullerene, where the biscalix[5]arene undergoes an anti to syn conformational change upon complexation with a fullerene to maximize the interaction between host and guest. Methyl viologen is one of the most widely used herbicides in the world. It is shown to be toxic to humans and animals and is linked to the development of Parkinson’s disease; accordingly, it is highly desirable to have a selective and sensitive method in the fast screening of methyl viologen. Currently, most of the detection of methyl viologen relies on 1H NMR titration experiments using various macrocycles such as calix[4]arenes, crown ethers, triptycenes, and pillar[5]arenes. There has been very few reports on the fluorescent sensing of methyl viologen. To the best of our knowledge, Wagner and Isaacs were the first to report a fluorescent sensing of methyl viologen relying on 1H NMR titration experiments. To the best of our knowledge, Wagner and Isaacs were unable to exchange at room temperature because of the restricted rotation of the C9−C11 or C10−C12 bonds of the β-amino-α,β-unsaturated ketones of anthracene.

RESULTS AND DISCUSSION

The synthetic pathways for biscalix[4]arenes 5, 7, and 10 are depicted in Scheme 1. Our synthetic strategy for linking two calix[4]arenes started with the double 1,3-dipolar cycloaddition reactions between aryl dinitrile oxides (prepared in situ from 3 and 4) and propargyl ether to yield 5 and 7 in 43% and 62% yield, respectively. In principle, the quadruple cycloaddition reactions, of two bispropargyloxyxcalix[4]arenes 2 with two anthracene-9,10-bis(carbonitrile oxide) 4, should lead to a doubly bridged biscalix[4]arene 10; however, when 2 (5.5 mM) was refluxed with 4 (5.5 mM) in THF for 24 h, the reaction mixture became very messy and was difficult to be purified by...
column chromatography. Alternatively, the doubly bridged biscalix[4]arene 10 could be synthesized via a two-step reaction sequence starting from 7. First, the bispropargyl ether substituted biscalix[4]arene 9 was obtained in 86% yield through S_N2 reaction of 7 with 2 equiv of propargyl bromide under basic conditions.

Second, a double 1,3-dipolar cycloaddition of the bispropargyl ether substituted biscalix[4]arene 9 with 4 afforded the doubly bridged biscalix[4]arene 10 in 32% yield. 1H NMR spectrum of the methylene bridge protons and the isoxazole protons of biscalix[4]arene 10 showed only two singlets implying that its structure was highly symmetrical.

The N−O bond cleavage of the isoxazole units of biscalix[4]arenes 5 by Mo(CO)_6-mediated ring-opening reaction led to the formation of 1,4-bisketoenaminophenyl biscalix[4]arene 6 and recovered calix[4]arene in 32 and 40% yield, respectively. Under similar reaction conditions, the ring-opening reaction of 7 gave the 9,10-bisketoenaminoanthyl biscalix[4]arenes 8a and 8b, as a mixture of atropisomers, in 67% yield (Scheme 2). 1H NMR spectra of these compounds showed that the amino protons of the ketoenaminos appeared as two singlets: one around δ10.0−10.2 (due to H-bonding with the carbonyl groups) and the other around δ 5.6−5.8 ppm. The structures of all products (5−10) were fully characterized by spectral data including 1H and 13C NMR (Figures S12−S27, Supporting Information), mass, and high resolution mass spectrometry (Experimental Section). Furthermore, the structure of biscalix[4]arene 10 was confirmed by a single-crystal X-ray crystallography analysis (Figure 1). The X-ray crystal structure of 10 clearly shows that it contains a rectangular cone cavity. This biscalix[4]arene is a nanometer-sized macrocycle (3.0 nm long) with two parallel anthracene moieties, and the distance between the two anthracene planes is 4.0 Å. The two anthracenes are not in juxtaposition; they are slightly staggered. The cavity of 10 is constructed by the walls of two parallel anthracene moieties and two tail-to-tail calix[4]arenes; therefore, it has a potential for π−π interaction and recognition of dication by the two bridged calix[4]arenes. To this end, we envisaged that methyl viologen and its analogues may have the potential to be snugly fit into the rectangular cavity of biscalix[4]arene 10.
Unexpectedly, the $^1$H NMR spectra of the ring-opened products 8 clearly showed two sets of signals (Figure 2b), indicating the existence of two conformational isomers or so-called atropisomers.$^{15}$ In contrast, the ring-opened product 6, from the reaction of 1,4-bisoxazolylphenyl substituted biscalix[4]arene 5, showed only one set of proton signals (Figures 2a, S1, and S2, Supporting Information).

To determine whether steric hindrance between the anthryl and the ketoenamino groups or steric bulkiness of the calix[4]arene plays the crucial role in making compounds 8 atropisomers, we synthesized a control compound 12, in which the two calix[4]arenes were replaced by two para- t-butylphenyl ether groups (Scheme 3). The $^1$H NMR spectrum of 12 at room temperature gives rise to two well-resolved sets of signals (Figure S26, Supporting Information). The results imply that adding a bulky substituent or not at a remote position from the 9,10-bisketoenamino substituted anthracene did not affect its atropisomeric properties. There is no need to replace t-butyloxy group with a bulkier substituent, such as calix[4]arene, to achieve atropisomeric properties in the 9,10-bisketoenamino substituted anthracene. Note that no atropisomeric properties were found for the phenyl bridged 1,4-biscalix[4]arene 6 (Figure 2a); thus, the hindered rotation in the 9,10-bisketoenamino substituted anthracene of 8 or 12 plays a key role in forming atropisomers.

$^1$H NMR spectra of the two biscalixarenes 8a and 8b show that some of their signals are separated and allowed for area integrations. At room temperature (298 K), the ring-opened products 8a and 8b exist as a mixture of conformers with a ratio of 46:54 in CDCl$_3$ (Figures S2 and S3, Supporting Information). However, the assignment of the cis- or trans-atropisomers cannot be unambiguously determined yet. We tried to separate the atropisomers 8a and 8b by HPLC using various columns; however, it was unsuccessful. Variable-temperature NMR studies at temperatures as high as 393 K (sample started to decompose) showed that the two sets of proton signals of 8a and 8b did not have any symptoms of merging (Figures S4 and S5, Supporting Information), implying a very high energy barrier for the rotations of C$_9$−C$_{11}$ and C$_{10}$−C$_{12}$ bonds.$^{15e,f}$ The energy barriers for the restricted rotation in

Scheme 2. Syntheses of Ring-Opened Biscalix[4]arene 6 and Atopisomers 8a and 8b

Figure 1. (a) X-ray single crystal structure of biscalix[4]arene 10 and (b) a snapshot of the structure in (a) by 90$^\circ$ rotation in its horizontal-axis.
9-phenylanthracenes have been predicted by DFT calculations\textsuperscript{15} and confirmed experimentally by VT NMR\textsuperscript{15e,17} to be \( \sim 21 \text{ kcal mol}^{-1} \). On the other hand, the simplicity of the NMR spectra of \( 7 \) even at \(-50^\circ\text{C} \) (Figures S6, Supporting Information) implies that rapid rotation occurs at this temperature and that there is a very low energy barrier of the rotations of \( \text{C}_9-C_{11} \) and \( \text{C}_{10}-C_{12} \) in \( 7 \). The rotational energy barrier of the bis-isoxazole substituted anthracene \( 7 \) is estimated to be smaller than \( 10 \text{ kcal mol}^{-1} \).\textsuperscript{18}

The normalized fluorescence spectra of biscalix[4]arenes \( 7, 10 \) and control compound \( 11 \) are shown in Figure 3. Biscalix[4]arene \( 10 \) displayed a broader emission band (\( \lambda_{\text{max}} \) at 443 nm) compared to those of biscalix[4]arene \( 7 \) and control compound \( 11 \) (both showed a \( \lambda_{\text{max}} \) at 432 nm). The results implied that an intramolecular \( \pi-\pi \) interaction of the two parallel anthracenes of biscalix[4]arene \( 10 \) should have occurred in cosolvent MeOH/CHCl\(_3\) (v/v, 1:2), which led to a longer emission wavelength.

Since biscalix[4]arene \( 10 \) contains anthracenes as fluorophores, we then used it in fast screening on a series of aromatic guests, alkyldiamines, and methyl viologen (G1–G13, Chart 1) using fluorescence spectroscopy. The binding properties of \( 10 \) in cosolvent MeOH/CHCl\(_3\) (v/v, 1:2) were assessed by adding 200 equiv of various guests, and their relative fluorescence intensity changes are shown in Figure 4. There was basically no (or very small) change in the fluorescence spectra of biscalix[4]arene \( 10 \) when it was mixed with excess aromatic guests (G1–G5) and alkyldiamines (G7–G13). To our delight, only methyl viologen (G6) caused a significant quenching on the fluorescence of biscalix[4]arene \( 10 \) (Figures 4 and 5). The fluorescence quantum yield of \( 10 \) was determined to be \( 0.80 \pm 0.02 \) using 9,10-diphenylanthracene.

**Figure 2.** \(^1\text{H} \) NMR spectra of the ring-opened products (a) 6 and (b) 8, where * denotes signals from the residual of chloroform-d. In spectrum (b), the signals labeled with a prime come from atropisomers.

**Scheme 3. Synthesis of Atropisomers 12a and 12b**
as a standard. Upon titration with G6, the fluorescence intensity of 10 gradually decreased, which gave a fluorescence quantum yield of 0.57 ± 0.01 (30% decrease) at 200 equiv of G6. The association constant of complex 10·G6 was determined to be 137.4 ± 7.6 M⁻¹ by a Stern–Volmer plot (Figure Sb). Furthermore, the excimer emission of 10 was slightly blue-shifted at high equivalents of G6, indicating that the π–π interaction of the two parallel anthracenes of biscalix[4]arene 10 was reduced. The results imply that G6 might have been embedded into the cavity of biscalix[4]arene 10, hence favoring the monomer emission compared to that of the excimer.

1H NMR titration experiments of biscalix[4]arene 10 with methyl viologen (G6) were also carried out to shed light on its binding mode (see Figures S7 and S8, Supporting Information). The proton signals of the anthracene of the host 10 were slightly upfield shifted by the addition of G6, which is consistent with the inclusion of G6 in the cavity of 10. Moreover, we also found that the proton signals of G6 were broadened and high field shifted in the presence of 10 equiv of 10 (Figure S8, Supporting Information). Diffusion-ordered NMR spectroscopy (DOSY) has been particularly useful in the characterization of complex host–guest systems in solution. Thus, 2D DOSY experiments were used to investigate the complex between biscalixarene 10 and G6. When a 1:1 mixture of 10 and G6 was measured in CD₃OD/CDCl₃ (v/v, 1/2) at 295 K, the diffusion coefficients for host 10 and guest G6 were determined to be 3.16 × 10⁻¹⁰ and 6.03 × 10⁻¹⁰ m²/s, respectively. However, when 100 equiv of G6 with 1 equiv of 10 were measured by 2D DOSY, a new species with a different diffusion coefficient (4.17 × 10⁻¹⁰ m²/s) appeared. This indicates that biscalixarene 10 and methyl viologen G6 form a complex. (Figure S9, Supporting Information)

In order to know whether the rectangular cavity of biscalix[4]arene 10 is necessary for the recognition of methyl viologen, we synthesized a control compound 11, in which the two calix[4]arene units are replaced by two para-t-butylphenyl groups. Furthermore, the fluorescence study of the open-chained biscalix[4]arene 7 toward methyl viologen G6 was also used for comparison (Figure 4). The fluorescence of the open-chained biscalix[4]arene 7 showed very little change at 200 equiv of G6, however, the fluorescence quantum yield of the other control compound 11 did show some quenching by G6. The quenching effect of methyl viologen G6 on the open-chain bis-para-t-butylphenyl 11 was smaller (ΦF decreased by 20%) compared to that on the biscalix[4]arene 10 (ΦF decreased by 30%). The association constant of complex 11·G6 was determined to be 77.6 ± 0.6 M⁻¹ by a Stern–Volmer plot (Figure S10, Supporting Information). The 1H NMR titration spectra of control compound 11 with G6 showed no change even with 10 equiv of G6 (Figure S11, Supporting Information). On the basis of these observations, we conclude that not only the cation–π interaction but also a proper cavity size must have played important roles in the binding of methyl viologen (G6) by biscalix[4]arene 10.

Finally, an optimized geometry of 10 with G6 was calculated by the molecular modeling DMol³ and simulated in CHCl₃ environment (Figure 6 and Tables S4–S5, Supporting Information). The DMol³ method from Material Studio 5.0 is developed by Accelrys Inc., in which the wave functions are expanded in terms of an accurate numerical basis set. We used a double-numeric quality basis set with polarization functions (DNP). The size of the DNP basis set is comparable to Gaussian 6-31G**, but DNP is more accurate than a...
energy, gradient, and displacement convergences were 2 × 10⁻³ Ha, 4 × 10⁻³ Ha Å⁻¹, and 5 × 10⁻³ Å, respectively. The optimized geometries of 10 with G6 by calculation showed a sandwich-like structure. The distance between two anthracenes increased from 4.0 Å (crystal) to ca. 6.5 Å when the G6 was embedded into the cavity of biscalix[4]arene 10. The results explain why the excimer emission of 10 was slightly blue-shifted.

■ CONCLUSION

Using a two-step reaction sequence, we have successfully synthesized a novel fluorescent biscalix[4]arene 10 with rectangular cavity. The biscalix[4]arene 10, with two parallel anthracene units, was found to show some affinity to dication molecules such as methyl viologen (G6). Although the binding constant of biscalix[4]arene 10 with G6 is small (137.4 ± 7.6 M⁻¹), it has the advantages of fast and easy screening by fluorescence spectroscopy. From a comparison of the results with two other control compounds (7 and 11), we believe that the cation–π interaction as well as a proper cavity size play key roles in the complexation of biscalix[4]arene 10 with G6. Moreover, 2D DOSY experiments provided strong evidence to support the complex formation between 10 and G6.

We also found that not only 9,10-bisketoenaminoanthryl biscalix[4]arenes (8a and 8b) but also 9,10-bisketoenaminoanthryl bis-t-butyl-phenol ethers (12a and 12b) are atropisomers, where hindered rotation between the ketoenamin group and the nearby C=H hydrogens of the anthracene were the key features. The estimated energy barriers for the restricted rotation of in the 9,10-bisketoenaminoanthryl derivatives 8a,b are ≥23 kcal mol⁻¹ from VT NMR. In sharp contrast, the isoxazole substituted 9,10-bisoxazolylanthryl biscalix[4]arene 7 has a much lower energy barrier on the rotation of C_9−C_11; therefore, even at temperatures as low as −50 °C, it did not show any symptom of proton NMR signal splitting between its atropisomers.

■ EXPERIMENTAL SECTION

General Methods. 1H NMR spectra were measured with either a 300 or 500 MHz spectrometer. Natural abundance 13C NMR spectra were measured using pulse Fourier transform techniques, with a 300 or 500 MHz spectrometer. Natural abundance 13C NMR spectra were measured with spectrometer and spectrofluorimeter using HPLC-grade solvents.

1,4-Bis-isoazolyl-phenylmethyl Linked Biscalix[4]arene, 5. Triethylamine (0.35 mmol) in ethanol (1.9 mL) was slowly added to a well-stirred solution of 1 (0.60 g, 0.69 mmol) and hydroximoyl chloride 3 (0.07 g, 0.31 mmol) in ethanol (30 mL). The reaction mixture was stirred at reflux for 24 h under N₂ (g). After evaporation of the solvent, the mixture was washed with water and extracted with dichloromethane. The organic phase was dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/n-hexane as eluent to give 0.20 g (42.7%) of 5 as a yellow solid: mp 178−180 °C; Rᶠ = 0.45 (ethyl acetate/n-hexane = 1:4); 1H NMR (CDCl₃, 300 MHz) δH (s, 2H), 9.16 (s, 4H), 8.03 (s, 4H), 7.12−6.99 (m, 16H), 5.39 (s, 4H). 3.43 (d, 4H, J = 13.2 Hz), 4.26 (d, 4H, J = 13.7 Hz), 3.46 (d, 4H, J = 13.2 Hz), 3.44 (d, 4H, J = 13.7 Hz), 1.22−1.20 (m, 72H) ppm; 13C NMR (CDCl₃, 75.5 MHz) δC 167.6 (Cq), 162.1 (Cq), 149.0 (Cq), 148.9 (Cq), 148.3 (Cq), 147.5 (Cq), 143.7 (Cq), 143.2 (Cq), 133.2 (Cq), 130.4 (Cq), 128.1 (Cq), 127.7 (Cq), 127.6 (CH), 127.4 (Cq), 126.7 (CH), 125.8 (CH), 125.7 (CH), 125.6 (CH), 102.8 (CH), 68.1 (Cq), 34.3 (Cq), 34.0 (Cq), 33.9 (Cq), 32.9 (CH₃), 32.2

Figure 5. (a) Fluorescence emission spectra of biscalix[4]arene 10 (10 µM) in the presence of various equivalents of methyl viologen (G6) and (b) its corresponding Stern–Volmer plot using the intensity at 443 nm as a parameter (KSV = 137.4 ± 7.6 M⁻¹). All measurements were in a cosolvent of MeOH/CHCl₃ (v/v, 1:2), and the excitation wavelength was 395 nm.

Figure 6. A possible binding mode of the complexation of biscalix[4]arene 10 with G6 (a) side view and (b) top view.
7.61 (3H); 1H NMR (300 MHz, CDCl$_3$) $\delta$ 80.0–7.96 (m, 4H), 7.51–7.48 (m, 4H), 7.25–7.67 (m, 22H), 5.40 (s, 4H), 4.54 (d, 4H, $J = 2.3$ Hz), 4.36 (d, 4H, $J = 13.2$ Hz), 4.31 (d, 4H, $J = 13.4$ Hz), 3.39 (d, 4H, $J = 13.2$ Hz), 3.32 (d, 4H, $J = 13.4$ Hz), 2.13 (s, 2H, $J = 2.3$ Hz), 1.30–1.15 (m, 17H); 13C NMR (75.5 MHz) $\delta$ 168.5 (Cq), 161.0 (Cq), 150.4 (Cq), 149.5 (Cq), 147.6 (Cq), 147.5 (Cq), 141.7 (Cq), 132.6 (Cq), 132.4 (Cq), 130.2 (Cq), 127.8 (Cq), 127.8 (Cq), 126.6 (CH), 126.1 (CH), 125.8 (CH), 125.7 (CH), 125.1 (CH), 107.9 (CH), 78.2 (Cq), 76.2 (Cq), 68.2 (CH), 63.3 (CH3), 37.1 (Cq), 33.9 (Cq), 33.8 (Cq), 32.1 (CH3), 31.9 (CH3), 31.7 (CH3), 30.9 (CH3) ppm; FAB-MS: m/z 1709 (M + H$^+$), 1700 (M$^+$); HRMS (FAB) calc for C$_{193}$H$_{215}$O$_{11}$N$_{13}$ 4623.9040, found 4624.8255.

---


A mixture of 1 (0.20 g, 0.03 mmol) and 4 (0.04 g, 0.01 mmol) in THF (15 mL) was heated at reflux for 24 h under $\text{N}_2$ (g). After evaporation of the solvent, the mixture was washed with water and extracted with dichloromethane. The organic phase was dried over MgSO$_4$ and the solvent was removed under reduced pressure.

The residue was purified by silica gel column chromatography with ethyl acetate/n-hexane as eluent to give 0.04 g (62.2%) of 7 as a yellow solid; mp 180–182°C; $R_f = 0.35$ (ethyl acetate/n-hexane (v/v, 1:1)).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.13 (s, 2H); 9.34 (s, 4H); 8.78–8.08 (m, 4H), 7.61–7.58 (m, 4H), 7.28–7.07 (m, 18H), 6.53 (s, 4H), 4.55 (s, 4H, $J = 13.2$ Hz), 4.33 (d, 4H, $J = 13.8$ Hz), 3.61 (d, 4H, $J = 13.2$ Hz), 3.51 (d, 4H, $J = 13.8$ Hz), 1.33–1.29 (m, 27H) ppm; 13C NMR (CDCl$_3$, 75.5 MHz) $\delta$ 167.2 (Cq), 161.4 (Cq), 149.1 (Cq), 148.8 (Cq), 148.3 (Cq), 147.7 (Cq), 144.3 (Cq), 143.3 (Cq), 133.5 (Cq), 130.3 (Cq), 128.1 (Cq), 127.7 (Cq), 127.7 (Cq), 126.8 (CH), 126.0 (CH), 125.9 (CH), 125.7 (CH), 125.7 (CH), 125.5 (Cq), 108.8 (CH), 67.6 (CH$_2$), 34.3 (Cq), 33.9 (Cq), 32.9 (CH), 32.4 (CH), 31.5 (CH$_2$), 31.2 (CH$_3$) ppm; FAB-MS: m/z 1633 (M$^+$ + H$^+$); HRMS (FAB) calc for C$_{167}$H$_{184}$N$_{12}$O$_{10}$ 4392.9340, found 4396.0001.

---


A mixture of 7 (0.10 g, 0.06 mmol), Mo(OCH$_3$)$_3$ (0.07 g, 0.025 mmol), and H$_2$O (0.2 mL) was stirred and heated at reflux for 5 h. The solvent was removed under a vacuum, and the residue was dissolved in 10 mL of dichloromethane. Then, to the solution was added 10 mL of NH$_4$OH (aq) to remove remaining molybdenum salts. After stirring for 1 h, the organic layer was washed with water and 1 M EDTA (aq). The organic phase was dried over MgSO$_4$ and the solvent was removed under reduced pressure.

The residue was purified by neutral silica gel column chromatography with ethyl acetate/n-hexane (v/v, 1:5) as eluent to give 0.016 g (31.9%) of yellow solid 6 with para-tartaric calix[4]arene (40%) as a side product.

mp 182–184°C; $R_f = 0.1$ in ethyl acetate/n-hexane (v/v, 1:3); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.28 (s, 2H), 10.07 (bs, 2H), 9.55 (s, 4H), 7.83 (s, 4H), 7.09–6.98 (m, 16H), 6.04 (s, 2H), 5.56 (bs, 2H), 4.85 (s, 4H), 4.53 (d, 4H, $J = 12.9$ Hz), 4.29 (d, 4H, $J = 13.8$ Hz), 3.44 (d, 4H, $J = 13.5$ Hz), 3.41 (d, 4H, $J = 12.9$ Hz), 1.50–1.36 (m, 72H) ppm; 13C NMR (CDCl$_3$, 75.5 MHz) $\delta_{\text{C}}$ 193.6 (Cq), 193.5 (Cq), 193.2 (Cq), 161.5 (Cq), 161.2 (Cq), 161.0 (Cq), 154.7 (Cq), 149.8 (Cq), 147.9 (Cq), 141.9 (Cq), 132.6 (Cq), 129.8 (Cq), 127.5 (Cq), 126.4 (CH$_2$), 126.0 (CH$_2$), 125.7 (CH$_2$), 125.6 (CH$_2$), 125.4 (CH$_2$), 125.3 (CH$_2$), 125.2 (CH$_2$), 107.1 (CH$_2$), 68.2 (CH$_2$), 34.1 (Cq), 33.9 (Cq), 33.8 (Cq), 32.0 (CH$_3$), 31.7 (CH$_3$), 30.9 (CH$_3$) ppm; FAB-MS: m/z 1709 (M + 2), 1708 (M + H$^+$), 1700 (M$^+$); HRMS (FAB) calc for C$_{132}$H$_{156}$N$_{12}$O$_{10}$ 3962.8785, found 3962.8744.
C42H40O4N2 636.2988, found 636.2994.

(CH), 125.6 (CH), 114.0 (CH), 95.8 (CH), 72.0 (CH2), 34.1 (Cq),

products

by neutral silica gel column chromatography with ethyl acetate/

solvent was removed under reduced pressure. The residue was purified

6.79 (m, 2H), 5.82 (s, 1H), 5.78 (s, 1H), 5.50 (bs, 1H) 5.43 (bs, 2H),

8.11

1 M EDTA (aq). The organic phase was dried over MgSO4, and the

1181.

° 7.46 (m, 4H), 7.28

C (decomposed);

products were added to 10 mL of dichloromethane. Then, to the solution was

was added 10 mL of NH4OH (aq) to remove remaining molybdenum salts.

After stirring for 1 h, the organic layer was washed with water and

1 M EDTA (aq). The organic phase was dried over MgSO4, and the

solvent was removed under reduced pressure. The residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified

neutral silica gel column chromatography with ethyl acetate/n-

hexane (1/5) as eluent to give trace amount of yellow solid 2. The

organic phase was dried over MgSO4, and the

residue was purified
excitation at 388 nm for 7 and 384 for 11 and from 395 to 650 nm for 10 with excitation at 391 nm. The relative fluorescent quantum yield for 7, 10, and 11 are 0.70 ± 0.02, 0.80 ± 0.02, and 0.96 ± 0.02, respectively. The relative quantum yields were calculated using equation: 
\[
\Phi_F = \left( \frac{A_{\text{ref}}}{A} \right) \times \left( \frac{F}{F_{\text{ref}}} \right) \times \left( \frac{n_{\text{chloroform}}}{n_{\text{cyclohexane}}} \right) \times \Phi_{\text{ref}},
\]