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Synthesis and Characterization of 5,10- and 5,15-Disubstituted Porphodimethenes

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The four porphodimethene isomers, 5,10- and 5,15-disubstituted, have been synthesized in a one-pot reaction by the Lindsey protocol. Three of them have been characterized by X-ray crystallography. Structures show that two of them are 5,15-porphodimethenes: one is *syn*-equatorial, another is *anti*-configuration; the third one is 5,10-porphodimethene. In the 5,10-porphodimethene, the tripyrrane subunit remains planar conformation. ^{1}H NMR and UV-vis spectra have also been characterized. Both spectra reveal remarkable difference between 5,10- and 5,15-disubstituted isomers.

Keywords calixphyrin, porphodimethene, Lindsey protocol, isomers

Introduction

Calix[4]phyrins are a class of hybrid molecules that lie at the structural crossroads between porphyrins and calix[4]pyrroles. A typical feature of porphyrins is full conjugation throughout the macrocyclic skeleton,[1-3] while calixphyrins possess a mixture of sp^2- and sp^3-hybridized *meso* carbon bridges and have been shown to be good receptors for cations and anions.[4-8] Because of such bonding features, calixphyrins possess reasonably flexible frameworks as well as rigid π-conjugated networks, whose characters vary considerably depending on the number and position of the sp^3 *meso*-carbon atoms. They are observed in numerous porphyrinic intermediates known as porphomethenes, porphodimethenes, isoporphyrins or phlorins.[9,10]

Porphodimethenes belong to an intermediate class of calix[4]phyrins.[11-19] They possess two sp^2- and two sp^3-hybridized *meso* carbon centers, which have the potential to possess both the binding properties of calixpyrroles and the biological affinity of (hydro)-porphyrins.[20] This disruption in the π-electronic conjugation has been shown to cause drastic conformational changes and significant modifications of their overall properties.[21-23] But such species are unstable in many cases. Porphodimethenes have been intensively investigated by several groups. For example, Sessler *et al.* have established convenient methods for the synthesis of a series of calix[*n*]phyrins and systematically investigated their structures and conformational mobilities in relation to calix[*n*]pyrrole chemistry.[24-27] Senge *et al.* have independently developed their own approaches to this class of compounds.[20,28-32] Among those porphodimethenes, 5,15-porphodimethenes can be synthesized by MacDonald-like condensation-based approaches.[33-35] For example, Scott and coworkers have reported that the reaction between dipyrromethanes and acenaphthenequinone led to the formation of the corresponding 5,15-porphodimethenes and they were subsequently converted into dinaphthylporphyrin dicarboxylic acids.[34] They also converted *tert*-butyl substituted acenaphthenequinones into 5,15-porphodimethenes and then made unusual fused ring porphyrins.[13] But the synthesis of 5,10-porphodimethenes is more difficult, and few studies have been reported.[24,29,36,37] Considering acenaphthenequinone may lead to spirocyclic structure which could stabilize the corresponding porphodimethenes species, we have synthesized the 5,10- and 5,15-porphodimethene isomers in a one-pot reaction with mixed acenaphthenequinone, benzaldehyde and pyrrole by the Lindsey protocol.[38-40] The four isomers have been characterized by X-ray crystallography, mass spectroscopy, ^{1}H NMR and UV-vis spectroscopy, *etc.*

Experimental

Materials and general methods

Acenaphthenequinone (Alfa Aesar) and tetrachloro-1,4-benzoquinone were used as received. Pyrrole and

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methylene chloride were freshly distilled before use. Other solvents were used as received. UV-vis spectra were measured on a Shimadzu UV-3150 spectrometer. ^{1}H NMR spectra were carried out using a Bruker AVANCE 400 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra were taken with Agilent 6220 Accurate-Mass TOF LC/MS.

Preparation of the four porphodimethene isomers

The reaction was carried out under anaerobic condition. Acenaphthenequinone (2.52 g, 13.8 mmol), benzaldehyde (1.33 mL, 13.8 mmol) and pyrrole (1.9 mL, 27.6 mmol) were dissovled in methylene chloride (500 mL). BF_3•OEt_2 (1 mL, 7.90 mmol) was added to the above solution and stirred for 1 h at room temperature, then tetrachloro-1,4-benzoquinone (6.72 g, 27.6 mmol) was added. After 2 h under reflux, triethylamine (8.0 mL) was added, and the mixture was stirred for another 0.5 h. When it was cooled down to r.t., it was filtered by sintered glass funnel. The filtrate was evaporated to dryness under vacuum, the black solid was further purified by column chromatography [silica, $V(CH_2Cl_2)$ ∶ V(petroleum ether)=1 ∶ 1]. The first (**1a**), second yellow band (**1b**) and second (**2a**), third purple band (**2b**) were collected respectively. (The first purple species is TPP, tetraphenylporphyrin.)

For **1a**, yield 0.18 g (6.8%); UV-vis (CH_2Cl_2) λ_{max} [ε/(L•mol^{-1}•cm^{-1})]: 323 (0.27×10^5), 439 (0.74×10^5), 498 (0.057×10^5) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.96 (s, 2H), 8.82 (d, J=6.7 Hz, 2H), 8.21 (d, J=8.1 Hz, 2H), 8.15 (d, J=7.0 Hz, 2H), 8.08—7.93 (m, 4H), 7.81 (t, J=7.6 Hz, 2H), 7.45—7.29 (m, 10H), 6.37 (d, J=3.4 Hz, 4H), 6.20 (d, J=3.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.08, 155.34, 141.81, 141.78, 141.64, 139.86, 137.43, 132.62, 132.09, 131.33, 131.06, 129.86, 129.43, 128.86, 128.50, 127.61, 125.12, 124.61, 123.31, 116.87, 61.54; IR(KBr) v: 3447, 1711, 1580, 1505, 1470, 1433, 1383, 1311, 1259, 1228, 1162, 1127, 1045, 1017, 962, 925, 829, 780, 719 cm^{-1}; LC-ESI-MS: 769.26 (calcd for $[M+H]^+$ 769.25, M=$C_{54}H_{32}N_4O_2$). Anal. calcd for $C_{54}H_{32}N_4O_2$•$0.3CH_2Cl_2$: C 82.10, H 4.14, N 7.05; found C 81.88, H 4.15, N 7.01.

For **1b**, yield 0.12 g (4.5%); UV-vis (CH_2Cl_2) λ_{max} [ε/(L•mol^{-1}•cm^{-1})]: 321 (0.28×10^5), 441 (1.00×10^5), 505 (0.076×10^5) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.98 (s, 2H), 8.18 (d, J=8.1 Hz, 2H), 8.12 (d, J=7.0 Hz, 2H), 8.03 (d, J=8.3 Hz, 2H), 7.97 (d, J=6.9 Hz, 2H), 7.87—7.76 (m, 4H), 7.49—7.42 (m, 2H), 7.37 (d, J=4.2 Hz, 4H), 7.31 (s, 4H), 6.32 (d, J=4.2 Hz, 4H), 6.00 (d, J=4.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.84, 154.25, 142.42, 141.92, 138.83, 137.76, 131.99, 131.20, 131.14, 131.05, 130.75, 129.11, 128.99, 128.59, 127.48, 125.58, 124.32, 124.22, 116.94, 62.13; IR(KBr) v: 3436, 1729, 1580, 1494, 1473, 1430, 1385, 1324, 1222, 1153, 1125, 1053, 1002, 961, 919, 830, 782, 719 cm^{-1}; LC-ESI-MS: 769.26 (calcd for $[M+H]^+$ 769.25, M = $C_{54}H_{32}N_4O_2$). Anal. calcd for $C_{54}H_{32}N_4O_2$• $0.2CH_2Cl_2$: C 82.84, H 4.16, N 7.13; found C 83.08, H 4.06, N 7.15.

For **2a**, yield 0.11 g (4.1%); UV-vis (CH_2Cl_2) λ_{max} [ε/(L•mol^{-1}•cm^{-1})]: 341 (0.46×10^5), 371 (0.44×10^5), 543 (0.26×10^5), 578 (0.28×10^5) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.26 (s, 1H), 11.90 (s, 1H), 8.13 (d, J=7.9 Hz, 2H), 7.92 (d, J=8.5 Hz, 4H), 7.82—7.76 (m, 2H), 7.76—7.66 (m, J=7.1 Hz, 4H), 7.51—7.33 (m, 10H), 6.64 (s, 2H), 6.19 (s, 2H), 6.05 (s, 2H), 5.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.62, 171.12, 152.75, 142.15, 140.82, 139.87, 139.19, 138.12, 136.93, 131.99, 131.64, 131.22, 131.07, 129.20, 129.11, 128.79, 128.71, 127.71, 125.76, 125.04, 123.64, 123.58, 123.12, 106.30, 62.40; IR (KBr) v: 3446, 1712, 1590, 1500, 1440, 1390, 1250, 1232, 1201, 1175, 1072, 1015, 962, 825, 781, 700 cm^{-1}; LC-ESI-MS: 769.26 (calcd for $[M+H]^+$ 769.25, M = $C_{54}H_{32}N_4O_2$). Anal. calcd for $C_{54}H_{32}N_4O_2$•$0.5CH_2Cl_2$: C 80.68, H 4.10, N 6.91; found C 80.49, H 4.4, N 6.68.

For **2b**, yield 0.17 g (6.4%); UV-vis (CH_2Cl_2) λ_{max} [ε/(L•mol^{-1}•cm^{-1})]: 332 (0.41×10^5), 364 (0.37×10^5), 540 (0.24×10^5), 578 (0.27×10^5) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.97 (s, 1H), 11.29 (d, J=24.9 Hz, 1H), 8.11 (d, J=8.1 Hz, 2H), 7.98 (d, J=7.0 Hz, 2H), 7.91 (d, J=8.3 Hz, 2H), 7.78 (d, J=6.9 Hz, 2H), 7.70 (dd, J=15.0, 7.1 Hz, 4H), 7.48—7.35 (m, 10H), 6.58 (d, J=4.6 Hz, 2H), 6.14 (s, 2H), 5.87 (d, J=4.6 Hz, 2H), 5.58 (d, J=2.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.07, 172.08, 152.19, 142.33, 140.10, 139.91, 138.65, 138.47, 137.29, 132.01, 131.84, 131.17, 131.06, 128.96, 128.72, 128.63, 127.65, 127.58, 125.66, 125.14, 123.91, 123.52, 123.18, 107.37, 80.85, 62.45; IR (KBr) v: 3439, 1724, 1585, 1493, 1433, 1382, 1256, 1224, 1193, 1158, 1066, 1005, 959, 923, 831, 783, 701 cm^{-1}; LC-ESI-MS: 769.26 (calcd for $[M+H]^+$ 769.25, M=$C_{54}H_{32}N_4O_2$). Anal. calcd for $C_{54}H_{32}N_4O_2$•$0.6CH_2Cl_2$: C 79.99, H 4.08, N 6.83; found C 80.13, H 4.29, N 6.61.

X-ray crystallography

The single crystals of **1a**, **1b** and **2b** were obtained through the diffusion of their methylene chloride/hexane solutions. All X-ray data collections were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo Kα (λ=0.071073 nm) at 223(2) K. Their structures were solved by direct methods and refined on F^2 using full matrix least-squares methods with SHELXTL version 97.[41] All non-hydrogen atoms were refined anisotropically. In the three structures, all the N—H hydrogen atoms were found in difference Fourier maps, and their coordinates and isotropic temperature factors were refined, other hydrogen atoms were theoretically added and riding on their parent atoms. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates are given in the cif file (CCDC number: 872251, 872252 and 872253). For **1a**, one asymmetric unit contains one independent porphodimethene molecule and one disorder methylene chloride solvate. For **2b**, one asymmetric unit contains

two independent porphodimethene molecules (molecules **C** and **D**), one ordered methylene chloride molecule and one disordered methylene chloride solvate.

For **1b**, one asymmetric unit contains two independent porphodimethene molecules (molecule **A** and **B**) and methylene chloride solvate. In one of the porphodimethenes, one naphthalene ring and one phenyl ring were found to be disordered over two positions, a major and a minor position. Both components were refined as rigid groups, and their thermal displacement parameters were restrained. In the final refinement, the occupancy for the major component is 0.54 and 0.62, respectively. For **1b**, methylene chloride molecules were badly disordered. SQUEEZE[42] was used to model the disordered methylene chloride solvate. The residue electron count in the interporphyrins voids amounted to 212 electrons per unit-cell (corresponding roughly to 1.25 molecule of CH_2Cl_2 per porphodimethene). Brief crystal data for these structures are listed in Table 1.

Results and Discussion

The synthesis of compounds **1a**, **1b** and **2a**, **2b** is summarized in Scheme 1. Briefly, these four isomers were prepared in a one-pot reaction by the Lindsey protocol. These compounds have been characterized by electrospray-ionization (ESI) mass spectrometry. It revealed the ion peaks at m/z=691.25 for all four species, (corresponding to $[M+H]^+$), which confirmed they are isomers. By comparison, we also did reaction between 5-phenyldipyrromethane and acenaphthenequinone with 2∶2 ratio, only **1a** and **1b** were obtained. So **1a** and **1b** are most likely 5,15-porphodimethenes, while **2a** and **2b** are not. Theoritically, our reaction could lead to porphyrinoid systems with one, three or four acenaphthenequinone units. But we did not obtain these species, one possible reason is that their yields could be too low. These new compounds have been further investigated by X-ray crystallography, ^{1}H NMR and UV-vis spectroscopy *etc*.

Table 1 Crystallographic data for **1a, 1b** and **2b**[a]

Complex	**1a**	**1b**	**2b**
Empirical formula	$C_{55}H_{34}Cl_2N_4O_2$	$C_{108}H_{64}N_8O_4$	$C_{110}H_{68}Cl_4N_8O_4$
Formula weight/(g•mol^{-1})	853.76	1537.67	1707.52
Temperature/K	223(2)	223(2)	223(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
space group	*P*2(1)/*n*	*P*-1	*P*-1
Unit cell dimensions	*a*=16.477(3) Å	*a*=13.725(3) Å	*a*=13.244(3) Å
	b=11.827(2) Å	*b*=17.162(3) Å	*b*=16.274(3) Å
	c=22.737(5) Å	*c*=19.852(4) Å	*c*=20.582(4) Å
	α=90°	*α*=84.00(3)°	*α*=110.16(3)°
	β=110.63(3)°	*β*=82.56(3)°	*β*=92.90(3)°
	γ=90°	*γ*=87.05(3)°	*γ*=91.33(3)°
Volume/Å^3	4146.6(14)	4607.9(16)	4155.0(14)
Z	4	2	2
ρ/(g•cm^{-3})	1.368	1.108	1.365
F(000)	1768	1600	1768
Crystal size/mm^3	0.20×0.60×0.55	0.30×0.60×0.40	0.20×0.40×0.4
Theta range for data collection	3.15° to 25.00°	3.01° to 25.00°	3.02° to 25.00°
Limiting indices	−14≤*h*≤19	−16≤*h*≤15	−14≤*h*≤15
	−13≤*k*≤14	−20≤*k*≤20	−17≤*k*≤19
	−27≤*l*≤124	−22≤*l*≤23	−24≤*l*≤24
Reflections collected/unique	20200/7251	38708/16175	34886/14571
Data/restraints/parameters	7251/56/602	16175/406/1179	14571/65/1175
GOF	1.158	1.009	1.131
R_1,wR_2 [$I>2\sigma(I)$]	R_1=0.0827	R_1=0.0890	R_1=0.0912
	wR_2=0.1939	wR_2=0.2370	wR_2=0.1797
R_1,wR_2 (all data)	R_1=0.0973	R_1=0.1395	R_1=0.1394
	wR_2=0.2049	wR_2=0.2648	wR_2=0.2027
Largest diff. peak and hole/(e•Å^3)	0.220 and −0.527	0.314 and −0.269	1.044 and −0.416

[a] $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$.

Crystal structures

The solid state structures of **1a**, **1b** (molecule **B**) and **2b** (molecule **D**) are shown in Figures 1, 2 and 3, respectively. ORTEP diagrams of **1b** (molecule **A**) and **2b** (molecule **C**) are provided in SI. Structures clearly show that compounds **1a** and **1b** are 5,15-disubstituted porphodimethenes, while **2b** is a 5,10-disubstituted species. Porphodimethenes with unsymmetrically substituted carbon atoms at the *meso* sp^3 centers can exist in three configurations: *syn*-axial, *syn*-equatorial and *anti*.[26,43] In our case, compound **1a** has *anti* configuration, **1b** has *syn*-equatorial configuration (two carbonyl oxygens face to each other). As one kind of calixphyrins, the typical feature of porphodimethenes is a mixture of sp^2- and sp^3-hybridized bridging *meso* carbon centers. In compounds **1a** and **1b**, the 5,15-carbons are sp^3-hybidized, and 10,20- carbons are sp^2-hybidized, which are confirmed by the corresponding bond number, bond distances and angles. Related values are listed in Table 2 and SI.

For **1a**, the structure shows the two saturated carbon atoms force the tetrapyrrolic macrocycle to adopt a strong rooflike folded structure with an interplanar roof angle defined by the dipyrromethene units of 117.8°. The two O···O distance is 3.26 Å. In **1b**, there are two independent molecules (molecules **A** and **B**), the corresponding angles are 130.5° and 130.8°. The dipyrromethene moieties in **1a** are quite planar with the dihedral angles of the pyrrole conjugated units 4.59° and 5.99°, respectively. But the two conjugated pyrrole units within the each dipyrromethene moieties in **1b** are more distorted, the corresponding dihedral angles are 2.63° and 13.12° for molecule **A**, 16.21° and 19.63° for molecule **B**.

In our experiments, we did not obtained *syn*-axial configuration (two carbonyl oxygens are away from each other). Considering about the structure, one possible reason is that such configuration causes both naphthyl groups toward each other, which will cause large repulsion.[44]

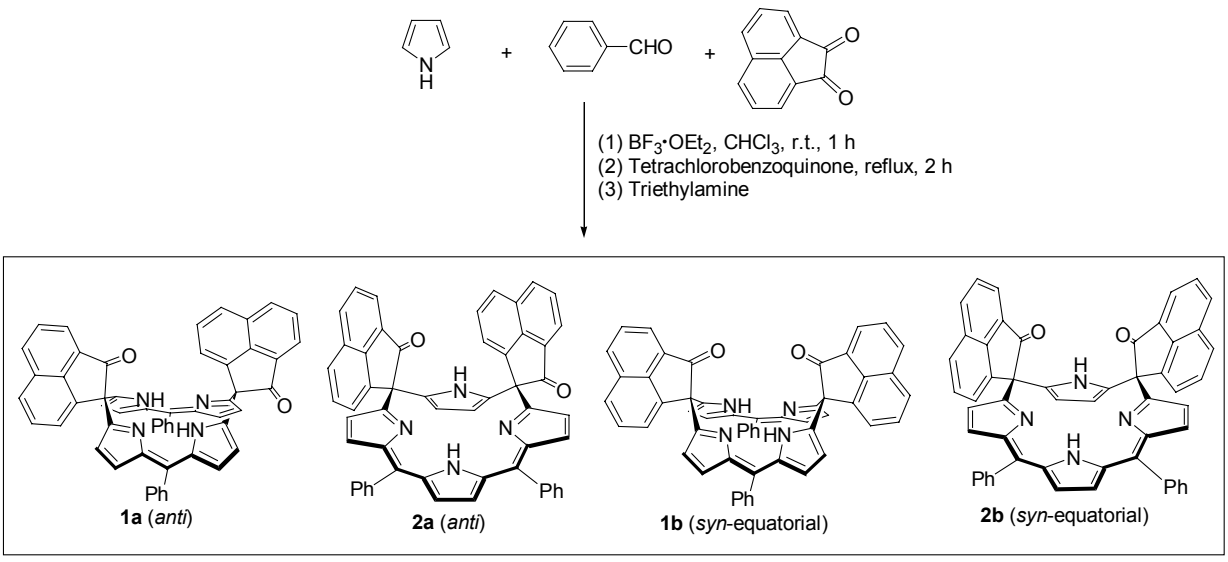
Compounds **2a** and **2b** can not be obtained by the MacDonald method. We were able to grow crystals of **2b** suitable for X-ray crystallographic analysis. In the crystal structure shown in Figure 3, it is clear that there are two sp^3 carbons. All the related bond distances, bond angles and bond numbers in Table S1 suggested the two sp^3 centers are at the 5- and 10-positions and the two sp^2 centers are at the 15- and 20-positions. It has *syn*-equatorial configuration, the two acenaphthylen-1(2*H*)-one subunits are located at the adjacent sp^3-hybirdized *meso* carbons, two carbonyl oxygens face to each other with the corresponding distance 3.640 Å for molecule **C** and 3.837 Å for molecule **D**. As expected, the macrocycle is nonplanar, the tetrapyrrole ring is divided into a conjugated tripyrrane unit and an isolated pyrrole unit. In this case, the tripyrrane subunit is almost planar, with the dihedral angle among the three conjugated pyrrole units 0.38°, 11.68° and 11.32° for molecule **C**, 8.32°, 8.54° and 9.21° for molecule **D**. It is much different from those in other structural characterized 5,10-porphodimethenes[45] which have nonplanar tripyrrane subunits. In the structure of **2b**, the tripyrrane and isolated pyrrole subunits display rotation angle of 64.82° for molecule **C** and 63.63° for molecule **D**.

We were not able to obtain the crystal structure of **2a**. But as similar reason to those 5,15-disubstituted porphodimethene, the *syn*-axial configuration of 5,10-disubstituted species could be unfavorable as well due to the repulsion involving naphthyl groups and the isolate pyrrole unit. So it is most likely compound **2a** has *anti*-configuration. But we can not completely rule out the possibility of *syn*-axial configuration.

^{1}H NMR analysis

In the fully conjugated porphyrin, TPP, the β-protons on the periphery of the macrocycle are strongly

Scheme 1 Synthetic route to 5,10- and 5,15-disubstituted porphodimethenes



CHINESE JOURNAL OF CHEMISTRY

Table 2 Selected bond lengths (Å) and angles (°) for **1a**

C(m1)—C(a2)	1.523(5)	C(A3)-C(m1)-C(11)	111.3(3)
C(m2)—C(a4)	1.422(4)	C(A2)-C(m1)-C(11)	113.6(3)
C(m3)—C(a6)	1.525(4)	C(A3)-C(m1)-C(1)	106.8(3)
C(m4)—C(a8)	1.424(5)	C(A2)-C(m1)-C(1)	112.5(3)
C(1)—O(1)	1.215(4)	C(11)-C(m1)-C(1)	102.1(3)
C(m1)—C(a3)	1.515(4)	C(A3)-C(m1)-C(A2)	110.1(3)
C(m2)—C(a5)	1.387(5)	C(A5)-C(m2)-C(A4)	124.5(3)
C(m3)—C(a7)	1.507(4)	C(A5)-C(m2)-C(21)	119.1(3)
C(m4)—C(a1)	1.389(5)	C(A4)-C(m2)-C(21)	116.3(3)
C(2)—O(2)	1.209(4)	C(A7)-C(m3)-C(A6)	110.1(3)
C(31)-C(m3-C(2)	101.9(2)	C(A7)-C(m3)-C(2)	108.6(3)
C(A6)-C(m3)-C(2)	109.6(2)	C(A1)-C(m4)-C(A8)	124.5(3)
C(A1)-C(m4)-C(41)	118.1(3)	C(A8)-C(m4)-C(41)	117.4(3)

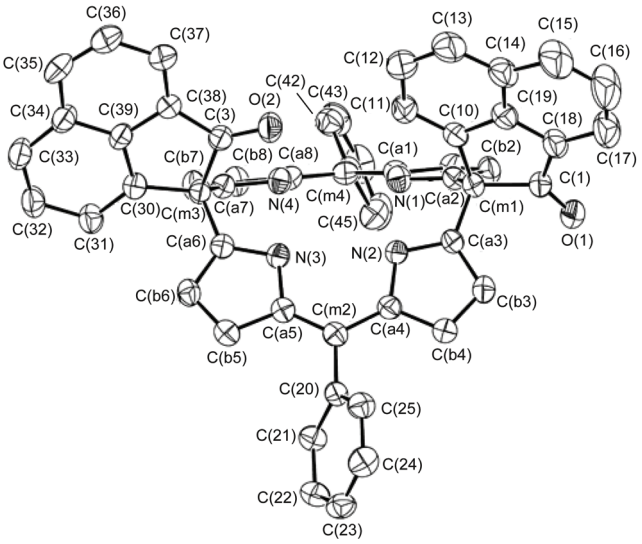


Figure 1 ORTEP view for **1a** at 50% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

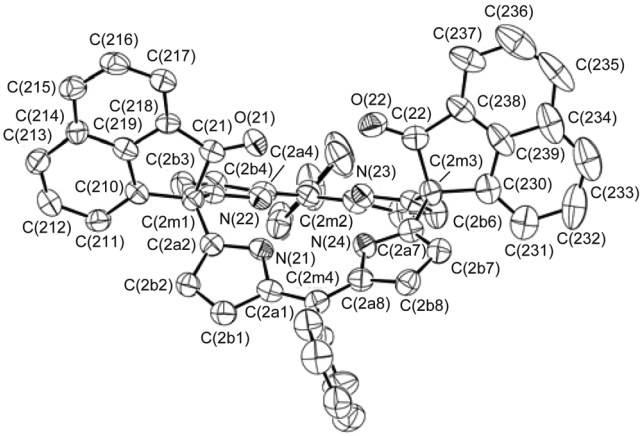


Figure 2 ORTEP view for **1b** (molecule **B**) at 50% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

deshielded by the diamagnetic ring current. They resonate at δ 8.87. The NH protons, in the core of the macrocycle,

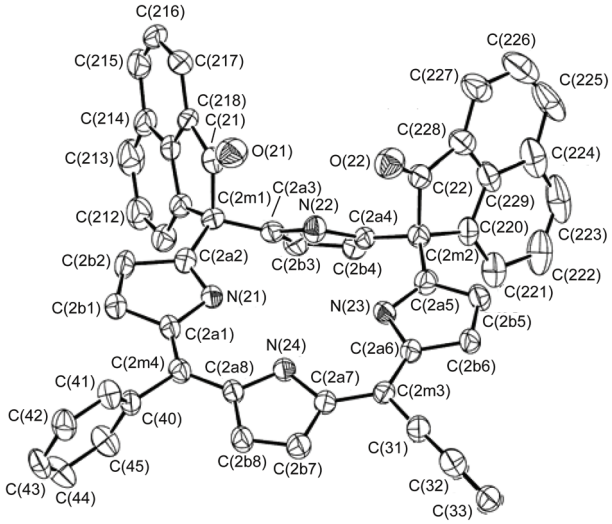


Figure 3 ORTEP view for **2b** (molecule **D**) at 50% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

are shielded by the ring current and resonate upfield at δ −2.72. As shown in Figure 4, in these four porphodimethenes, β-protons are still in the deshielding region, but less downfield, resonated at δ 5—7. The loss of aromaticity in the porphodimethenes causes a reverse effect on the chemical shifts of the NH protons, which results in a downfield shift to the range from δ 11 to 14. For two 5,15-substituted species, there is only single resonance for NH protons. But for 5,10-substituted species, there are two resonance signals. It is obviously due to the lower symmetry of 5,10-porphodimethene.

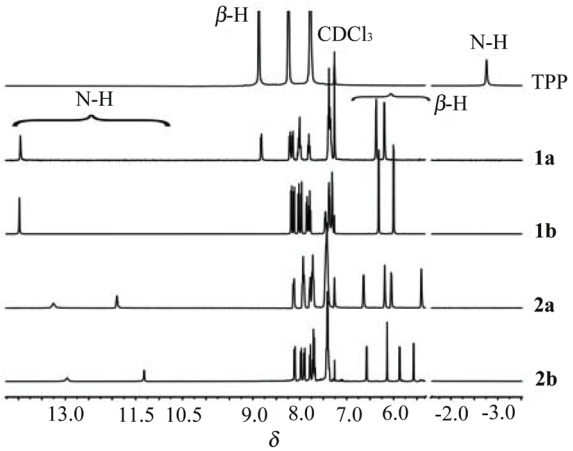


Figure 4 ^{1}H NMR spectra of TPP and four porphodimethene isomers in $CDCl_3$.

UV-vis analysis

Because of the presence of sp^3-hybridized centers, the overall macrocycles must adopt nonplanar conformations.[11-12,46] The photophysical properties of nonplanar macrocycles differ significantly from those of their planar analogues.[47-50] The two 5,15-porphodimethenes (**1a** and **1b**) are both bright orange solids and exhibit a characteristic absorption maxima in the UV-vis

spectra around 439 or 441 nm caused by two distinct linear conjugated π-system, and no Q band is observed (as shown in Figure 5). A weak broad shoulder around 502 nm is a characteristic feature of the porphodimethene.[51] Both **2a** and **2b** are purple solids. Their UV-vis spectra show two absorption bands at 350 and 550 nm. In 5,10-porphodimethenes, the tetrapyrrole ring is divided into a tripyrrane unit and an isolated pyrrole unit. The tripyrrane moiety is responsible for these two broad absorbances, with the absorption due to the isolated pyrrole unit being too weak to be measured.[20,52] This is considerably different from the absorption spectrum of a porphyrin, where there is an intense Soret band at 420 nm accompanied by four less intense Q bands at longer wavelengths.

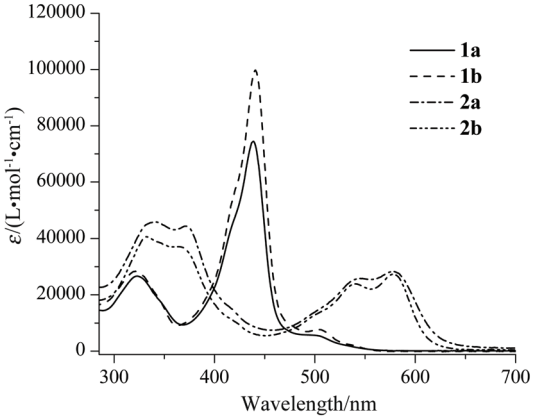


Figure 5 UV-vis spectra of the four isomers (1×10^{-5} mol•L^{-1}) in methylene chloride.

The absorption coefficients for all four porphodimethenes are much less intense than that of the free-base porphyrin. This is attributed to the interrupted conjugation in the macrocycles.[51] However, there is a remarkable difference between the UV-vis spectra of the 5,15-porphodimethenes and 5,10-porphodimethenes. The different conjugated pathway in these species could contribute to such difference. In the 5,15-porphodimethenes, the macrocycles were divided into two identical units containing two conjugated pyrrolic rings by sp^3-hybridized *meso* carbon centers, which shows a superimposed band which is more intense than the single two conjugated pyrrolic rings in UV-vis spectra; while in contrast, the macrocycles of the 5,10-porphodimethenes were divided into a tripyrrane unit and an isolated pyrrole unit. The tripyrrane containing three conjugated pyrrolic rings mainly contributed to the absorption bands, and two weak broad bands among 300—600 nm is a characteristic feature of three conjugated pyrrolic rings.[52] The spectra of **2a** and **2b** are very similar to that of 5,10-porphodimethene in Senge's study,[20] but their solid state structures are much different. It was reported the conformational changes of 5,15-porphodimethene can even lead to interconversion between C_2 and C_i symmetry forms.[26] So it is possible that in solution those conformers are flexible and can convert to each other, UV-vis absorption is the average contributions from all conformers.

Conclusions

In conclusion, we have successfully synthesized and isolated four porphodimethene isomers, especially, two 5,10-porphodimethenes, by a one-pot reaction. They have been characterized by X-ray crystallography, ^{1}H NMR and UV-vis spectroscopy *etc*. Structures suggest **1a** and **1b** are 5,15-porphodimethenes, and **2a** and **2b** are 5,10-porphodimethenes. As a 5,10-porphodimethene, **2b** shows the distinguished solid structure. Much different from the known 5,10-porphodimethenes, the tripyrrane subunit of **2b** adopt planar conformation. Consistent with the structural feature, 5,15-porphodimethenes and 5,10-porphodimethenes show remarkable different ^{1}H NMR and UV-vis spectra. We will further investigate their binding ability to ions in the future.

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