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Synthesis and spectroscopic characterization of *meso*-tetraarylporphyrins with fused phenanthrene rings

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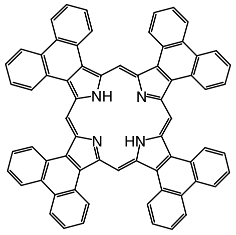
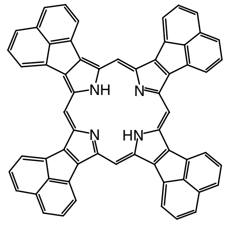
Abstract—A series of *meso*-tetraaryl porphyrins with fused phenanthrene rings have been synthesized from boron trifluoride-catalyzed Lindsey condensation of phenanthro[9,10-*c*]pyrrole with various *para*-substituted arylaldehydes at low temperature. Their structures were characterized by UV–vis, ^{1}H NMR, and mass spectroscopies. The UV–vis spectra of these compounds showed remarkable bathochromic shift of the Soret band to the wavelength around 577 nm and Q-bands into the near-infrared region.

Modified porphyrin chromophores with strong absorption in the red/near-infrared region have been extensively investigated due to their potential biomedical application in photodynamic therapy,[1] as well as a remarkable number of important functions in material science application, such as fluorescent probes,[2] conductive materials,[3] nonlinear optical materials,[4] near-infrared (NIR) dyes.[5] Increased conjugation usually induces a red-shift for a given chromophore, and various strategies including the synthesis of expanded porphyrins,[6] the introduction of *meso*-alkynyl substituents,[7] multiply connecting porphyrin oligomers,[8] and core modifications[9] have been reported to produce absorptions at long-wavelength. In addition, conformational distortions of the porphyrin macrocycle is responsible for some extent of bathochromic shifts.[10] Among them, one of the most effective and promising synthetic approaches might be the fusion of aromatic rings at the β-pyrrolic position which can lead to a significant alternation in the electronic and optical properties of the porphyrin core through the expansion of its π-electronic system. Several modified porphyrin structures with fused benzene, 1,2-naphthalene, acenaphthylene, phenathroline, and 9,10-phenanthrenene rings have been investigated.[11]



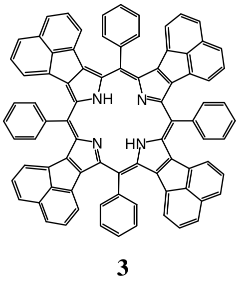
1

Tetraphenanthroporphyrin



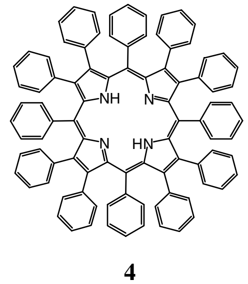
2

Tetraacenaphthoporphyrin



3

Tetraphenyltetraacenaphthoporphyrin



4

Dodecaphenylporphyrin

However, fusion with these aromatic subunits showed relatively small influence on the values of Soret band, even fusion with four phenanthrene moieties (**1**, Chart 1) produces the Soret band at 482 nm, which is only 80 nm red-shift compared to that of octaethylporphyrin (OEP).[11,12] The corresponding acenaphthoporphyrin **2** (Chart 1) shows a disproportionate longer Soret band at 528 nm.[12a,13a,b] Lash and co-workers further

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Keywords: Exocyclic rings; Phenanthrene ring; Ring-fused porphyrins; Synthesis.

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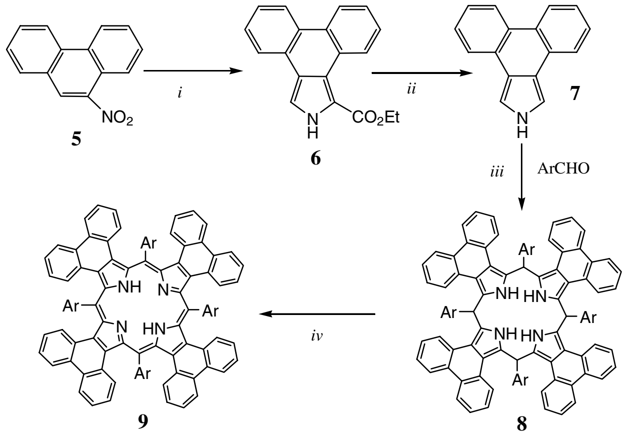

a. Ar = Ph; b. Ar = 4-FC_6H_4; c. Ar = 4-ClC_6H_4; d. Ar = 4-BrC_6H_4; e. Ar = 4-IC_6H_4

Scheme 1. Reagents and conditions: (i) $CNCH_2CO_2Et$, DBU, THF, rt, 24 h; (ii) KOH, $(CH_2OH)_2$, 170 °C, 2 h; (iii) $BF_3{\cdot}OEt_2$, CH_2Cl_2, Ar, −50 °C, 24 h; (iv) DDQ, Et_3N, 1 h.

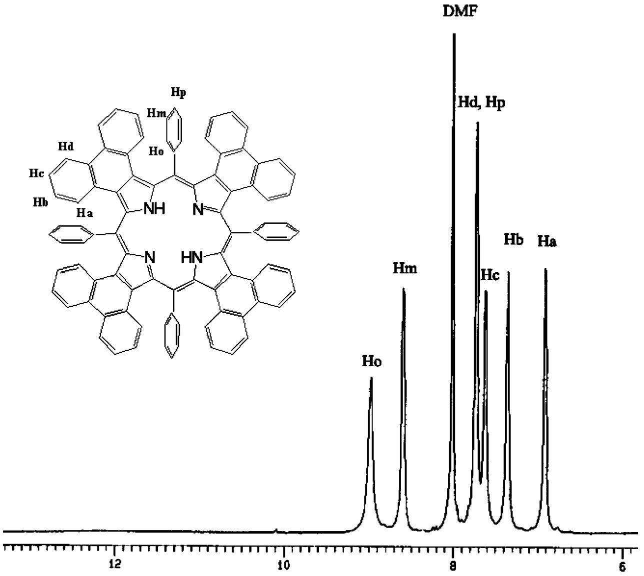

Figure 1. Partial 500 MHz ^{1}H NMR spectrum of **9a** in deuterio-*N*,*N*-dimethylformamide.

increased this value to 556 nm by introducing *meso*-phenyl substituents (**3**, Chart 1).[13b] However, *meso*-aryl phenanthroporphyrin could not be characterized due to the difficulty of preparation under normal Lindsey porphyrin condensation.[13b] Very recently, we reported the synthesis of *meso*-tetraphenyl-ethynylporphyrins at low temperature.[7a] Herein, we describe the synthesis and the spectroscopic property studies of a series of novel tetraaryltetraphenanthroporphyrins following our previous method.

The general procedure for the preparation of *meso*-tetraaryl substituted tetraphenanthroporphyrins **9a–e** was summarized in Scheme 1. Ethyl phenanthro[9,10-*c*]pyrrole-2-carboxylate **6** was readily obtained from the reaction of 9-nitrophenanthrene **5** with ethyl isocyanoacetate in the presence of the non-nucleophilic base 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU).[12d] The ethoxycarbonyl group of **6** was removed by heating with potassium hydroxide in ethylene glycol at 170 °C to give the unsubstituted tetracycle **7** in excellent yield. To the solution of **7** in dry dichloromethane, argon was purged and the flask was cooled to −50 °C, a solution of benzaldehyde in CH_2Cl_2 was added dropwise, followed by addition of catalytic amount of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at low temperature for three hours and warmed to room temperature overnight and after oxidation with DDQ gave the desired tetraphenyltetraphenanthroporphyrin **9a** in 17% yield. The successful synthesis of **9a** encouraged us to examine a series of related compounds with *para*-substituted aryl subunits. A series of *para*-substituted benzaldehydes (R = F, Cl, Br, and I) were condensed with phenanthropyrrole **7** as described above to give the corresponding porphyrins **9b–e** in 10–15% yields. These compounds showed increased solubility in comparison to *meso*-unsubstituted tetraphenanthroporphyrin **1** in $CHCl_3$. Their structures were characterized by MALDI-TOF MASS, ^{1}H NMR, IR, and UV–vis spectroscopies.[14]

The proton NMR spectrum of **9a** in deuterio-*N*,*N*-dimethylformamide (Fig. 1) showed six types of aromatic protons which were consistent with the proposed highly symmetrical porphyrin-like structure. The phenanthrene protons closest to the phenyl subunits were shielded by the adjacent phenyl rings and gave an upfield doublet resonance at 6.93 ppm.[12b] The *ortho*-protons on the phenyl units were deshielded by the adjacent π-systems and afforded a downfield doublet at 8.98 ppm. The remaining protons fell into the typical aromatic range of 7.3–8.0 ppm. The chemical shift of the internal NH appeared at 1.11 ppm, indicating that **9a** had a highly distorted conformation in solution. The structure was further supported by MALDI-TOF mass spectrometry, which gave the expected $[M+H]^+$ peak at $m/z = 1216.38$. Porphyrins **9b–e** gave satisfactory spectroscopic data that were in accordance with their proposed structures.[14]

The UV–vis spectrum of **9a** in chloroform showed a maximum peak at 577 nm which is typical for Soret band, and two Q-bands were observed at 725 and 796 nm that extended into the near-infrared region (Fig. 2). These values compared to those of the corresponding tetraphenyltetraacenaphthoporphyrin **3** (556 (Soret), 638, 705 nm) were red-shifted by 21 nm for Soret band and near 90 nm for the Q-bands. It is very interesting to note that in the case of *meso*-unsubstituted ring-fused porphyrins, the absorption of tetraacenaphthoporphyrins **2** (528 (Soret), 647, 702 nm) is more red-shifted than that of tetraphenanthroporphyrin **1** (482 (Soret), 615, 668 nm). In addition, the Soret band of **9a** is around 100 nm red-shifted compared to the value of 482 nm for the *meso*-unsubstituted tetraphenanthroporphyrin dication **1** and 468 nm for the highly distorted dodecaphenylporphyrin **4**,[15] suggesting that fusion with phenanthrene rings and the severe conformational distortions induced by the *meso*-aryl subunits with the relatively 'wider' phenanthrene rings are responsible for such a remarkable bathochromic shift. The UV–vis absorption spectra of **9b–e** in chloroform showed that as the electron withdrawing ability of the

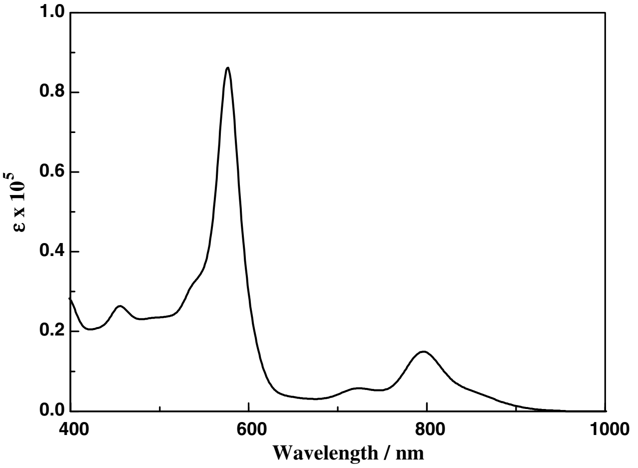

Figure 2. UV–vis spectra of **9a** in $CHCl_3$.

para-subunits on the phenyl moieties decreased in the order of F > Br > Cl > I, both the Soret band and Q-bands were slightly red-shifted with respect to that of **9a**, indicating that different substituents on *meso*-aryl groups had minor additional influence on the porphyrin electronic properties.

In conclusion, we synthesized a series of *meso*-aryl substituted tetraphenanthroporphyrins that showed strong absorption in the red/infrared region. Introduction of *meso*-aryl substituents and fusion with phenanthrene rings to the porphyrin chromophore are responsible for such a significant red-shift of the porphyrin absorption spectra. These properties are desirable as photosensitizers for PDT application. Further studies on the construction of oligomeric porphyrin arrays based on these conjugated structures are currently under investigation.

Acknowledgements

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14. Selected spectral data for **9a**–**e**. Compound **9a**: dark red powder; 17% yield; mp > 300 °C; ^1H NMR (500 MHz, DMF-d_7): δ 1.11 (2H, b), 6.93 (8H, d, $J = 8.2$ Hz),

7.36–7.38 (8H, m), 7.71–7.74 (12H, m), 7.95–7.97 (8H, m), 8.59–8.63 (8H, m), 8.98 (8H, d, $J = 8.2$ Hz); IR (KBr): $\nu_{\max}$/cm^{-1} 3424, 3081, 1629, 1443, 1352, 1048, 759, 726; UV–vis (CHCl$_3$) $\lambda_{\max}$/nm ($\varepsilon \times 10^5$) 577 (0.861), 725 (0.0574), 796 (0.149); MS (MALDI-TOF) *m*/*z* 1216.38 (M+H$^+$). Anal. Calcd for $C_{92}H_{54}N_4·2H_2O$: C, 88.29; H, 4.67; N, 4.48. Found: C, 88.46; H, 4.68; N, 4.51. Compound **9b**: dark red powder; 10% yield; mp > 300 °C; ^{1}H NMR (500 MHz, DMF-d_7): δ 0.89 (2H, b), 6.91–6.94 (8H, m), 7.46–7.49 (8H, m), 7.60–7.63 (8H, m), 7.86–7.88 (8H, m), 8.65–8.67 (8H, m), 8.86–8.88 (8H, m); IR (KBr): $\nu_{\max}$/cm^{-1} 3426, 3086, 1597, 1449, 1352, 1158, 1048, 758, 724; UV–vis (CHCl$_3$) $\lambda_{\max}$/nm ($\varepsilon \times 10^5$) 576 (0.553), 721 (0.038), 796 (0.0941); MS (MALDI-TOF) *m*/*z* 1288.10 (M+H$^+$). Anal. Calcd for $C_{92}H_{50}F_4N_4·3H_2O$: C, 82.37; H, 4.21; N, 4.18. Found: C, 82.46; H, 4.28; N, 4.21. Compound **9c**: dark red powder; 13% yield; mp > 300 °C; ^{1}H NMR (500 MHz, DMF-d_7): δ 0.84 (2H, b), 7.02–7.05 (8H, m), 7.42–7.44 (8H, m), 7.57–7.59 (8H, m), 7.78–7.81 (8H, m), 8.68–8.71 (8H, m), 8.92–8.95 (8H, m); IR (KBr): $\nu_{\max}$/cm^{-1} 3421, 3084, 1586, 1447, 1350, 1047, 1092 758, 726; UV–vis (CHCl$_3$) $\lambda_{\max}$/nm ($\varepsilon \times 10^5$) 582 (0.833), 722 (0.0798), 799 (0.160); MS (MALDI-TOF) *m*/*z* 1353.86 (M+H$^+$). Anal. Calcd for $C_{92}H_{50}Cl_4N_4$: C, 81.66; H, 3.72; N, 4.14. Found: C, 81.45; H, 3.80; N, 4.21. Compound **9d**: dark red powder; 11% yield; mp > 300 °C; ^{1}H NMR (500 MHz, DMF-d_7): δ 0.86 (2H, b), 6.99–7.03 (8H, m), 7.40–7.43 (8H, m), 7.55–7.59 (8H, m), 7.83–7.86 (8H, m), 8.66–8.69 (8H, m), 8.85–8.88 (8H, m); IR (KBr): $\nu_{\max}$/cm^{-1} 3422, 3082, 1630, 1442, 1350, 1077, 1047, 759, 725; UV–vis (CHCl$_3$) $\lambda_{\max}$/nm($\varepsilon \times 10^5$) 583 (0.938), 726 (0.0711), 801 (0.163); MS (MALDI-TOF) *m*/*z* 1531.95 (M+H$^+$). Anal. Calcd for $C_{92}H_{50}Br_4N_4·3H_2O$: C, 69.71; H, 3.56; N, 3.53. Found: C, 69.94; H, 3.59; N, 3.42. Compound **9e**: dark red powder; 15% yield; mp > 300 °C; ^{1}H NMR (500 MHz, DMF-d_7): δ 0.82 (2H, b), 6.98–7.05 (8H, m), 7.19–7.25 (8H, m), 7.38–7.46 (8H, m), 7.57–7.63 (8H, m), 8.02–8.10 (8H, m), 8.67–8.72 (8H, m); IR (KBr): $\nu_{\max}$/cm^{-1} 3424, 3080, 1576, 1446, 1348, 1060, 758, 727 617; UV–vis (CHCl$_3$) $\lambda_{\max}$/nm ($\varepsilon \times 10^5$) 585 (0.5998), 804 (0.1035), 857 (0.09); MS (MALDI-TOF) *m*/*z* 1719.99 (M+H$^+$). Anal. Calcd for $C_{92}H_{50}I_4N_4·1/2H_2O$: C, 63.94; H, 2.97; N, 3.24. Found: C, 63.74; H, 2.99; N, 3.42.

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