Quinone recognition by amide hydrogen bonding in porphyrin systems

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Received (in Cambridge) 24th August 1998, Accepted 15th December 1998

5,15-*cis*-Bis(2-trifluoroacetamidophenyl)porphyrin **2c** and its pentafluorobenzamidophenyl analogue **2e** have significant recognising ability for *p*-benzoquinone **3a**, which is explained by the large negative enthalpy change of the **2c**–**3a** complex and by the small entropy change of the **2e**–**3a** complex, respectively. Porphyrin **2e** recognises electron-rich *p*-benzoquinone more effectively than electron-deficient *p*-benzoquinone, which is ascribed to the enthalpy change of the complexation induced by the hydrogen bonding of amide protons of **2e** with oxygen atoms of the substituted *p*-benzoquinone.

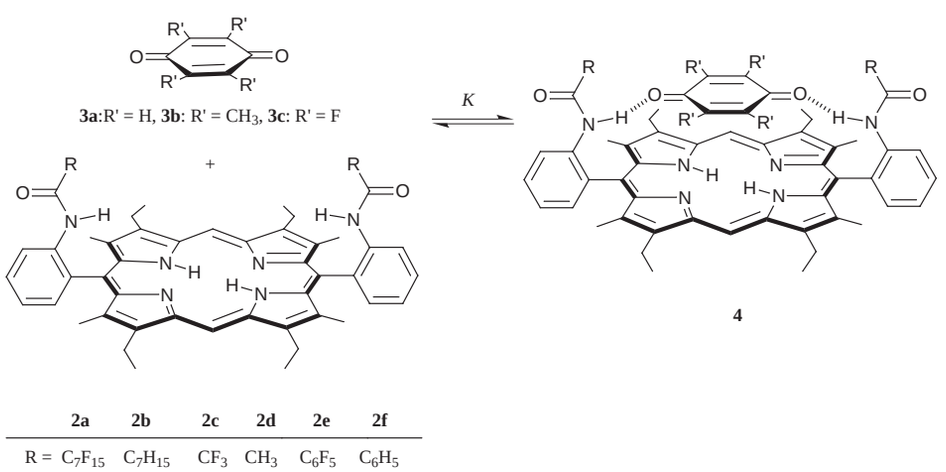
Introduction

In the photoinduced electron transfer in bacterial photosynthetic reaction centres, quinone derivatives, which are bound to the protein by hydrogen bonding to the carbonyl oxygens, play an important role as the electron acceptor.[1–4] Constructions of the artificial porphyrin–quinone assembly have been attained by considering noncovalent interactions based on the two- and four-point hydrogen bonding of *meso* substituted naphthols on the porphyrin ring,[5–8] the redox coupling of hydroquinone attached to the porphyrin ring,[9] and the amide hydrogen bonding of the macrocyclic tetraamide which fulfils the role of a scaffold by the incorporation of a metalloporphyrin coordination.[10,11] More direct hydrogen bonding of the amide substituents attached to the porphyrin ring affords another promising strategy for the porphyrin–quinone assembly,[12] since the acidity of the amide hydrogen can be controlled by varying the attached acyl group and, moreover, the multipoint hydrogen bonding can be constructed by the introduction of a functionalized acyl group. In this paper, we would like to demonstrate the *p*-benzoquinone recognition ability of 5,15-*cis*-bis(2-amidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrins **2** and, in particular, to focus upon the effect of the introduced acyl group on the association constant for the porphyrin–*p*-benzoquinone complexation.

Results and discussion

The recognising ability for *p*-benzoquinone (**3a**) was evaluated with respect to perfluoroheptanecarboxamido-, heptanecarboxamido-, trifluoroacetamido-, acetamido-, pentafluorobenzamido-, and benzamidoporphyrins (**2a**, **2b**, **2c**, **2d**, **2e**, and **2f**, respectively), together with the *trans*-isomer of **2a** (**2a**-*trans*) and 5,15-*cis*-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**1**). Porphyrins **2c** and **2d** were prepared by the acylation of **1** with the corresponding anhydride in 78 and 71% yield, respectively.[13] Porphyrins **2a**, **2b**, **2e**, and **2f** were obtained by the acylation of **1** with the corresponding acyl chloride in 73, 80, 63, and 98% yield, respectively (Scheme 1). The *trans*-isomer (**2a**-*trans*) was prepared from the *trans*-isomer of **1** in 80% yield.

Determination of the association constant for the porphyrin–**3a** complexation was first attempted by UV titration; however, it was found that the absorption change in the presence of varying amounts of **3a** was too small for the titration. The Stern–Volmer plot for the fluorescence quenching of porphyrin with **3a** indicates a linear correlation, which must be based on intermolecular collision of photoexcited porphyrin and a quinone molecule. The reliable intracomplex quenching, which can make possible the Benesi–Hildebrand treatment, is not realised. The ^{1}H NMR technique is another plausible method for the titration. The ^{1}H NMR spectrum of a mixture of porphyrin **2a** and **3a** showed sharp and single resonances for downfield-shifted amide protons of **2a** and for upfield-shifted protons of **3a**, which are consistent with the face-to-face structure **4**. The association constant for the porphyrin–**3a** complexation was evaluated from the ^{1}H NMR titration for the change of the downfield-shifted amide protons of porphyrin, the con-



Scheme 1

Table 1 Association constants (K/M^{-1}) for porphyrin–*p*-benzoquinone **3a** complexation in $C_6D_5CD_3$–$CDCl_3$ (10:1)[a]

2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2a-*trans***	**1**
$(2.4 \pm 0.3) \times 10$[b]	$(3.5 \pm 0.4) \times 10$[b]	$(1.5 \pm 0.1) \times 10^2$[c]	$(9.7 \pm 0.4) \times 10$[c]	$(1.7 \pm 0.2) \times 10^2$[c]	8.3 ± 4.6[c]	2.7 ± 0.5[b]	6.2 ± 1.2[b]

[a] The association constants were determined by ^{1}H NMR titration, the concentration of porphyrin being 2.5×10^{-3} M. [b] Determined at 293 K. [c] Determined at 298 K.

Table 2 Association constants (K/M^{-1}) and thermodynamic parameters for porphyrin–*p*-benzoquinone complexation in $C_6D_5CD_3$–$CDCl_3$ (10:1)[a]

	K					$\Delta G°_{298}$/	$\Delta H°$/	$T\Delta S°_{298}$/
	253 K	263 K	273 K	298 K	313 K	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
2c–3a	$(1.3 \pm 0.1) \times 10^3$	$(7.5 \pm 0.3) \times 10^2$	$(4.6 \pm 0.1) \times 10^2$	$(1.5 \pm 0.1) \times 10^2$	$(8.9 \pm 0.6) \times 10$	-3.0 ± 0.1	-7.1 ± 0.1	-4.1 ± 0.1
2d–3a	$(7.2 \pm 0.7) \times 10^2$	$(4.2 \pm 0.4) \times 10^2$	$(2.6 \pm 0.2) \times 10^2$	$(9.7 \pm 0.4) \times 10$	$(5.8 \pm 0.2) \times 10$	-2.7 ± 0.1	-6.6 ± 0.1	-3.9 ± 0.1
2e–3a	$(9.0 \pm 0.1) \times 10^2$	$(5.6 \pm 0.7) \times 10^2$	$(3.8 \pm 0.3) \times 10^2$	$(1.7 \pm 0.2) \times 10^2$	$(1.1 \pm 0.1) \times 10^2$	-3.1 ± 0.1	-5.4 ± 0.1	-2.3 ± 0.2
2e–3b	$(1.7 \pm 0.3) \times 10^3$	$(1.0 \pm 0.1) \times 10^3$	$(5.6 \pm 0.3) \times 10^2$	$(2.2 \pm 0.1) \times 10^2$	$(1.3 \pm 0.1) \times 10^2$	-3.2 ± 0.1	-6.7 ± 0.2	-3.5 ± 0.2
2e–3c	$(1.1 \pm 0.1) \times 10^2$	$(7.6 \pm 0.5) \times 10$	$(6.1 \pm 0.4) \times 10$	$(3.3 \pm 0.4) \times 10$	$(2.9 \pm 0.2) \times 10$	-2.1 ± 0.1	-3.5 ± 0.2	-1.5 ± 0.3
2f–3a	$(2.0 \pm 0.5) \times 10$	$(1.5 \pm 0.5) \times 10$	$(1.2 \pm 0.4) \times 10$	8.3 ± 4.6	6.7 ± 3.7	-1.3 ± 0.3	-2.7 ± 0.2	-1.5 ± 0.5

[a] The association constants were determined by ^{1}H NMR titration, the concentration of porphyrin being 2.5×10^{-3} M.

centration of porphyrin being 2.5×10^{-3} M and that of **3a** being varied from 1 to 200 equimolar amount in $C_6D_5CD_3$–$CDCl_3$ (10:1).[14] The results are collected in Table 1.

The appreciable association constant of **2a**, compared with that of **2a**-*trans*, supports the two-point hydrogen bonding described in structure **4**. The negligible association constant of porphyrin **1** indicates not only the weak hydrogen bonding of amino protons but also the weak π–π stacking of the aminophenyl substituted porphyrin ring and of the aminophenyl ring itself with **3a**.[15] Porphyrin **2a** is expected to show more rigid complexation than **2b**, since the amide protons of **2a** are more acidic than those of **2b** because of the strongly withdrawing fluorine group. However, a slight preference of **2b** over **2a** in association constants is in evidence, which indicates that the complexation is affected by both the acidity of the amide protons and the steric effect of the substituent, because the non-flexibility of the perfluoroalkyl group, other than its electron-withdrawing effect, is well known.[16]

Trifluoroacetamidoporphyrin **2c**, the trifluoromethyl group of which is expected to be small enough for the complexation, was next evaluated; the association constant was attained and was found to be greater than that of acetamidoporphyrin **2d**. It is remarkable that pentafluorobenzamidoporphyrin **2e** recognises **3a** effectively, its association constant being comparable to that of trifluoroacetamidoporphyrin **2c**, and this is in sharp contrast to the negligible association constant of benzamidoporphyrin **2f**.

The complexation equilibria of the selected porphyrins **2c**, **2d**, **2e**, and **2f** with *p*-benzoquinone **3a** were next followed by similar ^{1}H NMR titration at various temperatures. The obtained association constants are summarized in Table 2 and the satisfactorily linear van't Hoff plot, giving the relationship between the association constants and temperature, is described in Fig. 1. The thermodynamic parameters, which are evaluated by the van't Hoff equation, are also collected in Table 2. As was expected, the sufficiently negative free energy change of the complex with **2c** is mainly affected not by entropy change but by enthalpy change, which shows that the trifluoromethyl group is acting as a strongly electron-withdrawing group of comparable size to the methyl group in **2d**. On the contrary, it is of interest that the small entropy change of the complex with **2e** overcomes a slight decrease in enthalpy change, compared with **2d**, and facilitates the formation of the complex. It is likely that the small entropy change is due to the mesomeric delocalization between the pentafluorophenyl group and the carbonyl group in both **2e** and its complex with **3a**, resulting in the restriction of the free rotation of the pentafluorophenyl group. It should be added that the small negative free energy change in the case of **2f** reflects the considerable decrease in the enthalpy change, rather than the entropy change, and this seems to be caused by the weakly electron-withdrawing property of the phenyl group in **2f**.

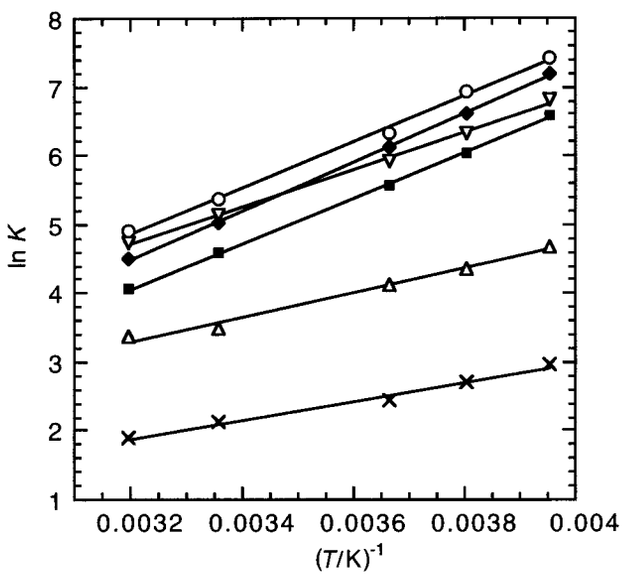


Fig. 1 van't Hoff plots for porphyrin–*p*-benzoquinone complexation in $C_6D_5CD_3$–$CDCl_3$ (10:1). ○, **2e–3b** ($r = 0.9985$); ◆, **2c–3a** ($r = 0.9998$); ▽, **2e–3a** ($r = 9990$); ■, **2d–3a** ($r = 0.9998$); △, **2e–3c** ($r = 0.9947$); ×, **2f–3a** ($r = 0.9936$).

The recognising ability for electron-rich tetramethyl-*p*-benzoquinone (**3b**) and electron-deficient tetrafluoro-*p*-benzoquinone (**3c**) was next evaluated using pentafluorobenzamidoporphyrin **2e.** As shown in Table 2, the electron-releasing methyl group brings about an outstanding increase in association constants and conversely the electron-withdrawing fluorine atom leads to a decrease in the association constant, compared with that of **3a**. This order **3b** > **3a** > **3c** in association constants is primarily caused by enthalpy change. It is realised that the small enthalpy change in the case of **3c** demonstrates the negligible contribution of the π–π stacking between electron-donating porphyrin and electron-accepting tetrafluorobenzoquinone **3c**. Hydrogen bonding of the amide protons of **2e** with the oxygen atoms of *p*-benzoquinones seems to play a main role in the complexation and it is supported by the calculated net charge of the oxygen atoms of *p*-benzoquinones; that is, the order of net charge -0.54 for **3b** > -0.52 for **3a** > -0.46 for **3c** is parallel to the decreasing association constants **2e–3b** > **2e–3a** > **2e–3c**.[17]

In conclusion, (2-trifluoroacetamido- and 2-pentafluorobenzamido)porphyrins **2c** and **2e** have significant recognising ability for *p*-benzoquinone **3a** and it should be noted that their recognising ability is as good as or slightly superior to that of (2-hydroxy-1-naphthyl)porphyrin analogues, association constants of which are reported to be $K = 5.5 \times 10\ M^{-1}$ in $CDCl_3$ (based on ^1H NMR titration) and $1.4 \times 10^2\ M^{-1}$ in benzene (based on UV–VIS titration) at 298 K. Moreover, **2e** recognises electron-rich *p*-benzoquinone more effectively than electron-deficient *p*-benzoquinone, which is ascribed to the enthalpy change of the complex, caused by the hydrogen bonding of amide protons of **2e** with oxygen atoms of the substituted *p*-benzoquinone.

Experimental

The IR spectra were recorded on a JASCO A-100 spectrometer and samples were run as potassium bromide pellets. UV–Visible spectra were recorded with a JASCO Ubest-50 spectrometer and measured in CH_2Cl_2. The ^1H NMR spectra were recorded with a JEOL JNM-GX270 (270 MHz) or -LA400 (400 MHz) spectrometer using tetramethylsilane as an internal standard, the chemical shifts being given in δ/ppm downfield. Samples were taken in $C_6D_5\ CD_3$–$CDCl_3$ (10 : 1) unless otherwise noted. The elemental analyses were measured with a Perkin-Elmer 2400 II CHN Analyzer.

5,15-*cis*-Bis(2-perfluoroheptanecarboxamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2a)

Triethylamine (200 mg, 1.98 mmol) was added dropwise to a solution of aminophenylporphyrin **1** (100 mg, 0.15 mmol) and perfluorooctanoyl chloride (800 mg, 1.85 mmol) in 10 mL of THF. After being stirred at room temperature for 1 h, the solution was evaporated to leave a residue which was dissolved in chloroform. The mixture was washed with water and brine, dried over magnesium sulfate, and evaporated. The resulting solid was chromatographed on silica gel (hexane–ethyl acetate, 5 : 1) to give 160 mg (73% yield) of **2a**. Further purification was carried out by recrystallization from hexane–chloroform: mp 191–193 °C; IR 3380 (NH), 1730 (C=O), 1210 and 1240 cm^{-1} (C–F); ^1H NMR δ −1.98 (s, 2H), 1.70 (t, J = 7.6 Hz, 12H), 2.48 (s, 12H), 3.85 (q, J = 7.6 Hz, 8H), 7.30 (t, J = 7.6 Hz, 2H), 7.60 (m, 4H), 8.0 (s, 2H), 8.85 (d, J = 8.6 Hz, 2H), 10.30 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 626.5 (3.05), 575 (3.34), 540 (3.37), 506.5 (3.72), 405.5 (4.79). Anal. Calcd. for $C_{60}H_{46}N_6F_{30}O_2$: C, 49.58; H, 3.19; N, 5.79. Found: C, 49.29; H, 3.12; N, 5.98%.

5,15-*trans*-Bis(2-perfluoroheptanecarboxamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2a-*trans*)

In a similar manner to the above, acylation of 5,15-*trans*-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin with perfluorooctanoyl chloride gave 80% yield of **2a**-*trans*: mp 239–241 °C (recrystallized from hexane–chloroform); IR 3375 (NH), 1730 (C=O), 1260, 1200, and 1140 cm^{-1} (C–F); ^1H NMR δ −2.0 (br s, 2H), 1.70 (t, J = 7.6 Hz, 12H), 2.50 (s, 12H), 3.85 (q, J = 7.6 Hz, 8H), 7.30 (t, J = 7.6 Hz, 2H), 7.60 (m, 4H), 8.00 (s, 2H), 8.90 (d, J = 8.6 Hz, 2H), 10.30 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 626.5 (3.04), 575 (3.34), 539.5 (3.37), 506 (3.73), 405 (4.79). Anal. Calcd. for $C_{60}H_{46}N_6F_{30}O_2$: C, 49.58; H, 3.19; N, 5.79. Found: C, 49.57; H, 2.83; N, 5.56%.

5,15-*cis*-Bis(2-heptanecarboxamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2b)

Similar acylation of **1** using octanoyl chloride afforded 80% yield of **2b**: mp 258–261 °C (recrystallized from hexane–chloroform); IR 3400 (NH), 1700 cm^{-1} (C=O); ^1H NMR δ −1.90 (br s, 2H), 0.3–0.95 (m, 30H), 1.70 (t, J = 7.6 Hz, 12H), 2.65 (s, 12H), 3.90 (q, J = 7.6 Hz, 8H), 6.90 (s, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.60 (m, 4H), 9.20 (d, J = 8.8 Hz, 2H), 10.27 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 626.5 (3.18), 575 (3.48), 540.5 (3.52), 506.5 (3.86), 406 (4.94). Anal. Calcd. for $C_{60}H_{76}N_6O_2$: C, 78.90; H, 8.39; N, 9.21. Found: C, 78.80; H, 8.11; N, 8.95%.

5,15-*cis*-Bis(2-trifluoroacetamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2c)

Similar acylation of **1** using trifluoroacetic anhydride afforded 78% yield of **2c**: mp 335–336.5 °C (dec.) (recrystallized from hexane–chloroform); IR 3375 (NH), 1735 (C=O), 1150 cm^{-1} (CF_3); ^1H NMR δ −1.90 (br s, 2H), 1.67 (t, J = 7.6 Hz, 12H), 2.49 (s, 12H), 3.82 (m, 8H), 7.24 (m, 2H), 7.51 (dd, J = 7.6, 1.5 Hz, 2H), 7.56 (m, 2H), 8.04 (s, 2H), 8.87 (dd, J = 8.5, 1.0 Hz, 2H), 10.28 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 626.5 (3.47), 575 (3.79), 540.5 (3.82), 506.5 (4.18), 406 (5.26). Anal. Calcd. for $C_{48}H_{46}N_6F_6O_2$: C, 67.58; H, 5.44; N, 9.86. Found: C, 67.20; H, 5.30; N, 9.48%.

5,15-*cis*-Bis(2-acetamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2d)

Similar acylation of **1** using acetic anhydride afforded 71% yield of **2d**: mp 313–314 °C (dec.) (recrystallized from hexane–ethyl acetate); IR 3400 (NH), 1695 cm^{-1} (C=O); ^1H NMR δ −1.84 (s, 2H), 0.60 (s, 6H), 1.70 (t, J = 7.6 Hz, 12H), 2.64 (s, 12H), 3.89 (m, 8H), 6.79 (s, 2H), 7.25 (m, 2H), 7.57 (dd, J = 7.6, 1.7 Hz, 2H), 7.64 (m, 2H), 9.14 (d, J = 8.5 Hz, 2H), 10.37 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 625.5 (3.21), 574 (3.77), 540.5 (3.73), 506.5 (4.18), 406.5 (5.29). Anal. Calcd. for $C_{48}H_{52}N_6O_2$–$CH_3CO_2C_2H_5$: C, 74.96; H, 7.26; N, 10.09. Found: C, 75.11; H, 7.17; N, 10.49%.

5,15-*cis*-Bis(2-pentafluorobenzamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2e)

Similar acylation of **1** using pentafluorobenzoyl chloride afforded 63% yield of **2e**: mp 312–313 °C (dec.) (recrystallized from hexane–chloroform); IR 3390 (NH), 1695 cm^{-1} (C=O); ^1H NMR δ −1.96 (br s, 2H), 1.68 (t, J = 7.6 Hz, 12H), 2.62 (s, 12H), 3.87 (m, 8H), 7.24 (m, 2H), 7.46 (dd, J = 7.6, 1.5 Hz, 2H), 7.62 (s, 2H), 7.63 (m, 2H), 9.22 (d, J = 8.0 Hz, 2H), 10.30 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 624.5 (3.44), 573 (3.83), 541 (3.83), 507 (4.20), 406.5 (5.28). Anal. Calcd. for $C_{58}H_{46}N_6O_2F_{10}$: C, 66.39; H, 4.42; N, 8.01. Found: C, 66.15; H, 4.24; N, 8.05%.

5,15-*cis*-Bis(2-benzamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2f)

Similar acylation of **1** using benzoyl chloride afforded 98% yield of **2f**: mp 294–295 °C (recrystallized from hexane–ethyl acetate); IR 3410 (NH), 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ −2.37 (s, 2H), 1.75 (t, J = 7.6 Hz, 12H), 2.60 (s, 12H), 4.02 (m, 8H), 6.49 (m, 4H), 6.65 (m, 4H), 6.80 (tt, J = 7.6, 1.2 Hz, 2H), 7.55 (m, 2H), 7.81 (dd, J = 7.6, 1.4 Hz, 2H), 7.90 (m, 2H), 8.06 (s, 2H), 9.05 (dd, J = 8.3, 1.0 Hz, 2H), 10.28 (s, 2H); UV λ_{max} nm (log ε/$dm^3\ mol^{-1}\ cm^{-1}$) 626.5 (3.32), 575.5 (3.76), 541.5 (3.74), 508 (4.14), 409 (5.22). Anal. Calcd. for $C_{58}H_{56}N_6O_2$: C, 80.14; H, 6.50; N, 9.67. Found: C, 80.11; H, 6.46; N, 9.43%.

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Paper 8/06621C