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Quinone-recognition by Four-point Hydrogen Bonding in Porphyrin System Having Urea Moiety

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5,15-*cis*-bis(Ureidophenyl)porphyrins have significant recognizing ability for *p*-benzoquinones through four-point hydrogen bonding. Although an unusual temperature-dependence of the complexation is observed with bis(*N′*-phenylureidophenyl) porphyrin, bis(*N′*-ethylureidophenyl)porphyrin shows a satisfactorily linear van't Hoff plot and recognizes an electron-rich *p*-benzoquinone such as tetramethyl-*p*-benzoquinone more effectively, which is ascribed to the large enthalpy change in the complex.

Keywords: Ureidoporphyrin; Quinone-recognition; Hydrogen bonding; Association constant

INTRODUCTION

In the mitochondrial respiratory chain, quinone derivatives bound to the protein by hydrogen bonding function as the acceptor and carrier of a photoinduced electron [1–4]. As a model for bacterial photosynthesis, the noncovalently linked porphyrin–quinone assembly has been studied for the construction of an artificial photo-separation system [5–11]. An intermediate of photoinduced electron transfer process has been reported to be detected in the noncovalent assembly of a meso-substituted (2-hydroxy-1-naphthyl)porphyrin derivative and quinone [12]. In our previous paper, we reported that hydrogen bonding of the amide substituents attached to the porphyrin ring afforded a promising strategy for the porphyrin–quinone assembly because of the controllable acidity of the amide hydrogen by varying the attached acyl group [13]. In fact, 5,15-*cis*-bis(2-pentafluorobenzamidophenyl)porphyrin has significant recognizing ability for *p*-benzoquinone, and its ability is comparable to or slightly superior to that of the corresponding (2-hydroxy-1-naphthyl)porphyrin analog and is mainly due to the enthalpy change in the complex caused by the hydrogen bonding of amide protons. A multipoint hydrogen bonding, which is expected to increase the enthalpy change in the complex, can be constructed by the introduction of a functionalized acyl group instead of a simple acyl group. A urea substituent can afford an attractive recognizing site through a multipoint hydrogen bonding [14–19]. In this paper, we wish to demonstrate the quinone recognition ability of 5,15-*cis*-bis(2-ureidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrins.

RESULTS AND DISCUSSION

The recognition of *p*-benzoquinone was first investigated with respect to *N′*-phenylureidoporphyrin (**1a**), which was prepared by the facile carbamoylation of 5,15-*cis*-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin with phenylisocyanate in 52% yield. The ^{1}H-NMR spectrum of porphyrin **1a** in $CDCl_3$ shows rather upfield-shifted phenyl protons and NH protons together with other downfield-shifted NH protons, as shown in Fig. 1. The upfield-shifted phenyl protons and NH protons are both due to the diamagnetic ring current of the porphyrin ring, so that the upfield- and downfield-shifted NH protons are, respectively, assigned to the ureido protons NH_b and the amide protons NH_a. Phenyl-, NH_a and NH_b

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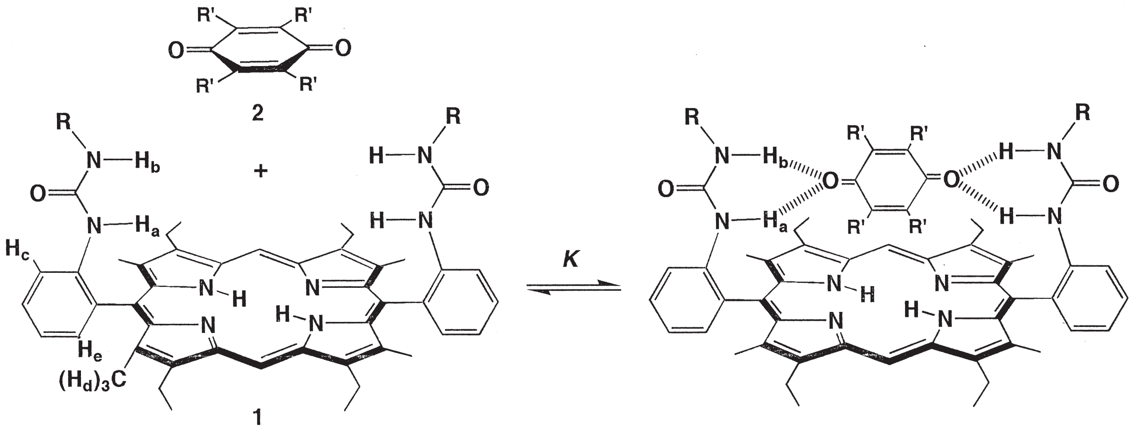

1a : R = C_6H_5, **1b** : R = C_2H_5
2a : R' = H, **2b** : R' = OCH_3, **2c** : R' = CH_3

SCHEME 1

protons are observed to be drastically shifted to the downfield in DMSO-d$_6$. Figure 1 also shows the prominent NMR spectrum for **1a**-*p*-benzoquinone complexation. Addition of one molar ratio of *p*-benzoquinone to a $CDCl_3$ solution of **1a** caused a considerable change in the chemical shifts of both the NH_a and NH_b protons of **1a** and the olefinic protons of *p*-benzoquinone. Large downfield shifts of NH_a and NH_b protons from 6.32 to 7.34 and from 5.49 to 6.74, respectively, indicate that the hydrogen bonding interaction between porphyrin and quinone is through both the NH_a and NH_b protons. The olefinic protons of *p*-benzoquinone shift upfield ($\Delta\delta = 1.30$ ppm) due to the diamagnetic ring current of the porphyrin ring. These results support that the complex is a four-point hydrogen-bonded structure where the quinone is situated above the porphyrin ring. It should be noted that the resonances of the phenyl groups in the complex considerably shift downfield, which supports the belief that the phenyl groups are raised by the complexation (Scheme 1).

The association constant for the 1:1 complexation of **1a** and *p*-benzoquinone was evaluated from the ^{1}H-NMR titration for the change in downfield-shifted NH_a protons, the estimated association constant being $K = 1.2 \times 10^3\,M^{-1}$ in $CDCl_3$ at 298 K[†]. The recognizing ability of **1a** is rather superior to that of 5,15-*cis*-bis(2-pentafluorobenzamido)porphyrin, the association constant of which is $K = 1.7 \times 10^2\,M^{-1}$ in $CDCl_3$/toluene-d$_8$ (1/10) at 298 K. The ^{1}H-NMR titration of **1a** was difficult to carry out at low temperature because of its low solubility and broadening of the NH_a resonances. The complexation behavior was next monitored by UV–Vis spectroscopic titration. The *Q*-band in the range of 475–700 nm changes with the observation of several isosbestic points upon addition of *p*-benzoquinone, as shown in Fig. 2. A sufficient change in the *Q*-band absorbance made it possible to estimate the association constant, which was evaluated to be $K = 2.3 \times 10^3\,M^{-1}$ in toluene at 298 K[‡].

To determine the temperature-dependence of the binding ability, the relationships between $1/T$ and $\ln K$, van't Hoff plots, of the complexation were evaluated (Fig. 3). However, an unusual temperature-dependence is observed; that is, the association constants are minimal around room temperature and gradually increase with lowering temperature and even with elevating temperature. The temperature-dependence was also found to be affected by the solvent polarity. In more polar solvents such as toluene/ethyl acetate (9/1 and 4/1), the binding behavior becomes close to the ordinary trend where the association constants decrease with elevating temperature.

From the reported facts that urea-substituted hosts assemble through intermolecular or intramolecular hydrogen bondings [14–19], the unusual temperature- and solvent polarity-dependence of the quinone recognition of **1a** will be explained by the assumption of the existence of a porphyrin dimer or oligomer, which no longer binds quinone. The presence of a porphyrin dimer or oligomer is suggested by a nuclear overhauser effect (NOE) in

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[†] Association constant is obtained by the slope and intercept of the plot based on the following equation, $1/\Delta\delta_{obsd}(NH_a) = \{1/\Delta\delta_{comp}(NH_a)\} + (1/K)\{1/\Delta\delta_{comp}(NH_a)\}\{1/[p\text{-benzoquinone}]_{total}\}$, where $\Delta\delta_{obsd}(NH_a) = \delta_{obsd}(NH_a) - \delta_{\mathbf{1a}}(NH_a)$, $\Delta\delta_{comp}(NH_a) = \delta_{comp}(NH_a) - \delta_{\mathbf{1a}}(NH_a)$, and $\delta_{\mathbf{1a}}(NH_a)$ is the chemical shift of NH_a protons of the free porphyrin **1a** [8].

[‡] A 1:1 complex follows to the equation, $C_H C_G/(A - A_H) = (\varepsilon_{HG} - \varepsilon_H)^{-1} \times C_G + (\varepsilon_{HG} - \varepsilon_H)^{-1} \times K^{-1}$ (where C_H and C_G mean the initial host concentration and the added guest concentration, respectively; A and A_H mean the measured absorbance and the initial host absorbance, respectively; ε_{HG} and ε_H mean the molar absorption coefficients of the complex and of the host, respectively). On the basis of a plot of C_G vs. $C_H C_G/(A - A_H)$, the association constant K is estimated from the slope divided by the intercept.

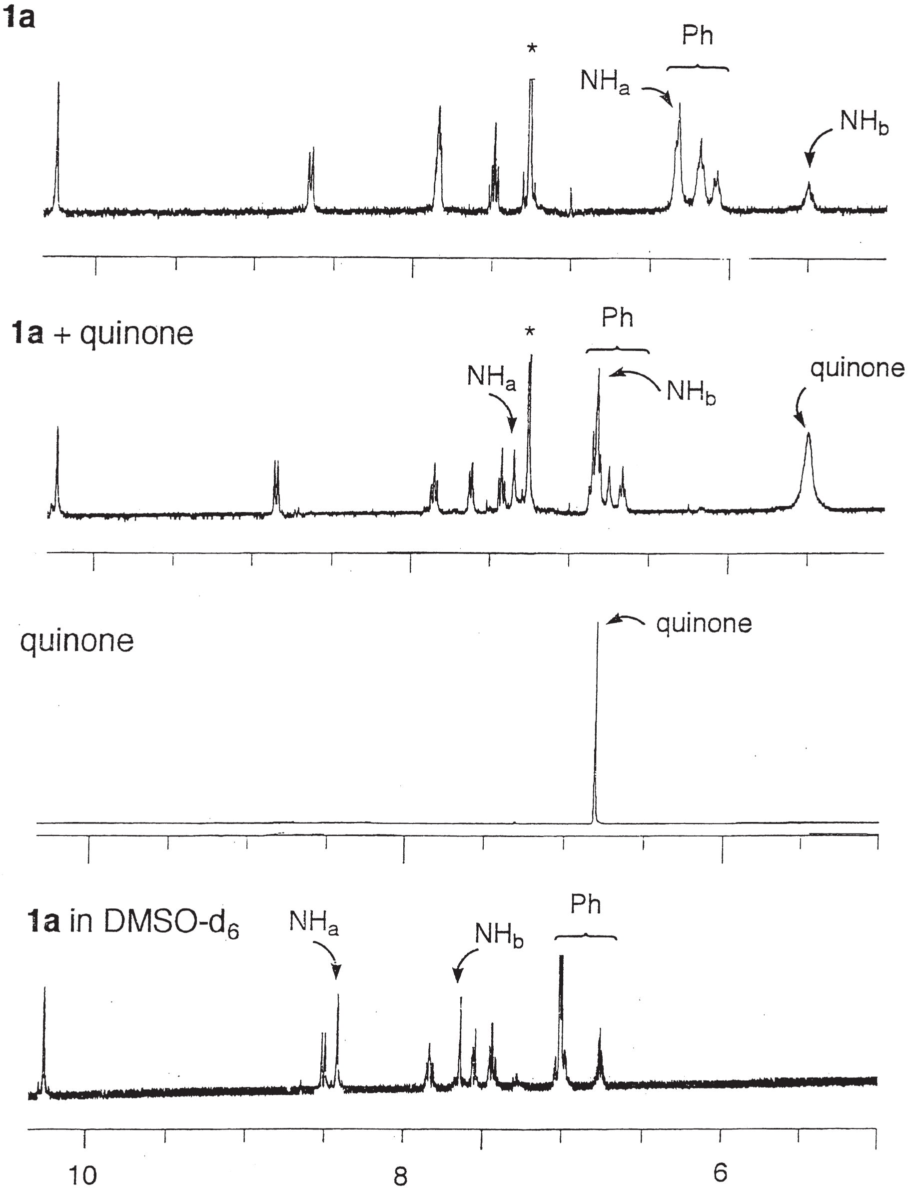

FIGURE 1 ^{1}H-NMR spectra **1a**. Measured in $CDCl_3$, unless otherwise noted. *contaminant of $CDCl_3$.

the ^{1}H-NMR spectra [20]. When the signals of the *N*′-phenyl group of **1a** were irradiated, a positive NOE was observed with the aromatic hydrogen (H_c) and the hydrogen (H_d) of methyl group bonding to the porphyrin ring (Table I). These connectivities cannot result from through-space interactions within a single molecule because these hydrogens are not sufficiently close to interact in the same molecule. Therefore, the NOE connectivities should come from intermolecular interaction, which is responsible for the formation of a porphyrin dimer or oligomer. The NOE of *N*′-ethylureidoporphyrin **1b** was examined for comparison to **1a**. The signals of the methyl group of the *N*′-ethyl substituent in **1b** were also irradiated, but the NOE connectivity was not observed with any hydrogens (Table I). These results support that **1b** exists as a monomer in the $CDCl_3$ solution.

Investigation was next focused on the quinone recognition of **1b**, which exists as the monomer in $CDCl_3$. Similarly to the case of **1a**, addition of one molar ratio of *p*-benzoquinone to a $CDCl_3$ solution of **1b** caused considerable downfield shifts of the NH_a and NH_b protons of porphyrin and an upfield shift of the olefinic protons of *p*-benzoquinone. The association constant for the complexation was evaluated from the ^{1}H-NMR titration for the change in the downfield-shifted amide protons NH_a, the concentration of *p*-benzoquinone being varied from 10 to 200 equimolar amounts. The temperature-dependence of the association constants are collected in Table II, and the satisfactorily linear van't Hoff plot is described in Fig. 4. The thermodynamic parameters, which are evaluated by the van't Hoff equation, are also collected in Table II. The binding ability of **1b** is

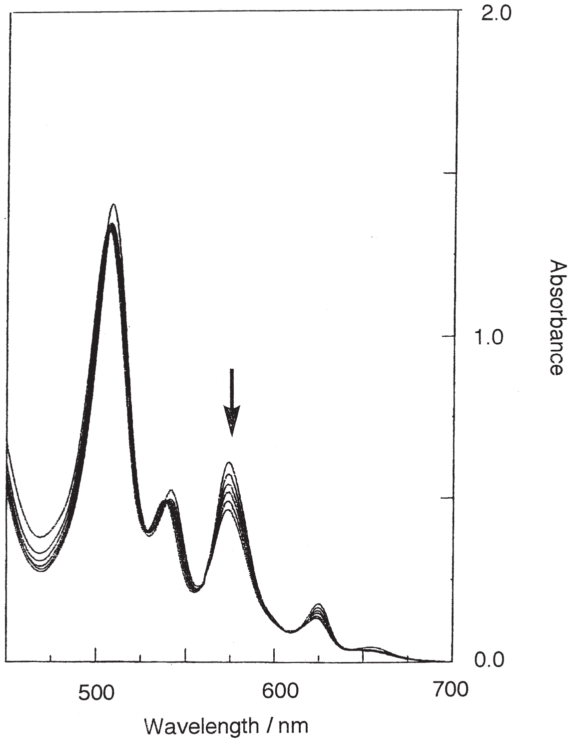

FIGURE 2 UV–Vis spectra change for **1a**-*p*-benzoquinone complexation in toluene at 298 K. [**1a**] = 1.0×10^{-4} M, [*p*-benzoquinone] = 1.0×10^{-4}–2.0×10^{-2} M.

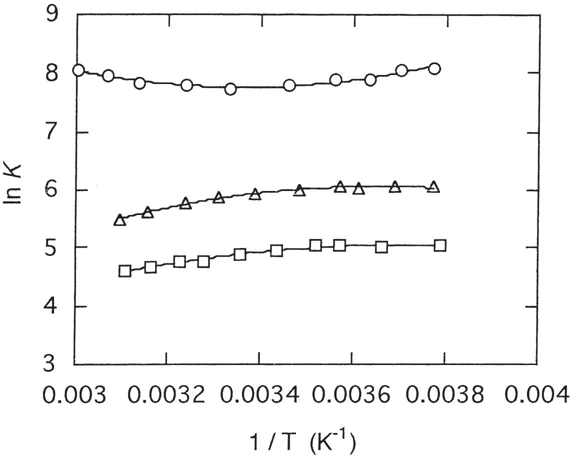

FIGURE 3 Temperature-dependence of the complexation of **1a** with *p*-benzoquinone. (○) in toluene, (△) in toluene/ethyl acetate (9/1) and (□) in toluene/ethyl acetate (4/1).

TABLE I NOE connectivity in porphyrins **1a** and **1b***

Porphyrin	H_c (%)	H_d (%)	H_e (%)
1a	8.4	5.7	0
1b	0	0	0

* *N′*-Phenyl group in **1a** and methyl group of *N′*-ethyl substituent in **1b** were irradiated.The measurements were carried out in $CDCl_3$.

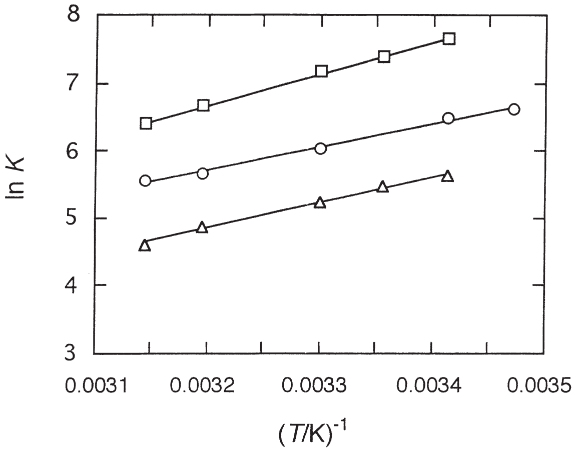

FIGURE 4 van't Hoff plots for the **1b**-quinone complexation in $CDCl_3$. (○) **1b**–**2a** ($r = 0.9965$), (△) **1b**–**2b** ($r = 0.9967$) and (□), **1b**–**2c** ($r = 0.9991$).

superior to that of the analogous 5,15-*cis*-bis(2-pentafluorobenzamidophenyl)porphyrin, its thermodynamic parameters being reported to be $\Delta G^0 = -3.1\,\text{kcal mol}^{-1}$, $\Delta H^0 = -5.4\,\text{kcal mol}^{-1}$ and $T\Delta S^0 = -2.3\,\text{kcal mol}^{-1}$ in toluene-ds–$CDCl_3$ (10:1) [13]. Tetramethoxy-*p*-benzoquinone **2b** caused a slight decrease in the association constants, and reversely, an outstanding increase in the association constants was found in the case of quinone **2c**, having an electron-releasing methyl group. It is realized that the relatively large enthalpy change in the case of **2c** contributes to the large free energy change. This seems to reflect the large hydrogen bondings of NH_a and NH_b of **1b** with the oxygen atoms of **2c**, which have a relatively large negative charge. In contrast, the relatively large entropy change in the complexation of **2b** contributes to the small free energy change, and this seems to come from the steric repulsion of the bulky methoxy groups.

In conclusion, bis(*N′*-phenylureidophenyl)porphyrin **1a** has significant recognizing ability for *p*-benzoquinone through four-point hydrogen bonding, but an unusual temperature-dependence is observed in the complexation. On the other hand, bis(*N′*-ethylureidophenyl)porphyrin **1b** shows a satisfactorily linear van't Hoff plot. Moreover, **1b** recognizes an electron-rich *p*-benzoquinone such as tetramethyl-*p*-benzoquinone more effectively, which is ascribed to the large enthalpy change in the complex.

EXPERIMENTAL

The IR spectra were recorded on a JASCO A-100 spectrometer, and samples were run as potassium bromide pellets. UV–Vis spectra were recorded with a JASCO Ubest-50 spectrometer and measured in toluene. The ^{1}H-NMR spectra were recorded with a

TABLE II Association constant (K, M^{-1}) and thermodynamic parameter for the **1b**-quinone complexation in $CDCl_3$*

	T (K)						ΔG^0_{293} (kcal mol^{-1})	ΔH^0 kcal mol^{-1}	$T\Delta S^0_{293}$ (kcal mol^{-1})
	288	293	298	303	313	318			
1b–2a	7.4×10^2	6.6×10^2	–	4.2×10^2	2.9×10^2	2.6×10^2	−3.8	−6.7	−2.9
1b–2b	–	2.8×10^2	2.4×10^2	1.9×10^2	1.3×10^2	1.0×10^2	−3.3	−7.6	−4.3
1b–2c	–	2.1×10^3	1.6×10^3	1.3×10^3	7.8×10^2	6.0×10^2	−4.5	−9.2	−4.7

*The association constants were determined by ^{1}H-NMR titration, concentration of **1b** being 5.0×10^{-4} M. Errors in K's are ≤10%.

JEOL JNM-LA400 (400 MHz) spectrometer using tetramethylsilane as an internal standard, the chemical shifts being given in δ (ppm) downfield. Samples were taken in $CDCl_3$ unless otherwise noted. The elemental analyses were measured with a Perkin Elmer 2400 II CHN Analyzer. Toluene, dichloromethane and ethyl acetate for spectroscopy were of the highest quality from KOKUSAN Chemical and were used without purification. 5,15-*cis*-bis(2-Aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin and tetramethoxy-*p*-benzoquinone were prepared by the previously reported methods [21,22].

5,15-*cis*-bis[2-(N'-Phenyl)ureidophenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (1a)

A solution of phenylisocyanate (60 mg, 0.50 mmol) in 5 ml of toluene was added dropwise to a solution of 5,15-*cis*-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (100 mg, 0.15 mmol) in 15 ml of toluene. After stirring 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, 3/1) to give 70 mg (52% yield) of **1a**. Further purification was carried out by recrystallization from hexane–chloroform: mp 230°C (dec.); IR 3375 (NH), 1680 (C=O) cm^{-1}; ^{1}H-NMR δ − 2.13 (br s, 2H), 1.77 (t, $J = 7.6$ Hz, 12H), 2.58 (s, 12H), 4.02 (m, 8H), 5.49 (s, 2H), 6.08 (m, 2H), 6.18 (m, 4H), 6.32–6.34 (m, 6H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.81–7.86 (m, 4H), 8.65 (d, $J = 8.3$ Hz, 2H), and 10.25 (s, 2H); $\lambda_{max}(CH_2Cl_2)$ (nm), ($\log \varepsilon$ M^{-1} cm^{-1}) 622.5 (3.21), 571.5 (3.74), 542.5 (3.67), 508.5 (4.07), and 408 (5.18). Found: C, 77.36; H, 6.56; N, 12.49%. Calcd for $C_{58}H_{58}N_8O_2$: C, 77.48; H, 6.50; N, 12.46%.

5,15-*cis*-bis[2-(N'-Ethyl)ureidophenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (1b)

Similar carbamoylation of 5,15-*cis*-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin using ethylisocyanate at 40°C for 12 h afforded 83% yield of **1b**: mp 265°C (dec.) (recrystallized from hexane–ethyl acetate); IR 3350 (NH), 1660 (C=O) cm^{-1}; ^{1}H-NMR δ −2.01 (br s, 2H), 0.38 (m, 6H), 1.76 (t, $J = 7.6$ Hz, 12H), 2.44 (m, 4H), 2.57 (s, 12H), 3.29 (br s, 2H), 4.01–4.04 (m, 8H), 5.75 (s, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.78–7.83 (m, 4H), 8.55 (d, $J = 8.1$ Hz, 2H), and 10.26 (s, 2H); $\lambda_{max}(CH_2Cl_2)$ (nm), ($\log \varepsilon$ M^{-1} cm^{-1}) 624 (3.37), 572 (3.93), 543 (3.85), 508 (4.28), and 408 (5.38). Found: C, 74.58; H, 7.27; N, 13.78%. Calcd for $C_{50}H_{58}N_8O_2$: C, 74.78; H, 7.28; N, 13.95%.

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