# Hydrogen Bonds Not Only Provide a Structural Scaffold to Assemble Donor and Acceptor Moieties of Zinc Porphyrin—Quinone Dyads but Also Control the Photoinduced Electron Transfer to Afford the Long-Lived Charge-Separated States

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A series of zinc porphyrin-quinone linked dyads [**ZnP-CONH-Q**, **ZnP-NHCO-Q**, and **ZnP**-*n*-**Q** (n = 3, 6, 10)] were designed and synthesized to investigate the effects of hydrogen bonds which can not only provide a structural scaffold to assemble donor and acceptor moieties but also control the photoinduced electron-transfer process. In the case of **ZnP-CONH-Q** and **ZnP-NHCO-Q**, the hydrogen bond between the N-H proton and the carbonyl oxygen of Q results in the change in the reduction potential of Q. The strong hydrogen bond between the N-H proton and the carbonyl oxygen of Q<sup>•-</sup> in **ZnP-CONH-Q**<sup>•-</sup>, **ZnP-NHCO-Q**<sup>•-</sup>, and **ZnP-n-Q**<sup>•-</sup> (n = 3, 6, 10) generated by the chemical reduction has been confirmed by the ESR spectra, which exhibit hyperfine coupling constants in agreement those predicted by the density functional calculations. In the case of **ZnP-n-Q** (n = 3, 6, 10), on the other hand, the hydrogen bond between two amide groups provides a structural scaffold to assemble the donor (ZnP) and the acceptor (Q) moiety together with the hydrogen bond between the N-H proton and the carbonyl oxygen of Q, leading to attainment of the charge-separated state with a long lifetime up to a microsecond.

# Introduction

In the bacterial photosynthetic reaction center (bRC) from Rhodobacter (Rb) sphaeroides, an electron is transferred from the singlet excited state of (BChl)<sub>2</sub> via bacteriochlorophyll (BChl) and bacteriopheophytin (Bphe) to the primary quinone  $(Q_A)$  and finally to the secondary quinone  $(Q_B)$ .<sup>1</sup> Although  $Q_A$ and Q<sub>B</sub> are virtually identical, the difference in the hydrogen bonds with the amino acids makes it possible to transfer an electron from  $Q_A$  to  $Q_B$ .<sup>1-3</sup> Hydrogen bonds are formed between  $Q_A$  and the amide groups of D2  $Phe^{261}$  and D2  $His^{214},$  whereas  $Q_B$  is hydrogen-bonded with D1 Ser<sup>264</sup>, D1 His<sup>215</sup>, and the amide group of D1 Phe<sup>265</sup> in photosystem II (PS II).<sup>2b</sup> In this case, the hydrogen bonds can not only provide a structural scaffold but also control the direction of electron transfer (ET).<sup>1-3</sup> Thus, the hydrogen bond has emerged as the paramount synthon for selfassembly to investigate ET dynamics in supramolecular electron donor (D) and acceptor (A) ensembles.<sup>4–10</sup> However, there has so far been no systematic study to elucidate the effects of hydrogen bonds on control of both the structure and redox reactivity of D-A ensembles.

On the other hand, extensive efforts have so far been devoted to elucidating the distance and orientation dependence of ET from electron donors (D) to acceptors (A) in a variety of D–A linked systems.<sup>11–16</sup> In particular, covalently and noncovalently linked porphyrin–quinone dyads constitute one of the most extensively investigated photosynthetic models, in which the fast photoinduced electron transfer from the porphyrin singlet excited state to the quinone occurs to produce the charge-separated (CS) state, mimicking well the photosynthetic electron transfer.<sup>17–24</sup> However, the charge recombination rates of the

charge-separated state of porphyrin—quinone dyads are also fast and the lifetimes are mostly on the order of picoseconds or subnanoseconds in solution,<sup>17–22</sup> in contrast with the long-lived charge-separated state in the natural photosynthesis.<sup>1–3</sup>

We report herein the first systematic study to clarify the effects of hydrogen bonds which can not only provide a structural scaffold to assemble the donor and acceptor moieties but also control the redox reactivity in a series of zinc porphyrin-quinone linked dyads [**ZnP**-**CONH-Q**, **ZnP**-**NHCO-Q**, and **ZnP**-*n*-**Q** (n = 3, 6, 10) shown in Chart 1]. In the case of **ZnP**-**CONH-Q** and **ZnP**-**NHCO-Q**, the hydrogen bond between the N-H proton and the carbonyl oxygen of Q results in the change in the redox potential of Q. In the case of **ZnP**-*n*-**Q** (n = 3, 6, 10), on the other hand, the hydrogen bond between two amide groups provides a structural scaffold to assemble the donor (ZnP) and the acceptor (Q) moiety, leading to attainment of the charge-separated state with a surprisingly long lifetime up to a microsecond.

#### **Experimental Section**

**General Methods.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a JEOL JNM-AL300 NMR spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-DX300 mass spectrometer. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight mass spectra (TOF) were measured on a Kratos Compact MALDI I (Shimadzu). IR spectra of solid samples were recorded on a Thermo Nicolet NEXUS 870 FT-IR instrument using 2 cm<sup>-1</sup> standard resolution at ambient temperature by KBr wafers containing 1% of the sample. IR spectra of samples in CH<sub>2</sub>Cl<sub>2</sub> were measured using an ASI ReactIR 1000 spectrometer (PE-Sciex).

**Materials.** All solvents and chemicals were of reagent grade quality, were obtained commercially, and were used without

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CHART 1



further purification unless otherwise noted. Benzonitrile (PhCN) was purchased from Aldrich Co., USA, and Tokyo Kasei Organic Chemicals, Japan, and purified by successive distillation over  $P_2O_5$ .<sup>25</sup> Tris(2,2'-bipyridyl)ruthenium(III) hexafluorophosphate [Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub>] was prepared according to the literature.<sup>26</sup> Thin-layer chromatography (TLC) and flash column chromatography were performed with Art. 5554 DC-Alufolien Kieselgel 60 F<sub>254</sub> (Merck), and Fujisilicia BW300, respectively. The synthetic procedures of synthetic precursors [H<sub>2</sub>P–CONH–(MeO)<sub>2</sub>Ph, H<sub>2</sub>P–CONMe–(MeO)<sub>2</sub>Ph, H<sub>2</sub>P–NHCO–(MeO)<sub>2</sub>Ph, H<sub>2</sub>P–*n*-COOH (n = 3, 6, 10), and H<sub>2</sub>P–n-(MeO)<sub>2</sub>Ph (n = 3, 6, 10)] and reference compounds (ZnP–NHCO-ref, ZnP–CONH-ref) are similar to those in our previous reports.<sup>27</sup> The synthetic details and characterizations are described in Supporting Information (S1–S7).

ZnP-CONH-Q. A dichloromethane solution of boron tribromide (BBr<sub>3</sub>; 0.26 mmol) was added to a dichloromethane solution (30 mL) of H<sub>2</sub>P-CONH-(MeO)<sub>2</sub>Ph (2) (140 mg, 0.13 mmol) at 0 °C under argon. After the solution was stirred at 0 °C for 3 h, BBr3 was quenched by adding water and saturated aqueous sodium hydrogen carbonate. The organic phase was dried over sodium sulfate and filtrated. After removal of solvent, the residue was purified by column chromatography (SiO<sub>2</sub>, chloroform). The purified compound (H<sub>2</sub>P-CONH-(HO)<sub>2</sub>Ph) was further stirred under Ar with PbO<sub>2</sub> (250 mg) in dichloromethane (30 mL) at room temperature for 2 h. PbO<sub>2</sub> was removed carefully by suction filtration. After removal of solvent, the residue was purified by column chromatography (SiO<sub>2</sub>, chloroform). The H<sub>2</sub>P-CONH-Q was refluxed in dichloromethane with a methanolic solution of zinc acetate (Zn(OAc)<sub>2</sub>). After water was added to the solution, the organic phase was dried over sodium sulfate and filtrated. After removal of solvent, the column chromatography on silica gel with chloroform as the eluent and subsequent recrystallization from chloroform and hexane gave ZnP-CONH-Q as a deep redpurple solid. (45 mg, 0.039 mmol, 30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.17 (s, 1H(NH)), 9.02 (d, 1H(Ph), J = 5 Hz), 9.01 (s, 8H( $\beta$ )), 8.87 (d, 1H(Ph), J = 5 Hz), 8.41 (d, 1H(Ph), J =8 Hz), 8.27 (d, 1H(Ph), J = 8 Hz), 8.09 (m, 6H(Ar)), 7.94 (m, 1H(Q)), 7.80 (m, 3H(Ar)), 6.90 (m, 2H(Q)), 1.53 (s, 54H-('Bu)). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  188 (Q, C=O), 183 (Q, C=O), 166 (amide, C=O), 148 (ring, C-N). UV-vis (CHCl<sub>3</sub>, nm): 426, 553, 597. TOF-MS: *m*/*z* 1163.9. FAB-MS (FAB+): *m*/*z* 1164.4. HR-MS (FAB+): *m*/*z* 1163.5621 (calcd for C<sub>75</sub>H<sub>81</sub>N<sub>5</sub>O<sub>3</sub>Zn, 1163.5644). FT-IR (KBr): 1701 (amide, C=O), 1668 (C=O), 1651 (C=O), 1593 (alkene), 1493 (N-H). FT-IR (CH<sub>2</sub>Cl<sub>2</sub>): 1701 (amide, C=O), 1669 (C=O), 1652 (C=O), 1593 (alkene), 1498 (N-H). TLC (SiO<sub>2</sub>): *R*<sub>f</sub> = 0.70 in CHCl<sub>3</sub>.

ZnP-CONMe-Q. The same synthetic procedures as those from H<sub>2</sub>P-CONH-(MeO)<sub>2</sub>Ph to ZnP-CONH-Q were employed for preparation of ZnP-CONMe-Q using H<sub>2</sub>P-CONMe-(MeO)<sub>2</sub>Q as the precursor. The column chromatography for purification of  $H_2P$ -CONMe-Q(OH)<sub>2</sub> was performed using chloroform:MeOH = 50:1 in silica gel. The column chromatography on silica gel with chloroform as the eluent and subsequent recrystallization from chloroform and hexane gave ZnP-CONMe-Q as a deep red-purple solid (131 mg, 0.11 mmol, 61%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.00 (s, 8H( $\beta$ )), 8.75 (d, 1H(Ph), J = 8 Hz), 8.22 (d, 1H(Ph), J = 8 Hz), 8.07 (m, 6H(Ar)), 7.87 (d, 2H(Ph), J = 8 Hz), 7.78 (m, 1H(Q)), 7.77 (m, 3H(Ar)), 6.83 (m, 2H(Q)), 3.60 (s, 3H(N-Me)) 1.53 (s, 54H(<sup>t</sup>Bu)). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  187 (Q, C=O), 182 (Q, C=O), 172 (amide, C=O), 150.6 (ring, C-N). UV-vis (CHCl<sub>3</sub>, nm): 425, 552, 596. TOF-MS: *m*/*z* 1177.3. FAB-MS (FAB+): *m*/*z* 1178.5. HR-MS (FAB+): *m/z* 1177.5796 (calcd for C<sub>76</sub>H<sub>83</sub>N<sub>5</sub>O<sub>3</sub>Zn, 1177.5801). FT-IR (KBr): 1678 (amide, C=O), 1675 (Q, C=O), 1653 (Q, C=O), 1592 (alkene), 1338 (N-Me). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>): 1682 (amide, C=O), 1680 (Q, C=O), 1653 (Q, C=O), 1592 (alkene), 1340 (N-Me). TLC:  $R_f = 0.50$  in CHCl<sub>3</sub>.

**ZnP**–**NHCO-Q.** This compound was prepared in the same manner as **ZnP**–**CONH-Q**. The residue was purified by column chromatography (SiO<sub>2</sub>, chloroform:ethyl acetate = 9:1). **ZnP**–**NHCO-Q** was obtained as a deep red-purple solid (80 mg, 0.069 mmol, 38%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  11.5 (s, 1H(NH)), 9.00 (s, 8H( $\beta$ )), 8.28 (d, 2H(Ph), J = 8 Hz), 8.09 (m, 6H(Ar)), 8.03 (d, 2H(Ph), J = 8 Hz), 7.78 (s, 3H(Ar)), 7.53

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(s, 1H(Q)), 6.97 (s, 2H(Q)), 1.53 (s, 54H('Bu)). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  186 (Q, C=O), 182 (Q, C=O), 163 (amide, C=O), 148 (ring, C-N). UV-vis (CHCl<sub>3</sub>, nm): 425, 552, 595. TOF-MS: m/z 1164.7. FAB-MS (FAB+): m/z 1164.6. HR-MS (FAB+): m/z 1163.5647 (calcd for C<sub>75</sub>H<sub>81</sub>N<sub>5</sub>O<sub>3</sub>-Zn, 1163.5644). FT-IR (KBr): 1697 (amide, C=O), 1680 (C=O), 1659 (C=O), 1591 (alkene), 1530 (N-H). FT-IR (CH<sub>2</sub>Cl<sub>2</sub>): 1693 (amide, C=O), 1678 (C=O), 1663 (C=O), 1592 (alkene), 1536 (N-H). TLC (SiO<sub>2</sub>):  $R_f = 0.26$  in CHCl<sub>3</sub>.

ZnP-3-Q. This compound was prepared in the same manner as **ZnP-CONH-Q** using H<sub>2</sub>P-3-(MeO)<sub>2</sub>Ph as the precursor. The column chromatography for purification was performed using chloroform: MeOH = 95:5 in silica gel. Removal of solvent gave ZnP-3-Q as a deep red-purple solid. (100 mg, 0.080 mmol, 73%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.00  $(s, 8H(\beta)), 8.95 (m, 2H(NH)), 8.19 (d, 2H(Ph)), J = 8 Hz), 8.09$ (m, 6H(Ar)), 7.92 (d, 2H(Ph), J = 8 Hz), 7.78 (m, 3H(Ar)), 7.71 (m, 1H(Q)), 6.79 (m, 2H(Q)), 2.72 (t, 2H(-CH<sub>2</sub>-CONHQ), J = 7 Hz), 2.67 (t, 2H(NHCO-CH<sub>2</sub>-), J = 7 Hz), 1.53 (s, 54H(<sup>t</sup>Bu)), 1.25 (m, 2H(-CH<sub>2</sub>-)). UV-vis (CHCl<sub>3</sub>, nm): 425, 552, 596. TOF-MS: m/z 1248.9. FAB-MS (FAB+): m/z 1250.6. FT-IR (KBr): 1722 (amide, C=O), 1703 (amide, C=O), 1666 (Q, C=O), 1658 (Q, C=O), 1592 (alkene), 1525 (N-H), 1497 (N-H). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>): 1725 (amide, C=O), 1677 (amide, C=O), 1661 (Q, C=O), 1637 (Q, C=O), 1592 (alkene), 1535 (N-H), 1494 (N-H). TLC:  $R_f = 0.30$  in CHCl<sub>3</sub>.

ZnP-6-Q. This compound was also prepared in the same manner as ZnP-3-Q. The column chromatography for purification was performed using chloroform in silica gel. Removal of solvent gave ZnP-6-Q as a deep red-purple solid (45 mg, 0.035 mmol, 29%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.92 (s, 8H(β)), 8.88 (s, 1H(NH)), 8.87 (s, 1H(NH)), 8.22 (d, 2H(Ph), J = 8 Hz), 8.01 (m, 6H(Ar)), 7.92 (m, 1H(Q)), 7.82 (d, 2H(Ph), J = 8 Hz), 7.71 (m, 3H(Ar)), 6.67 (m, 2H(Q)), 2.48 (m, 2H(NHCO-CH<sub>2</sub>-)), 2.37 (m, 2H(-CH<sub>2</sub>-CONHQ)), 1.48 (s, 54H(<sup>t</sup>Bu)), 1.25 (m, 8H(-CH<sub>2</sub>-)). UVvis (PhCN, nm): 431, 560, 601. TOF-MS: m/z 1291.0. FAB-MS (FAB+): m/z 1290.5. FT-IR (KBr): 1717 (amide, C=O), 1699 (amide, C=O), 1667 (Q, C=O), 1653 (Q, C=O), 1592 (alkene), 1524 (N-H), 1498 (N-H). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>): 1727 (amide, C=O), 1713 (amide, C=O), 1672 (Q, C=O), 1654 (Q, C=O), 1590 (alkene), 1512 (N-H), 1501 (N-H). TLC:  $R_f =$ 0.50 in CHCl<sub>3</sub>.

ZnP-10-Q. This compound was also prepared in the same manner as ZnP-3-Q. The column chromatography on silica gel with chloroform gave ZnP-10-Q as a deep red-purple solid. (40 mg, 0.030 mmol, 18%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.00 (m, 8H( $\beta$ )), 8.98 (s, 1H(NH)), 8.97 (s, 1H(NH)), 8.18 (d, 2H(Ph), J = 8 Hz), 8.08 (m, 6H(Ar)), 7.97 (m, 1H(Q)), 7.91 (d, 2H(Ph), J = 8 Hz), 7.78 (m, 3H(Ar)), 6.75 (m, 2H(Q)), 2.42 (t,  $2H(NHCO-CH_2-)$ , J = 7 Hz), 2.28 (t,  $2H(NHCO-CH_2-), J = 7 Hz), 1.52 (s, 54H(^tBu)), 1.25 (m,$ 16H(-CH<sub>2</sub>-)). UV-vis (CHCl<sub>3</sub>, nm): 426, 559, 600. TOF-MS: *m*/*z* 1347.0. FAB-MS (FAB+): *m*/*z* 1346.7. FT-IR (KBr): 1720 (amide, C=O), 1700 (amide, C=O), 1661 (O, C=O), 1652 (Q, C=O), 1592 (alkene), 1540 (N-H), 1508 (N-H). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>): 1732 (amide, C=O), 1718 (amide, C=O), 1685 (Q, C=O), 1661 (Q, C=O), 1592 (alkene), 1508 (N-H), 1500 (N-H). TLC:  $R_f = 0.55$  in CHCl<sub>3</sub>.

**Electrochemical Measurements.** Electrochemical measurements were performed on a BAS 100W electrochemical analyzer in deaerated PhCN containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) as supporting electrolyte at 298 K. A conventional three-electrode

cell was used with a platinum working electrode (surface area of 0.3 mm<sup>2</sup>) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO<sub>3</sub> (0.01 M) reference electrode. All potentials (vs Ag/Ag<sup>+</sup>) were converted to values vs SCE by adding 0.29 V.<sup>28</sup> All electrochemical measurements were carried out under an atmospheric pressure of Ar.

ESR Measurements. The radical anions, ZnP-CONH-Q<sup>•-</sup>, ZnP-CONMe-Q<sup>•-</sup>, ZnP-NHCO-Q<sup>•-</sup>, and ZnP-*n*-Q<sup>•-</sup>, were produced by the chemical reduction with tetramethylsemiquinone radical anion  $(1.0 \times 10^{-5} \text{ M})$ , which was obtained by the reaction between hydroquinone and *p*-benzoquinone in the presence of tetramethylammonium hydroxide.29 The radical cation, ZnP<sup>•+</sup>-CONH-Q, was generated by the chemical oxidation with  $Ru(bpy)_3^{3+}$ . A solution containing the radical anion or the radical cation was transferred to an ESR tube under an atmospheric pressure of Ar. The ESR spectra were recorded on a JEOL X-band spectrometer (JES-RE1XE) with a quartz ESR tube (1.2 mm i.d.). The ESR spectra were measured under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signalto-noise (S/N) ratio of the observed spectra. The g values were calibrated with an  $Mn^{2+}$  marker, and the hyperfine coupling (hfc) constants were determined by computer simulation using Calleo ESR Version 1.2 program coded by Calleo Scientific on an Apple Macintosh personal computer. For the detection of the charge-separated state, a quartz ESR tube (internal diameter, 4.5 mm) containing a deaerated PhCN solution of **ZnP-10-Q** dyad (5.0  $\times$  10<sup>-5</sup> M) was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg lamp (Ushio-USH1005D) through an aqueous filter at low temperatures. The internal diameter of the ESR tube is 4.5 mm, which is small enough to fill the ESR cavity but large enough to obtain good signal-to-noise ratios during the ESR measurements under photoirradiation. The ESR spectra in frozen PhCN were measured under nonsaturating microwave power conditions at 173 K with a JEOL X-band spectrometer (JESRE1XE) using an attached variable-temperature apparatus.

**Fluorescence Quenching.** Fluorescence measurements of **ZnP**–*n*-**Q**, **ZnP**–**NHCO-ref**, and **ZnP**–**CONH-ref** were carried out on a SHIMADZU spectrofluorophotometer (RF-5000). The excitation wavelength of ZnP was set at  $\lambda = 560$  nm in MeCN, PhCN, CH<sub>2</sub>Cl<sub>2</sub>, tetrahydrofuran (THF), and toluene. Typically, CH<sub>2</sub>Cl<sub>2</sub> and THF solutions were deaerated by five freeze–pump–thaw cycles. MeCN, PhCN, and toluene solutions were deaerated by argon purging for 15 min prior to the measurements. Time-resolved fluorescence spectra were measured by a Photon Technology International GL-3300 with a Photon Technology International GL-3300 with a four-channel digital delay/pulse generator (Stanford Research System Inc. DG535) and a motor driver (Photon Technology MD-5020).

The excitation wavelength was 431 nm using POPOP (Wako Pure Chemical Ind. Ltd., Japan) as a dye. The fluorescence lifetimes of ZnP–CONH-ref were determined as  $\tau = 2.04$  ns in MeCN,  $\tau = 2.04$  ns in PhCN,  $\tau = 1.88$  ns in CH<sub>2</sub>Cl<sub>2</sub>,  $\tau = 2.10$  ns in THF, and  $\tau = 2.15$  ns in toluene by an exponential curve fit of the fluorescence decay using a microcomputer. The fluorescence lifetimes of ZnP–NHCO-ref were also determined as  $\tau = 1.77$  ns in MeCN,  $\tau = 1.91$  ns in PhCN,  $\tau = 1.81$  ns in CH<sub>2</sub>Cl<sub>2</sub>,  $\tau = 2.13$  ns in THF, and  $\tau = 2.06$  ns in toluene. All samples were excited at 431 nm

TABLE 1: Edge-to-Edge Distances ( $R_{ee}$ ) and Center-to-Center Distances ( $R_{cc}$ ), Redox Potentials, and Driving Forces of Electron Transfer ( $-\Delta G_{ET}$ ,  $-\Delta G_{BET}$ )

duad	D a Å	$\mathbf{p} = a b \mathbf{\hat{\lambda}}$	D a.c. Å	D a Å	$E_{\rm ox},^{d} \rm V$	$E_{\rm red},^{d} V$	$-\Lambda C$ e $\gamma V$	$-\Lambda C$ $aV$
uyau	$\Lambda_{ee}$ ," A	$\Lambda_{ee}$ , $A$	$\Lambda_{ee}$ , $\Lambda$	$\Lambda_{cc}$ ," A	ZIIP 7/ZIIP	Q/Q	$-\Delta G_{\rm ET}$ , ev	$-\Delta G_{\text{BET}}, ev$
ZnP-CONH-Q	3.78			12.66	0.78	-0.36	0.91	1.14
	(3.83)			(12.59)				
	(2102)			(				
ZnP-CONMe-O	3 78			12.66	0.77	-0.46	0.82	1 23
	(2.78)			(12.60)	0.77	0.10	0.02	1.25
	(3.78)			(12.04)				
7nD - NUCOO	2.91			12.66	0.77	0.17	1 11	0.04
ZIIF - MICO-Q	3.01			12.00	0.77	-0.17	1.11	0.94
	(3.80)			(12.85)				
					0.40	0.15		
FC-NHCO-Q					0.48	-0.15		
					(Fc <sup>+</sup> /Fc)			
Fc-NMeCO-O					0.52	-0.36		
-					$(Fc^{+}/Fc)$			
7nP-3-0	10.74	8 26		$12 20^{b}$	0.79	-0.40	0.86	1 10
Zili J-Q	10.74	(9.19)		(12.20)	0.79	-0.40	0.00	1.17
		(0.10)		(12.34)				
7nD-60	15 21	0.01	(1.26)	12 51b	0.70	0.29	0.88	1 17
ZIIP=0-Q	15.51	0.21	(4.20)	12.31	0.79	-0.58	0.00	1.1/
				$(12.44)^c$				
<b>Z D</b> 10.0	01.47	0.07	(1.20)	10.01h	0.70	0.07	0.00	1.1.6
ZnP=10-Q	21.47	8.27	(4.29)	10.81	0.79	-0.37	0.89	1.16
				$(10.82)^{c}$				

<sup>*a*</sup> Estimated from optimized structure (B3LYP/6-31G(d) or BLYP/6-31G(d)). The values in parantheses are those of Q<sup>•-</sup>. <sup>*b*</sup> Type A structure. <sup>*c*</sup> Type B structure. <sup>*d*</sup> vs SCE in the presence of 0.1 M TBAPF<sub>6</sub> in PhCN. <sup>*e*</sup> Photoinduced ET from <sup>1</sup>ZnP\* to Q in PhCN.



with a repetition rate of 10 Hz (pulse width, 3-4 ns), and the fluorescence signal was analyzed after passing through a monochromator set at the peak emission of the corresponding sample.

**Time-Resolved Absorption Measurements.** Nanosecond transient absorption measurements were carried out using a Panther OPO pumped by a Nd:YAG laser (Continuum, SLII-10, 4–6 ns full width at half-maximum (fwhm)) at 428–435 nm with the power of 10 mJ as an excitation source. The solution was deoxygenated by argon purging for 10 min prior to the measurements. The quantum yields of the charge-separated states of ZnP–*n*-Q (n = 3, 6, 10) were determined using a comparative method.<sup>30</sup> In particular, the strong zinc tetraphenylporphyrin triplet–triplet absorption (470 nm = 74 000 M<sup>-1</sup> cm<sup>-1</sup>;  $\Phi_{\rm T} = 0.88$ )<sup>30</sup> served as a probe to determine the quantum yields for formation of the CS state in PhCN.

**Theoretical Calculations.** Density-functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the BeckeLYP and 6-31G(d) basis set with unrestricted Hatree–Fock (UHF) formalism, Becke3LYP functional, and 6-31G(d) basis set<sup>31</sup> or BeckeLYP and 6-31G(d) basis set<sup>31</sup> with the restricted Hatree–Fock (RHF) formalism as implemented in the Gaussian 98 program.<sup>32</sup> Subsequently, the harmonic vibrational frequencies were calculated, where calculated frequencies have been scaled to avoid systematic errors.<sup>33,34</sup> The <sup>13</sup>C magnetic shielding tensors ( $\chi$ ) of DFT-optimized structures of Ph–CONH-Q, Ph–CONMe-Q, and Ph–NHCO-Q compounds, and tetramethylsilane (TMS) as reference, were obtained following the gauge-including atomic orbital (GIAO) approach at the DFT level.<sup>35</sup>

The NMR parameters for TMS were calculated and used as the reference compound in order to compare isotropic shielding with the experimentally observed chemical shifts. A natural population analysis<sup>36</sup> (NPA) was used to ascertain the location of the "extra" electron density in the radical anion species; geometries were optimized using BLYP at the 6-31G(d) level. The energy difference between the optimized structures of the A type and B type in the radical anion (**Ph**–**6**-**Q**<sup>•–</sup>, **Ph**–**10**-**Q**<sup>•–</sup>) was evaluated on the basis of BLYP/6-31G calculations with the ROHF formalism.

## **Results and Discussion**

Synthesis. The synthesis and characterizations of ZnP– CONH-Q, ZnP–CONMe-Q, ZnP–NHCO-Q, and ZnP–n-Q (n = 3, 6, 10) dyads, and ZnP–CONH-ref and ZnP–NHCOref are described in detail in Experimental Section and Supporting Information S1–S7.

Hydrogen Bond to Stabilize Q<sup>•-</sup> of ZnP–Q Dyads. The cyclic voltammograms of ZnP–CONH-Q exhibited two reversible one-electron redox couples of two redox-active moieties at 0.78 V for the ZnP<sup>•+</sup>/ZnP couple and -0.36 V for the Q/Q<sup>•-</sup> couple (vs SCE), as shown in Table 1, where similar one-electron redox potentials of the ZnP<sup>++</sup>/ZnP and Q/Q<sup>•-</sup> couples are obtained for ZnP–*n*-Q (n = 3, 6, 10). When the amide proton of ZnP–CONH-Q is replaced by the methyl group in ZnP–CONMe-Q, the one-electron reduction potential of Q ( $E^0_{red}$  vs SCE = -0.46 V) is negatively shifted as compared with the  $E^0_{red}$  value of Q in ZnP–CONH-Q, whereas the one-electron oxidation potential ( $E^0_{ox}$  vs SCE = 0.77 V) of the ZnP moiety in ZnP–CONMe-Q is virtually the same as the  $E^0_{ox}$ 



Figure 1. ESR spectra and the computer simulation spectra of (a)  $ZnP-CONH-Q^{--}$  and (b)  $ZnP-CONMe-Q^{--}$  ( $1.0 \times 10^{-5}$  M) in deaerated CH<sub>2</sub>Cl<sub>2</sub> at 263 K, and the optimized structures of (a) Ph-CONH-Q<sup>--</sup>, (b) Ph-CONMe-Q<sup>--</sup>, and (c) Ph-NHCO-Q<sup>--</sup> by Gaussian 98 with UBLYP/ 6-31G(d) basis set [the values (G) in parentheses are provided by Gaussian 98 with UBLYP/6-31G(d) basis set].

value (0.78 V) of **ZnP–CONH-Q**. Similarly the replacement of the amide proton by the methyl group results in a negative shift of the  $E^{0}_{red}$  value of Q in the ferrocene–quinone dyad: **Fc–NMeCO-Q** (-0.38 V) as compared with the  $E^{0}_{red}$  values of **Fc–NHCO-Q** (-0.15 V) and **ZnP–NHCO-Q** (-0.17 V), where the ZnP moiety is replaced by Fc. Such a negative shift of the  $E^{0}_{red}$  value of Q by the replacement of the amide proton by the methyl group indicates that Q<sup>•–</sup> is stabilized by formation of a hydrogen bond between the amide proton and the carbonyl oxygen of Q<sup>•–</sup>. The larger potential shift (0.19 eV) in **ZnP– NHCO-Q** by the replacement of the amide proton by the methyl group than that (0.10 eV) in **ZnP–CONH-Q** suggests that the hydrogen bond in **ZnP–NHCO-Q<sup>•–</sup>** is stronger than that in **ZnP–CONH-Q<sup>•–</sup>**.

The hydrogen-bonded Q<sup>•-</sup> species are detected by ESR. ZnP-CONH-Q<sup>•-</sup>, ZnP-CONMe-Q<sup>•-</sup>, and ZnP-NHCO-Q<sup>•-</sup> were produced by the electron-transfer reduction of ZnP-CONH-Q, ZnP-CONMe-Q, and ZnP-NHCO-Q by semiquinone radical anion in CH<sub>2</sub>Cl<sub>2</sub> at 298 K (see Experimental Section). Since the  $E^{0}_{red}$  value of *p*-benzoquinone (-0.50 V vs SCE)<sup>37</sup> is more negative that the  $E^{0}_{red}$  values of the Q moiety of the dyads, the electron transfer is thermodynamically favorable to produce Q<sup>•-</sup> in the dyads. The ESR spectra of **ZnP**–**CONH-Q**<sup>•-</sup>, **ZnP**–**CONMe-Q**<sup>•-</sup>, and **ZnP**–**NHCO-Q**<sup>•-</sup> are shown in Figure 1 together with the computer simulation spectra. The *g* value is determined as *g* = 2.0039, 2.0041, and 2.0048, respectively. The *g* value (2.0041) of **ZnP**–**CONMe-Q**<sup>•-</sup> is larger than the value (2.0039) in **ZnP**–**CONH-Q**<sup>•-</sup>. This indicates that more spin is localized on the oxygen atom which has a large spin–orbit coupling constant in **ZnP**–**CONHe-Q**<sup>•-</sup>.

The hyperfine coupling constants (*hfc*) determined by the computer simulation are shown in Figure 1. The *hfc* values of three protons of the Q<sup>•-</sup> moiety in **ZnP**–**CONH**-Q<sup>•-</sup> (3.80, 2.10, and 1.62 G) and in **ZnP**–**NHCO**-Q<sup>•-</sup> (4.30, 1.95, and 1.80 G) are highly inequivalent, whereas those in **ZnP**–**CONMe**-Q<sup>•-</sup> (2.62, 2.55, and 2.40 G) are rather equivalent.<sup>38</sup> The *hfc* values can be largely reproduced by the Gaussian 98



Figure 2. Optimized structures and selected bond lengths of (a) Ph-CONH-Q, (b) Ph-CONMe-Q, (c) Ph-NHCO-Q, (d) Ph-3-Q, (e) Ph-6-Q (type A), (f) Ph-6-Q (type B), (g) Ph-10-Q (type A), and (h) Ph-10-Q (type B) calculated by a DFT method with Gaussian 98 [B3LYP/6-31G(d) basis set for a-c and BLYP/6-31G(d) basis set for d-h].

calculation with the UBLYP/6-31G(d) basis set as indicated by the calculated hfc values in parentheses in Figure 1.<sup>38</sup> In these calculations, the porphyrin moiety is replaced by the phenyl group, since the porphyrin moiety is expected to have no significant effect on the structure and spin densities of the Q moiety. The comparison of the observed hfc values with the calculated values indicates that the formation of hydrogen bond in ZnP-CONH-Q<sup>•-</sup> and ZnP-NHCO-Q<sup>•-</sup> results in the less spin densities on the carbons adjacent to the carbonyl group of the Q<sup>•-</sup> moiety of which forms the hydrogen bond with the NH proton as compared with those adjacent to the other carbonyl group. This indicates that the negative charge is more localized on the carbonyl oxygen which forms the hydrogen bond with the N-H proton due to the electrostatic stabilization, when the spin is more localized on the carbons adjacent to the other carbonyl group. The DFT calculations also support the charge localization due to the formation of the hydrogen bond: the negative charge density of the hydrogen bonded carbonyl oxygen (-0.216 in ZnP-CONH-Q<sup>--</sup> and -0.222 in ZnP-**NHCO-Q**<sup>•-</sup>) is significantly larger than that of the other carbonyl oxygen (-0.171 in ZnP-CONH-Q<sup>•-</sup> and -0.143 in ZnP-NHCO-Q<sup>•-</sup>), whereas the difference in the narrative charge densities between the two carbonyl oxygens in ZnP-**CONMe-Q**<sup> $\bullet$ -</sup> becomes smaller (-0.199 and -0.168).

The optimized geometries of **Ph**–**CONH**-**Q**<sup>•–</sup>, **Ph**–**CONMe**-**Q**<sup>•–</sup>, and **Ph**–**NHCO**-**Q**<sup>•–</sup> are also shown in Figure 1. The O–H distances between the oxygen atom of **Q**<sup>•–</sup> and the amide hydrogen in Figure 1 are 1.97 Å in **Ph**–**CONH**-**Q**<sup>•–</sup> and 1.70 Å in **Ph**–**NHCO**-**Q**<sup>•–</sup>, which are much shorter than the calculated distances in the neutral state: **Ph**-**CONH**-**Q**, 2.10 Å; **Ph**–**NHCO**-**Q**, 1.87 Å, respectively (Figure 2a,c) by a DFT method with Gaussian 98 (B3LYP/6-31G(d) basis set). In accordance with such a decrease in the O–H hydrogen bond

distance, the C–O bond length of the hydrogen bonded carbonyl group in **Ph**–**NHCO-Q**<sup>•-</sup> (1.291 Å) becomes longer as compared with the distance in **Ph**–**CONH-Q**<sup>•-</sup> (1.285 Å) because of the weakening of the C–O bond by the stronger hydrogen bonding with the amide proton in **Ph**–**NHCO-Q**<sup>•-</sup> relative to **Ph**–**CONH-Q**<sup>•-</sup>. This is consistent with the larger potential shift (0.19 eV) in **ZnP**–**NHCO-Q** by the replacement of the amide proton by the methyl group than that (0.10 eV) in **ZnP**–**CONH-Q**<sup>•-</sup> (1.285 Å) also becomes the longer **C–O bond length** in the position of Q1 (see Chart 1) in **Ph**–**CONH-Q**<sup>•-</sup> (1.282 Å) due to formation of hydrogen bond in **Ph**–**CONH-Q**<sup>•-</sup>.

Formation of the much weaker hydrogen bond in the neutral state (Q) than in the reduced state (Q<sup>•-</sup>) was examined on the basis of wavenumbers of C=O stretching vibration in the position of Q1 in Chart 1 and the <sup>13</sup>C chemical shifts of the C=O of Q in the <sup>13</sup>C NMR spectra. The wavenumbers for C=O in the position of Q1 (Chart 1) in KBr as well as in CH<sub>2</sub>-Cl<sub>2</sub> solution (see Experimental Section) become larger in the following sequence: ZnP-NHCO-Q (1659 cm<sup>-1</sup> in KBr, 1663 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>), **ZnP-CONH-Q** (1668 cm<sup>-1</sup> in KBr, 1669 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>), and **ZnP–CONMe-Q** (1675 cm<sup>-1</sup> in KBr, 1680 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>); see Supporting Information S10. The chemical shifts for C=O carbons of the <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> (see S11) become larger in the following sequence: ZnP-CONMe-Q (182.1), ZnP-CONH-Q (183.0), and ZnP-NHCO-Q (185.6) in accordance with weakening of the C=O (Q1) bond strength as indicated in the IR spectra. The DFT calculations of Ph-CONH-Q, Ph-CONMe-Q, and Ph-NHCO-Q, with Gaussian 98 (B3LYP/6-31G(d) basis set), reproduce well the experimental wavenumbers and chemical



Figure 3. ESR spectra and the computer simulation spectra of (a)  $\mathbf{ZnP-3-Q^{--}}$ , (b)  $\mathbf{ZnP-6-Q^{--}}$ , and (c)  $\mathbf{ZnP-10-Q^{--}}$  ( $1.0 \times 10^{-5}$  M) in deaerated CH<sub>2</sub>Cl<sub>2</sub> at 258 K and optimized structures of (a)  $\mathbf{Ph-3-Q^{--}}$ , (b)  $\mathbf{Ph-6-Q^{--}}$ , and (c)  $\mathbf{Ph-10-Q^{--}}$  by Gaussian 98 with UBLYP/6-31G(d) basis set [the values (G) in parentheses are provided by Gaussian 98 with UBLYP/6-31G(d) basis set].

shifts in <sup>13</sup>C NMR (S10, S11). The estimated distance of C=O (Q1) bond becomes longer in the same order as IR spectra in KBr and CH<sub>2</sub>Cl<sub>2</sub> solution: **Ph**-**NHCO-Q** (1.232 Å), **Ph**-**CONH-Q** (1.228 Å), and **Ph**-**CONMe-Q** (1.225 Å) as shown in Figure 2a-c.

Hydrogen Bond Providing a Structural Scaffold To Assemble the Donor and Acceptor Moieties in ZnP-n-QDyads. The optimized structures of ZnP-n-Q (n = 3, 6, 10) are calculated using Gaussian 98 with BLYP/6-31G(d) basis set as shown in Figure 2d-h.<sup>39</sup> Ph-6-Q and Ph-10-Q afford two kinds of optimized structures: one is the same type as Ph-3-Q (type A); the other is the hydrogen-bonded structure of amide hydrogen with carbonyl oxygen in the Q<sup>•-</sup> moiety (type B). The type A of **Ph-6-Q** and **Ph-10-Q** is 12.5 and 13.2 kJ mol<sup>-1</sup> more stable than the type B. The O-H distance between the oxygen atom of Q and the amide proton shown in Figure 2d-h is 2.10 Å in the type A of **Ph-n-Q** irrespective of the difference in the number of methylene spacer (n = 3, 6, 10), which is the same as that (2.10 Å) in **Ph-CONH-Q**. The other O-H distance between two amide groups is 2.13 Å for **Ph-3-Q**, 2.09 Å for **Ph-6-Q**, and 2.16 Å for **Ph-10-Q**. The observed wavenumbers for C=O and N-H bonds both in KBr and in CH<sub>2</sub>Cl<sub>2</sub> for C=O and N-H bonds (S12) are virtually the same irrespective of the difference in methylene numbers

in accordance with the optimized structures in Figure 2. The two weak interactions (hydrogen bonds) between C=O bonds and N-H bonds may be formed.

The ESR spectra of ZnP-3-Q<sup>•-</sup>, ZnP-6-Q<sup>•-</sup>, and ZnP-**10-Q**<sup>•-</sup>  $(1.0 \times 10^{-5} \text{ M})$  are shown in Figure 3 together with the computer simulation spectra. The g values are determined as 2.0039, 2.0038, and 2.0037, respectively. At first glance, the hyperfine structure of **ZnP-3-Q**<sup>•-</sup> (five main lines) is quite different from those of ZnP-6-Q<sup>•-</sup> and ZnP-10-Q<sup>•-</sup> (eight main lines). The hyperfine coupling constants (*hfc*) are determined by the computer simulation as shown in Figure 3. The largest *hfc* value in the  $Q^{\bullet-}$  moiety of **ZnP-3-Q** $^{\bullet-}$  (3.36 G) is significantly smaller than that of ZnP-6-Q<sup>•-</sup> (4.70 G) and ZnP-10-Q<sup>-</sup> (4.30 G). This indicates that the hydrogen-bonded structure of ZnP-3-Q<sup>•-</sup> is different from that of ZnP-6-Q<sup>•-</sup> and **ZnP-10-Q**<sup>•-</sup> as supported by the DFT calculations. The most stable structure of Ph-3-Q<sup>•-</sup> calculated by a DFT method with Gaussian 98 (UBLYP/6-31G(d) basis set) contains two hydrogen bonds between amide protons and carbonyl oxygens, as shown in Figure 3 where the observed hfc values are wellreproduced by the calculated values using the optimized structure. The O-H distances between the oxygen atom of Q<sup>•-</sup> and the amide hydrogen in Figure 3 are 1.87 and 1.95 Å in Ph-3-Q<sup>•-</sup>, which are much shorter than the calculated distances in the neutral form: Ph-3-Q (2.13 and 2.10 Å) in Figure 2. In contrast to the case of the neutral form of Ph-6-Q and Ph-10-Q (type A in Figure 2), the most stable structure of Ph-6-Q<sup>•-</sup> and Ph-10-Q<sup>•-</sup> is type B in which the amide proton adjacent to the Ph moiety forms the hydrogen bond with carbonyl oxygen of the Q\*- moiety. The observed hfc values in Figure 3 can be well-reproduced by those in parentheses in Figure 3 calculated using the optimized structures of the type B in Ph-6-Q<sup>•-</sup> and Ph-10-Q<sup>•-</sup>. The energies of the type B structure of Ph-6-Q<sup>--</sup> and Ph-10-Q<sup>--</sup> are by 9.6 and 5.4 kJ  $mol^{-1}$  more stable than those of type A, respectively. The O-H distances in **Ph-6-Q**<sup>•-</sup> (1.80 Å) and **Ph-10-Q**<sup>•-</sup> (1.82 Å) are much shorter than those in the neutral state, Ph-6-Q (2.12 Å) and **Ph-10-Q** (2.25 Å).

**Photoinduced Electron Transfer in ZnP–Q Dyads.** The fluorescence intensities of **ZnP–CONH-Q** and **ZnP–***n***-Q** (n = 3, 6, 10) in PhCN were much smaller than that of the reference compound without Q (**ZnP–CONH-ref**). The occurrence of photoinduced ET was confirmed by observation of the ESR spectrum of **ZnP+**-**10-Q**<sup>•-</sup>, which was generated by photoirradiation of a deaerated PhCN solution of **ZnP–10-Q** at 173 K, as shown in Figure 4a. The ESR spectrum of **ZnP+**+**-10-Q**<sup>•-</sup> (g = 2.0028 in Figure 4a) consists of the superposition of the ESR signals of **ZnP+**+**-CONH-Q** (g = 2.0023 in Figure 4b) and **ZnP–CONH-Q**<sup>•-</sup> (g = 2.0043 in Figure 4c), produced by the chemical oxidation and reduction, respectively.

From the fluorescence quenching in Figure 5, the rate constant  $(k_{\rm ET})$  of ET from the singlet excited state of the ZnP moiety to the Q moiety in **ZnP**–**CONH-Q** is determined as  $1.5 \times 10^{10}$  s<sup>-1</sup> in PhCN by the comparison of the intensity of **ZnP**–**CONH-ref** ( $\tau = 2.04$  ns in MeCN,  $\tau = 2.04$  ns in PhCN,  $\tau = 1.88$  ns in CH<sub>2</sub>Cl<sub>2</sub>,  $\tau = 2.10$  ns in THF, and  $\tau = 2.15$  ns in toluene determined from fluorescence decay) using eq 1. The  $k_{\rm ET}$  values in

$$k_{\rm ET} = (\tau_{\rm ZnP-CONH-ref})^{-1} ([I_0/I] - 1)$$
(1)

with MeCN, CH<sub>2</sub>Cl<sub>2</sub>, THF, and toluene were also determined as summarized in Table 2 (see Experimental Section). The  $k_{\text{ET}}$ values of **ZnP–CONH-Q** in MeCN and PhCN are significantly



**Figure 4.** ESR spectra of (a) **ZnP**<sup>++</sup>–**10**-**Q**<sup>--</sup>, (b) **ZnP**<sup>++</sup>–**CONH-Q**, and (c) **ZnP**–**CONH-Q**<sup>--</sup> (1.0 × 10<sup>-5</sup> M), produced by the photo-irradiation in deaerated PhCN at 173 K.



Figure 5. Fluorescence spectra of ZnP–CONH-Q, ZnP–3-Q, ZnP–6-Q, ZnP–10-Q, and ZnP–CONH-ref  $(1.0 \times 10^{-5} \text{ M})$  in deaerated PhCN at 298 K.

larger than those of **ZnP–CONMe-Q**. Such an enhancement of the photoinduced electron-transfer results from the larger driving force ( $-\Delta G_{\text{ET}} = 0.91 \text{ eV}$ ) for **ZnP–CONH-Q**) than that ( $-\Delta G_{\text{ET}} = 0.82 \text{ eV}$ ) for **ZnP–CONMe-Q** due to the hydrogen bond (vide supra).

The rate constants ( $k_{\text{ET}}$ ) of photoinduced electron transfer from <sup>1</sup>ZnP\* to Q in **ZnP**–*n*-**Q** (n = 3, 6, 10) are also determined in several solvents by the comparison of the fluorescence decay of **ZnP**–**NHCO-ref** (see Experimental Section) using eq 2.<sup>40</sup>

$$k_{\rm ET} = (\tau_{\rm ZnP-n-Q})^{-1} - (\tau_{\rm ZnP-NHCO-ref})^{-1}$$
 (2)

The representative fluorescence decay curves of **ZnP**–*n*-**Q** (n = 3, 6, 10) in toluene are shown in Figure 6 as compared with the curve of **ZnP**–**NHCO-ref**. The  $k_{\text{ET}}$  values of **ZnP**–*n*-**Q** (n = 3, 6, 10) in several solvents are summarized in Table 2.

The plots of logarithm of the ET rate constants (log  $k_{\text{ET}}$ ) vs the methylene spacer numbers in ZnP-linked-Q dyads in several solvents are shown in Figure 7. The  $k_{\text{ET}}$  values for ZnP-3-Q, ZnP-6-Q, and ZnP-10-Q in several solvents are approximately the same irrespective of the difference in the number of the methylene spacer, whereas the  $k_{\text{ET}}$  values for ZnP-CONH-Q are much faster than those of ZnP-3-Q, ZnP-6-

TABLE 2: Rate Constants of Photoinduced ET (k<sub>ET</sub>) in MeCN, PhCN, CH<sub>2</sub>Cl<sub>2</sub>, THF, and Toluene

		K <sub>ET</sub> , S					
solvent	$\epsilon_{ m r}$	ZnP-CONH-Q	ZnP-CONMe-Q	ZnP-NHCO-Q	ZnP-3-Q	ZnP-6-Q	ZnP-10-Q
MeCN PhCN	37.5 25.2	$\begin{array}{l} 4.9 \times 10^{10a} \\ 1.5 \times 10^{10a} \end{array}$	$4.5 \times 10^{9 a}$ $2.0 \times 10^{9 a}$	$6.3 \times 10^{8 a}$	$\begin{array}{l} 4.7\times 10^{8b} \\ 8.4\times 10^{7b} \\ (1.7\times 10^{8a}) \end{array}$	$\begin{array}{c} 3.7\times 10^{8b} \\ 1.1\times 10^{8b} \\ (1.8\times 10^{8a}) \end{array}$	$\begin{array}{c} 3.1 \times 10^{8b} \\ 1.4 \times 10^{8b} \\ (2.4 \times 10^{8a}) \end{array}$
CH <sub>2</sub> Cl <sub>2</sub> THF toluene	8.93 7.58 2.38	$\begin{array}{l} 2.9 \times 10^{10a} \\ 1.4 \times 10^{10a} \\ 3.1 \times 10^{10a} \end{array}$			$\begin{array}{c} 6.6\times10^{8b}\\ 3.6\times10^{8b}\\ 6.9\times10^{8b} \end{array}$	$\begin{array}{c} 3.3\times10^{8b}\\ 1.6\times10^{8b}\\ 2.3\times10^{8b} \end{array}$	$\begin{array}{c} 1.3 \times 10^{8b} \\ 1.1 \times 10^{8b} \\ 1.8 \times 10^{8b} \end{array}$

 $^{a} k_{\text{ET}} = \tau_{(\text{ZnP-CONH-ref)}}^{-1} [(\phi_{\text{FL}}^{0} / \phi_{\text{FL}}) - 1]. \ ^{b} k_{\text{ET}} = \tau_{(\text{ZnP-3,6,10-Q})}^{-1} - \tau_{(\text{ZnP-NHCO-ref)}}^{-1}.$ 



Figure 6. Fluorescence decay curves of ZnP–3-Q, ZnP–6-Q, ZnP–10-Q, and ZnP–NHCO-ref ( $1.0 \times 10^{-5}$  M) in deaerated toluene at 298 K.



**Figure 7.** Plots of rate constants of photoinduced ET (log  $k_{\text{ET}}$ , solid line) and BET (log  $k_{\text{BET}}$ , broken line) vs numbers of methylene chains in **ZnP–CONH-Q**, **ZnP–3-Q**, **ZnP–6-Q**, and **ZnP–10-Q** in MeCN, PhCN, CH<sub>2</sub>Cl<sub>2</sub>, THF, and toluene.

**Q**, and **ZnP**–**10-Q**. Such a difference in the  $k_{\text{ET}}$  values is ascribed to the difference in the edge-to-edge distance ( $R_{ee}$ ) between ZnP and Q (see Table 1), since the  $R_{ee}$  value of **ZnP**–**CONH-Q** (3.78 Å) is much shorter than those of **ZnP**–**3-Q** (8.26 Å), **ZnP**–**6-Q** (8.21 Å), and **ZnP**–**10-Q** (8.27 Å), which are virtually the same (see Table 1).<sup>41</sup> Thus, the hydrogen-bond formation between two amide groups provides control of a structural scaffold even in polar solvent (MeCN), enabling the efficient photoinduced ET.<sup>42,43</sup>



**Figure 8.** (a) Time-resolved absorption spectra observed at 140 ns ( $\bullet$ ) and 6  $\mu$ s ( $\bigcirc$ ) after laser pulse excitation (428 nm) of a deaerated MeCN solution of **ZnP-3-Q** (5.0 × 10<sup>-6</sup> M) at 298 K. (b) First-order plots of absorbance at 480 nm after laser excitation (laser power, 3.5, 2.4, and 1.5 mJ, respectively) at 435 nm.

Back-Electron Transfer in ZnP-Q Dyads. The backelectron transfer (BET) processes in ZnP-Q dyads have also been investigated using nanosecond laser flash photolysis. The representative resolved-transient spectra of a deaerated MeCN solution of ZnP-3-Q excited at the ZnP moiety at 428 nm are shown in Figure 8a. The formation of the charge-separated state  $(ZnP^{\bullet+}-3-Q^{\bullet-})$  is clearly observed as indicated by the appearance of the absorption bands at 470 and 630 nm due to ZnP<sup>•+</sup>,<sup>44</sup> and also the band at 450 nm due to Q<sup>•-.45</sup> The absorption band corresponding to the CS state disappears by the BET process. The absorption decay at 630 nm obeys first-order kinetics as shown in Figure 8b, where the constant  $k_{\rm BET}$  value (1.0  $\times$  $10^6 \text{ s}^{-1}$ ) is obtained irrespective of the difference in the laser power. It should be noted that this is the first example of the long-lived CS state of porphyrin-quinone linked systems.<sup>17-24</sup> In the case of ZnP-CONH-Q, ZnP-CONMe-Q, and ZnP-NHCO-Q, the CS states were not detected due to the fast BET process. The  $k_{\text{BET}}$  values of **ZnP**-n-**Q** (n = 3, 6, 10) in MeCN and PhCN are summarized in Table 3 together with the quantum yield of CS ( $\Phi_{CS}$ ) determined by the comparative method using zinc tetraphenylporphyrin (see Experimental Section). The

TABLE 3: Rate Constants of BET ( $k_{BET}$ ) in MeCN and PhCN, and Quantum Yields of CS ( $\Phi_{CS}$ ) in PhCN

	solvent	ZnP-3-Q	ZnP-6-Q	ZnP-10-Q
$k_{\rm BET}$ , s <sup>-1</sup>	MeCN	$1.0 \times 10^{6}$	$1.1 \times 10^{7}$	$1.3 \times 10^{7}$
	PhCN	$1.6 \times 10^{6}$	$9.8 \times 10^{6}$	$1.0 \times 10^{7}$
$\Phi_{ m CS}$	PhCN	$0.36^{a}$	$0.29^{a}$	0.36 <sup>a</sup>
		$(0.26)^{b}$	$(0.28)^{b}$	$(0.33)^{b}$

<sup>*a*</sup> Determined by the comparative method. <sup>*b*</sup> Determined by the fluorescence quenching.

 $(1 - I/I_0)$  values (0.26–0.33 in parentheses in Table 3) obtained from fluorescence quenching agree with the  $\Phi_{CS}$  values (0.29–0.36) determined from the comparative method.

The plots of logarithm of the BET rate constants (log  $k_{BET}$ ) vs the number of methylene spacer of  $\mathbf{ZnP}-n-\mathbf{Q}$  in several solvents are also shown in Figure 7. The  $k_{BET}$  values of  $\mathbf{ZnP}^{\bullet+}-n-\mathbf{Q}^{\bullet-}$  (n = 6, 10) in MeCN and PhCN are much faster than those in  $\mathbf{ZnP}^{\bullet+}-\mathbf{3-Q}^{\bullet-}$  (see S13). In contrast to the BET process, the  $k_{ET}$  values of  $\mathbf{ZnP}-n-\mathbf{Q}$  are virtually the same irrespective of the number of methylene spacer of  $\mathbf{ZnP}-n-\mathbf{Q}$  (Figure 7). Such a difference between the ET and BET processes may result from the difference in the hydrogen-bonded structures between the neutral sate ( $\mathbf{ZnP}-n-\mathbf{Q}$ ) and the CS state ( $\mathbf{ZnP}^{\bullet+}-n-\mathbf{Q}^{\bullet-}$ ) (vide supra). The formation of hydrogen bond in the type B structure of  $\mathbf{ZnP}^{\bullet+}-n-\mathbf{Q}^{\bullet-}$  (n = 6, 10 in Figure 3) affords the closer distance between ZnP and Q (4.26 Å in  $\mathbf{ZnP}^{\bullet+}-\mathbf{6-Q}^{\bullet-}$  and 4.29 Å in  $\mathbf{ZnP}^{\bullet+}-\mathbf{10-Q}^{\bullet-}$ ) as compared with that in  $\mathbf{ZnP}^{\bullet+}-\mathbf{3-Q}^{\bullet-}$  (8.18 Å), leading to the faster BET.

The  $k_{\text{ET}}$  and  $k_{\text{BET}}$  values are evaluated using the Marcus equation for intramolecular ET (eq 3),<sup>46</sup> where *V* is the electronic coupling matrix element. The  $\lambda$  and *V* values are

$$k_{\rm ET} = (4\pi^3/h^2\lambda k_{\rm B}T)^{1/2}V^2 \exp[-(\Delta G_{\rm ET} + \lambda)^2/4\lambda k_{\rm B}T]$$
 (3)

evaluated from the  $k_{\rm ET}$  values and  $-\Delta G_{\rm ET}$  values of **ZnP–CONH-Q** ( $k_{\text{ET}} = 1.5 \times 10^{10} \text{ s}^{-1}, -\Delta G_{\text{ET}} = 0.91 \text{ eV}$ ), and those of **ZnP–NHCO-Q** ( $k_{\rm ET} = 6.3 \times 10^8 \, {\rm s}^{-1}$ ,  $-\Delta G_{\rm ET} =$ 1.11 eV) in PhCN using eq 3 as 0.57 eV and 17 cm<sup>-1</sup>, respectively. The predicted  $k_{\text{BET}}$  values are determined as  $4.0 \times 10^8$  s<sup>-1</sup> in **ZnP–CONH-Q** and  $1.0 \times 10^{10}$  s<sup>-1</sup> in ZnP-NHCO-Q using 0.57 eV and 17 cm<sup>-1</sup>. This is consistent with no observation of CS states in the nanosecond laser flash photolysis measurements. In the same manner, the  $\lambda$  and V values are determined from the  $k_{\rm ET}$  and  $k_{\rm BET}$  values with  $-\Delta G_{\rm ET}$ and  $-\Delta G_{\text{BET}}$  values in PhCN as 0.63 eV and 0.8 cm<sup>-1</sup> in **ZnP–3-Q**, where the  $R_{ee}$  distance (8.26 Å) in the neutral state is virtually the same as that (8.18 Å) in the radical anion state. The reorganization energy ( $\lambda = 0.63 \text{ eV}$ ) in **ZnP-3-Q** is larger than that in ZnP-CONH-Q and ZnP-NHCO-Q ( $\lambda$  = 0.57 eV) due to an increase in the solvent reorganization energy, whereas the V value decreases with an increase in the  $R_{ee}$ distance. Both the ET and BET processes in ZnP-3-Q  $(R_{ee} = 8.28 \text{ Å})$  are much slower than those in **ZnP–CONH-Q** and **ZnP–NHCO-Q** ( $R_{ee} = 3.78-3.81$  Å) due to the longer Ree distance. In the case of ZnP-6-Q and ZnP-10-Q, however, the structure is changed from type A before the ET process to type B after the ET process. The  $R_{ee}$  distances of the type B structure of the CS states  $(ZnP^{\bullet+}-6\text{-}Q^{\bullet-},\ ZnP^{\bullet+}-10\text{-}Q^{\bullet-})$ become significantly shorter than the  $R_{ee}$  distance in **ZnP**<sup>•+</sup>-3-Q<sup>--</sup>, affording the shorter CS lifetimes in ZnP-6-Q and ZnP-10-Q.

In conclusion, the hydrogen bond not only provides a structural scaffold to assemble the donor (ZnP) and the acceptor (Q) moiety but also controls the photoinduced electron-transfer

process, leading to attainment of the charge-separated state with a long lifetime up to a microsecond.

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**Supporting Information Available:** Synthetic details and characterizations of precursors of ZnP-linked-Q dyads (S1–S7), comparison of calculation methods of the *hfc* values of **ZnP–CONH-Q<sup>--</sup>**, **ZnP–CONMe-Q<sup>--</sup>**, **ZnP–NHCO-Q<sup>--</sup>**, and **ZnP–3-Q<sup>--</sup>** (S8) and that of **ZnP–***n***-Q<sup>--</sup>** (*n* = 6, 10) (S9), experimental and calculated wavenumbers of N–H, C=O bond (S10), experimental and calculated chemical shifts of <sup>13</sup>C NMR in **ZnP–CONH-Q**, **ZnP–CONMe-Q**, and **ZnP–NHCO-Q** (S11), experimental wavenumbers of N–H, C=O bond in **ZnP–***n***-Q** (*n* = 3, 6, 10) (S12), and decay profiles of **ZnP<sup>+</sup>–***n***-Q<sup>--</sup>** (*n* = 3, 6, 10) at 480 nm in MeCN (S13) (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.

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(38) The *hfc* values were also calculated using the B3LYP and ADF method. Of all the computational methods and basis sets tested, the BLYP/ 6-31G(d) basis set predicts the *hfc* values in closest agreement with experimental results in Figure 1 and Figure 3 (see S8, S9).

(39) The calculated energy of **Ph–6-Q** with a structure without hydrogen bond formation is by 14.8 kJ mol<sup>-1</sup> higher than that with the optimized structure (type A of **Ph–6-Q**); the calculations were performed using the BLYP/6-31G(d) basis set with the RHF formalism in Gaussian 98 program.

(40) The ET processes from  ${}^{1}ZnP^{*}$  to Q in **ZnP**-**CONH-Q** in several solvents are too fast to be determined by the fluorescence decay.

(41) The  $R_{cc}$  distances were estimated by the structures, which were provided by adding the optimized structure of ZnP calculated by the ADF calculation with II (large) basis set to **Ph–CONH-Q** and **Ph–***n***-Q**.

(42) The  $k_{\rm ET}$  value is known to decrease with increasing the distance  $(R_{\rm ee})$ , obeying  $k_{\rm ET} = k_{\rm ET}^0 \exp(-\beta R_{\rm ee})^{.43}$  From the distance dependence of  $k_{\rm ET}$  values in **ZnP–CONH-Q** and **ZnP–n-Q** (n = 3, 6, 10) in several solvents using the  $R_{\rm ee}$  values of **ZnP–CONH-Q** and **ZnP–n-Q** (n = 3, 6, 10) in Table 1, the  $\beta$  values were determined by the slope as 1.14 Å<sup>-1</sup> in MeCN, 1.15 Å<sup>-1</sup> in PhCN, 1.07 Å<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, 1.01 Å<sup>-1</sup> in THF, and 1.08 Å<sup>-1</sup> in toluene. The  $\beta$  values between 1.01 and 1.15 Å<sup>-1</sup> agree with those reported previously for saturated hydrocarbon spacers  $(0.8-1.4 \text{ Å}^{-1})^{14,43a-c}$  or protein  $(1.0-1.4 \text{ Å}^{-1})^{.43d,e}$ 

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