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Molecular recognition of viologen by zinc porphyrinic receptors with diarylurea sidearms. Toward construction of a supramolecular electron transfer system

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Abstract—A series of zinc porphyrinic receptors for a viologen substrate (hexyl viologen, $\mathbf{HV}^{2+}$) were synthesized, in which varying numbers of diarylurea moieties, from one to four, were appended at the porphyrin's *meso* positions. The increase in the number of the diarylurea moiety led to the increase in stability of the receptor–$\mathbf{HV}^{2+}$ complex, showing that the convergent dipoles set up on the porphyrin platform played an essential role in the complexation. In this system, formation of the stable electron donor–acceptor complex resulted in the effective electron transfer from the singlet excited state of the zinc porphyrin to $\mathbf{HV}^{2+}$.

1. Introduction

For a few past decades, photoinduced electron transfer systems employing organic molecules as well as metal complexes have received much attention because they do not only serve as models for photosynthetic electron relay systems but also give significant insights into the development of molecular-scale opto-electronic devices.[1] Especially, the supramolecular architecture of electron donor–acceptor complexes has been eagerly studied and established as one of powerful methods for construction of photochemically active ensembles,[2] where porphyrins and the related compounds have been widely used as electron donor components because of analogy to photosynthetic pigments. Thus, designing porphyrinic receptors for appropriate electron acceptors such as electron-deficient aromatics,[3] quinones,[4] fullerenes,[5] and viologens[6] has been one of major topics in supramolecular photochemistry. Many covalently-linked porphyrin–viologen donor–acceptor systems have so far been studied,[7] where the electron transfer effectively occurs via formation of a face-to-face donor–acceptor complex.[7d] However, despite such significance of the rational design of supramolecular porphyrin–viologen complexes, only a few examples of porphyrinic receptors for a bare viologen backbone have been so far reported.[6a,d,e]

We recently reported the doubly diarylurea-linked cofacial zinc porphyrin dimer (**DLD**), which formed a 1:1 complex with a viologen substrate (hexyl viologen perchlorate, $\mathbf{HV}^{2+}\cdot 2ClO_4^-$).[8] In this system, high stability of the complex ($K=546{,}000\ M^{-1}$ in

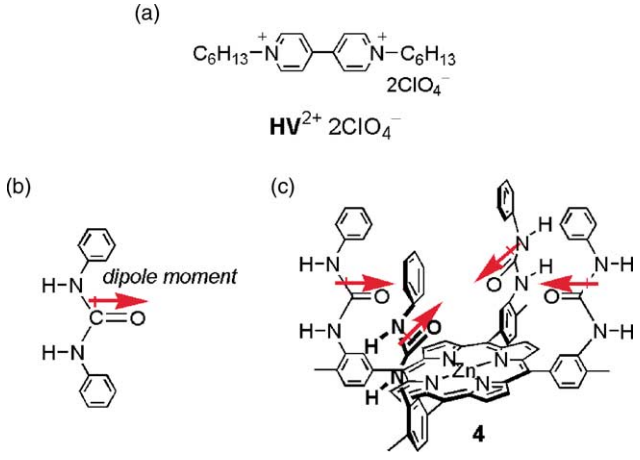

Figure 1. (a) Structure of a viologen substrate (hexyl viologen perchlorate), and illustrations of (b) the dipole moment on diphenylurea and (c) the convergent arrangement of four carbonyl dipoles in the receptor **4**.

Keywords: Molecular recognition; Diarylurea; Zinc porphyrin; Viologen; Photoinduced electron transfer; Supramolecular system.
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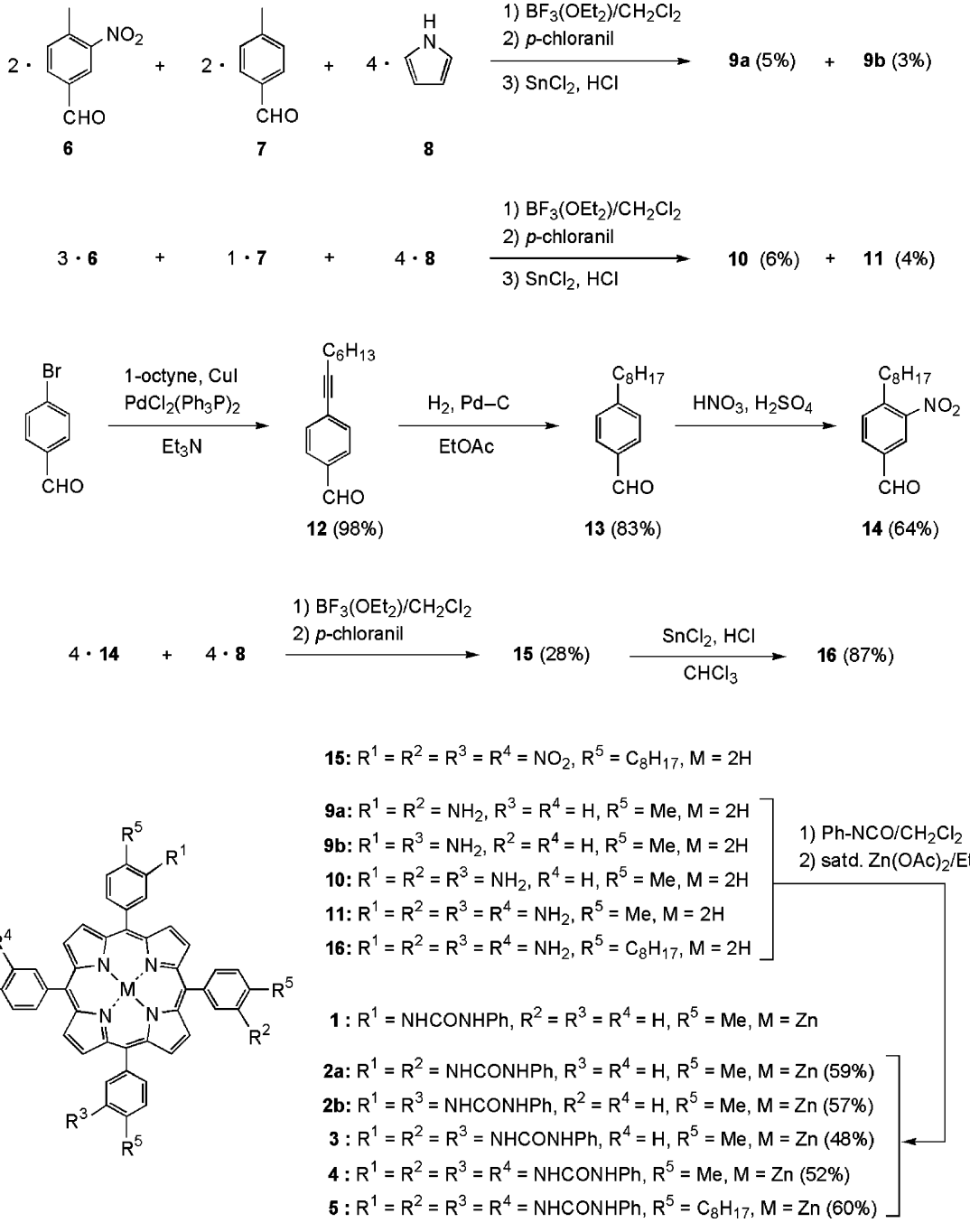
$CHCl_3$/DMSO, 10:1, v/v) was attributed to the dipole-cation interactions[9] between the diarylurea linkages and the viologen backbone. This interesting result impels us to design a more sophisticated porphyrinic receptor for viologen that is facilely prepared. Here we report complexation of a series of diarylurea-appended zinc porphyrins **1**–**4** with $\mathbf{HV}^{2+}$: arranging the carbonyl dipoles on the zinc porphyrin platform in a convergent manner should promise effective binding of $\mathbf{HV}^{2+}$ (Fig. 1). We also discuss the complexation-facilitated photoinduced electron transfer from steady-state fluorescence quenching studies and flash laser photolysis measurement.

2. Results and discussion

2.1. Synthesis of the zinc porphyrinic receptors

We have already reported the synthesis of the receptor **1** in the previous work.[10] In Scheme 1 are shown the syntheses of **2**–**5**. Acid-promoted ($BF_3 \cdot OEt_2$) condensation of 4-methyl-3-nitrobenzaldehyde **6**, *p*-tolualdehyde **7** and pyrrole **8** at the ratio of 2:2:4 (mol/mol/mol) followed by oxidation with chloranil afforded a mixture of 5,10-bis(3-nitro-4-methylphenyl)-15,20-bis(4-methylphenyl)porphyrin, and 5,15-bis(3-nitro-4-methylphenyl)-10,20-bis(4-methylphenyl)porphyrin, both of which were reduced



Scheme 1. Synthesis of porphyrinic receptors.

by $SnCl_2$ in concd HCl to yield a mixture of the corresponding amino-substituted porphyrins **9a** and **9b** in the yields of 3 and 5% based on **8**, respectively. Changing the ratio of the starting materials (**6**:**7**:**8**=3:1:4, mol/mol/mol), a similar procedure afforded **10** and **11** in 6 and 4% yields, respectively. The receptors **2**–**4** were easily obtained by the reactions of the corresponding amino-substituted porphyrins **9**–**11** with an excess amount of phenylisocyanate followed by zinc insertion in 48–60% yields. The more soluble, quadruply functionalized zinc porphyrin **5** was also prepared as an analogue of **4** for ^{1}H NMR spectroscopic studies. A Sonogashira cross-coupling reaction of 4-bromobenzaldehyde and 1-octyne yielded 4-(1-octyn-1-yl)benzaldehyde **12** in 98% yield, followed by hydrogenation on Pd–C to yield 4-octylbenzaldehyde **13** in 83% yield. Nitration of **13** by treatment with HNO_3 in H_2SO_4 yielded 3-nitro-4-octylbenzaldehyde **14** in 64% yield. Acid-promoted ($BF_3\cdot OEt_2$) condensation of **14** and **8** yielded a nitro-substituted porphyrin **15** in 28% yield, which was reduced to **16** in 87% yield. Treatment of **16** with a large excess of phenylisocyanate followed by zinc insertion yielded the receptor **5** in 60% yield. Each compound was identified by ^{1}H NMR, ^{1}H–^{1}H COSY, electronic absorption, IR, and FAB mass spectra as well as elemental analyses.

2.2. Complexation behavior of the zinc porphyrinic receptors with HV^{2+}

In Figure 2 are shown electronic absorption spectral changes of **4** in the Soret region upon addition of varying amounts of $\mathbf{HV}^{2+}\cdot 2ClO_4^-$. The red-shifted spectral changes with an isosbestic point at 434 nm showed saturation behavior. The stoichiometry of the **4**–$\mathbf{HV}^{2+}$ complex was confirmed as 1:1 by the Job's analysis using electronic absorption spectroscopy. The binding constant (K_{abs}) was determined as $(2.86\pm0.30)\times 10^6\ M^{-1}$ by the computer-assisted least squares analysis based on 1:1 complexation, which was larger than that of the **DLD**–$\mathbf{HV}^{2+}$ complex.[8] Similar complexation behavior was observed for **1**–**3** upon addition of $\mathbf{HV}^{2+}$, and K_{abs}s of **1**–**4** for $\mathbf{HV}^{2+}$ are summarized in Table 1. The increase in the number of the diarylurea moiety led to the increase in the stability of the complex, and the zinc porphyrin without any diarylurea moieties[11] did not exhibit any spectral changes even in the presence of an excess amount of $\mathbf{HV}^{2+}$. These results indicate that the diarylurea moieties play an essential role in binding of $\mathbf{HV}^{2+}$.

The complexation of $\mathbf{HV}^{2+}$ to the receptors was also confirmed by ^{1}H NMR titration experiments. In Figure 3 are shown ^{1}H NMR spectra of **5**, $\mathbf{HV}^{2+}$, and a 1:1 mixture of the both. The signals of H^a, H^b and H^c of $\mathbf{HV}^{2+}$ exhibited complexation-induced upfield shifts (1.4, 3.7, and 0.6 ppm, respectively) upon addition of an equimolar amount of **5**, and any other remarkable shifts of the signals of the alkyl protons in $\mathbf{HV}^{2+}$ were not observed (<0.2 ppm). As the proton was close to the center of viologen backbone, the upfield shift became large. These results were unambiguously due to ring-current anisotropy from the porphyrin π-plane, indicating that the bipyridinium backbone of $\mathbf{HV}^{2+}$ was located on the porphyrin ring. The free **5** exhibited the multiple signals of H^4 and two urea N–Hs as well as the broadened signals of H^1–H^6 (Fig. 3c), indicating that the receptor exists as a mixture of the atropisomers.[12]

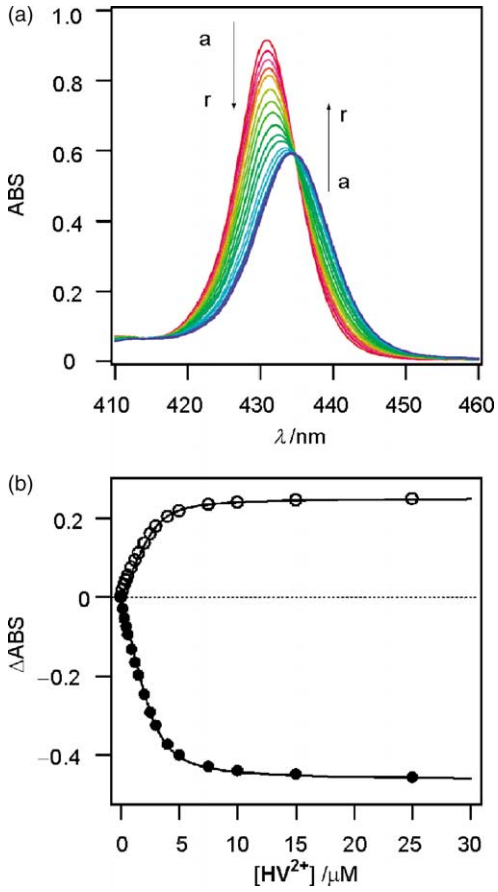


Figure 2. (a) Electronic absorption spectral changes of **4** (1.5 μM) upon addition of increasing amounts of $\mathbf{HV}^{2+}$ (a–r; 0, 0.15, 0.30, 0.45, 0.60, 0.90, 1.2, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 7.5, 10, 15, 25 and 50 μM) and (b) absorbance changes at 430 (●) and 438 nm (○) in $CHCl_3$–DMSO (10/1, v/v) at 293 K.

On the other hand, the complexed **5** exhibited singlet signals of H^4 and N–Hs as well as the sharp signals of H^1–H^6, although a small amount of metastable conformer was observed probably due to the flexibility of the diarylurea arms (Fig. 3b).[13] Taking it into consideration that the increase in the number of the diarylurea moiety gave rise to stabilization of the complex, one can see that all the diarylurea moieties participated in the binding of $\mathbf{HV}^{2+}$.

The contribution of the dipole-cation interaction to the complexation of $\mathbf{HV}^{2+}$ was quantitatively estimated by

Table 1. Binding constants of receptors **1**–**4** for $\mathbf{HV}^{2+}$ obtained by electronic absorption (K_{abs}) and fluorescence emission spectra (K_{em})[a]

Compound	K_{abs} (M^{-1})[b]	K_{em} (M^{-1})[c]	ΔG_{abs} (kJ mol^{-1})[d]
1	1100	2300	−17.1
2a	18,900	15,000	−24.0
2b	17,500	10,700	−23.8
3	195,000	216,000	−29.7
4	2,860,000	1,940,000	−36.2

[a] In $CHCl_3$–DMSO (10/1, v/v) at 293 K.
[b] Experimental errors were within 7% except for **4** (11%).
[c] Experimental errors were within 10% except for **4** (26%).
[d] ΔG_{abs}s were calculated from K_{abs}s.

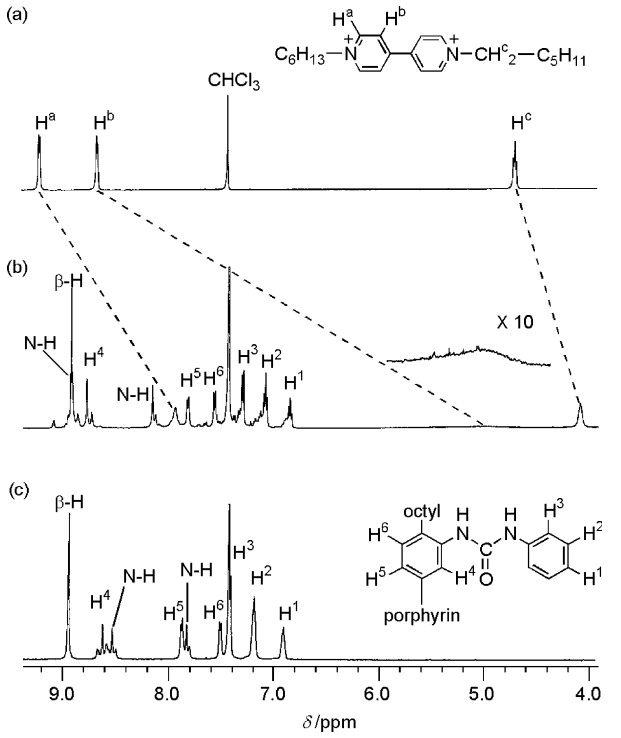


Figure 3. ^{1}H NMR spectral study of (a) $\mathbf{HV}^{2+}$ (1.8 mM), (b) $\mathbf{HV}^{2+}$ (1.8 mM) + **5** (1.8 mM), and **5** (1.8 mM) in $CDCl_3$–DMSO-d_6 (10/1, v/v) at 293 K.

plotting the free energy changes of the complexation (ΔG_{abs}s) against the number of the diarylurea moiety (Fig. 4). These plots showed good linearity, and the slope obtained (−6.28 kJ/mol) is attributed to the averaged free energy change given by one dipole-cation interaction between the diarylurea moiety and $\mathbf{HV}^{2+}$ (Fig. 5, ΔG_A). In addition, the intercept of the plots (−11.1 kJ/mol) is reasonably attributed to the free energy change of the interaction between the porphyrin platform and the viologen backbone (Fig. 5, ΔG_B), that is either electrostatic or solvophobic interaction, or the sum of both. It is noteworthy that such a good linear relationship also indicates that, in each receptor–$\mathbf{HV}^{2+}$ system, all diarylurea moieties contribute to binding of $\mathbf{HV}^{2+}$ in an induced-fit manner to achieve the multiple dipole-cation interaction.

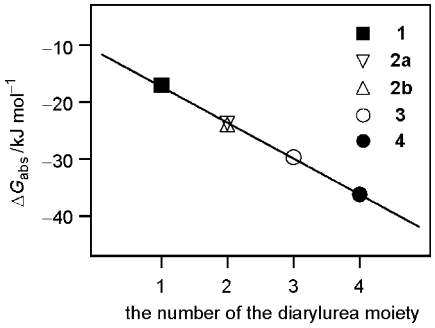


Figure 4. Plots for free energy changes on complexation of **1**–**4** with $\mathbf{HV}^{2+}$ against the number of the diarylurea moiety in the receptors in $CHCl_3$–DMSO (10/1, v/v) at 293 K. R^2 = 0.996.

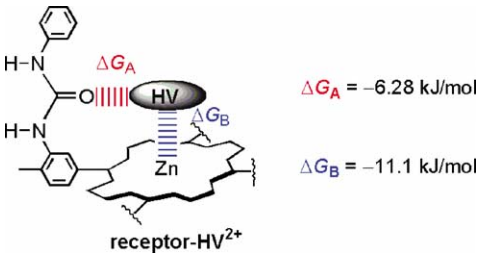


Figure 5. Schematic representation of contribution of the intermolecular interactions (ΔG_A and ΔG_B) to the complexation of the receptors **1**–**4** with $\mathbf{HV}^{2+}$.

2.3. Complexation-facilitated electron transfer from the zinc porphyrinic receptors to $\mathbf{HV}^{2+}$

Addition of $\mathbf{HV}^{2+}$ to solutions of **1**–**4** led to the fluorescence quenching due to photoinduced electron transfer from the zinc porphyrin unit to $\mathbf{HV}^{2+}$ (Fig. 6a).[6b,c,e,8] The binding constant K_{em} obtained from fluorescence emission spectroscopy validly corresponded with K_{abs} for each receptor (Table 1), indicating that fluorescence quenching occurred via formation of the electron donor–acceptor complex. As shown in Figure 6b, all titration curves finally reached plateaus but exhibited different fluorescence quenching efficiencies: the **3**–$\mathbf{HV}^{2+}$ and **4**–$\mathbf{HV}^{2+}$ systems showed quite efficient fluorescence quenching (97 and 100%, respectively, supposing that the receptor molecules fully complexed with $\mathbf{HV}^{2+}$), whereas the **2a**–$\mathbf{HV}^{2+}$ and **2b**–$\mathbf{HV}^{2+}$ showed quasi-effective (79 and 75%, respectively) and the **1**–$\mathbf{HV}^{2+}$ showed less effective quenching (24%). The **ZnPor**–$\mathbf{HV}^{2+}$ system hardly showed fluorescence quenching (**ZnPor**; [5,10,15,20-tetrakis(4-methylphenyl)-porphyrinato]zinc(II)). Therefore,

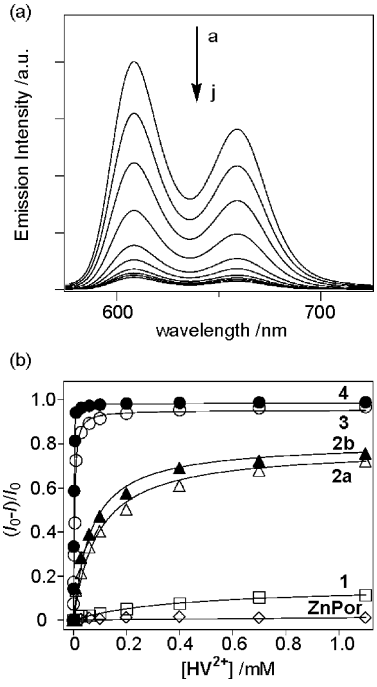


Figure 6. (a) Fluorescence emission spectral changes of **4** upon addition of increasing amounts of $\mathbf{HV}^{2+}$ (a–j; 0, 0.30, 0.60, 0.90, 1.2, 1.5, 2.0, 2.5, 3.0, and 4.0 μM; [**4**] = 1.5 μM) and (b) quenching titration profiles of **1**–**4** in $CHCl_3$–DMSO (10/1, v/v) at 293 K. λ_{ex} = 560 nm.

the increase in the thermodynamic stability of the receptor–$\mathbf{HV}^{2+}$ complex led to the increase of fluorescence quenching efficiency. These results indicated that multiple dipole-cation interactions as seen in **3**–$\mathbf{HV}^{2+}$ and **4**–$\mathbf{HV}^{2+}$ fixed $\mathbf{HV}^{2+}$ tightly on the receptor in a preferred manner to photoinduced electron transfer.

2.4. Photophysical properties of the 4–$\mathbf{HV}^{2+}$ complex

In order to clarify the efficient electron transfer in the **4**–$\mathbf{HV}^{2+}$ system, the detailed study on photophysics was carried out in a mixture of benzonitrile and tetrahydrofuran (1/1, v/v).[14] In this solvent system, the spectroscopic profiles of electronic absorption and fluorescence emission of **4** upon complexation with $\mathbf{HV}^{2+}$ were similar to those in $CHCl_3$–DMSO (10/1, v/v), although the binding constant of **4** to $\mathbf{HV}^{2+}$ significantly decreased to $3.98\times10^3\ M^{-1}$. The lifetime of the excited state of **4**, τ(**4**), was determined as 1.89 ns from the fluorescence emission decay at 650–700 nm, which was typical of the singlet excited state of zinc porphyrins.[15] Upon addition of $\mathbf{HV}^{2+}$(3.0 mM) to a solution of **4** (5.0 μM), the fast decay component τ_{CS} was observed (310 ps),[16] which was attributed to quenching by photoinduced electron transfer from the zinc porphyrin chromophore to $\mathbf{HV}^{2+}$. According to the Eqs. 1 and 2, the rate of charge separation k_{CS} and charge separation quantum yield Φ_{CS} were determined as $2.7\times10^9\ s^{-1}$ and 0.84, respectively:

$$k_{CS} = \tau_{CS}^{-1} - \tau(\mathbf{4})^{-1} \quad (1)$$

$$\Phi_{CS} = 1 - \tau_{CS}/\tau(\mathbf{4}) \quad (2)$$

The fast electron transfer from a porphyrin singlet state to a viologen in the stable complex has been reported by Willner et al.[6c] One can explain that the quite rapid charge separation process is caused by the intracomplex electron transfer in the **4**–$\mathbf{HV}^{2+}$ donor–acceptor ensemble.

Further information for the electron transfer process was obtained from the transient absorption spectra of **4**–$\mathbf{HV}^{2+}$ measured upon 558 nm laser irradiation. As shown in Figure 7a, the photoinduced electron transfer from **4** to $\mathbf{HV}^{2+}$ was confirmed by two characteristic bands of the viologen cation radical $\mathbf{HV}^{\bullet+}$ at 400 and 620 nm,[17] although the absorption of the porphyrin cation radical $\mathbf{4}^{\bullet+}$ at 640 nm[7c,18] was not clear because of the overlap with the absorption band of $\mathbf{HV}^{\bullet+}$. As seen in Figure 7b, the fast rise component of the viologen cation radical at 400 nm was indicative of the intracomplex electron transfer in the **4**–$\mathbf{HV}^{2+}$ complex.[6c] The slow rise component at 400 nm was also observed, which was attributed to the intermolecular electron transfer from the free **4** to the uncomplexed $\mathbf{HV}^{2+}$. The other characteristic band appeared at 470 nm, which was assigned to the zinc porphyrin triplet–triplet absorption.[6c,18c] The rate of the decay agreed well with the slow rise of the absorption of $\mathbf{HV}^{\bullet+}$, and thus, these results indicated that intermolecular electron transfer competitively occurred from the triplet state of **4**. However, as indicated by the fluorescence lifetime measurement, the efficient electron transfer should occur via the formation of the **4**–$\mathbf{HV}^{2+}$ complex. To clarify the intracomplex electron transfer process, the decay of the transient absorption of the triplet excited state of the porphyrinic receptor $^3\mathbf{4}^*$ was monitored in the presence of varying concentrations of $\mathbf{HV}^{2+}$(Fig. 8). The triplet–triplet absorption of **4** in the absence of $\mathbf{HV}^{2+}$ decayed obeying the first-order kinetics (190 μs^{-1}). The addition of $\mathbf{HV}^{2+}$ to a solution of **4** led to the decrease in the initial intensity of the triplet state absorption, along with the shortening of the triplet lifetime. This result clearly indicated that the rapid electron transfer disturbed the formation of $^3\mathbf{4}^*$ via the intersystem crossing. In other words, the complexation of **4** with $\mathbf{HV}^{2+}$ allowed the efficient electron transfer from the singlet state of **4** to $\mathbf{HV}^{2+}$. The charge recombination rate in the $\mathbf{4}^{\bullet+}$–$\mathbf{HV}^{\bullet+}$ supramolecular redox product could not be determined because the $\mathbf{HV}^{\bullet+}$ was formed via the two electron transfer pathways from both of the singlet and triplet excited states of **4**. However, it is noteworthy that the quick rise component at 400 nm (Fig. 7b) implies that the charge recombination rate is relatively slow. This is because the supramolecular redox product $\mathbf{4}^{\bullet+}$–$\mathbf{HV}^{\bullet+}$ dissociates to the individual redox species $\mathbf{4}^{\bullet+}$ and $\mathbf{HV}^{\bullet+}$ due to electrostatic repulsion.

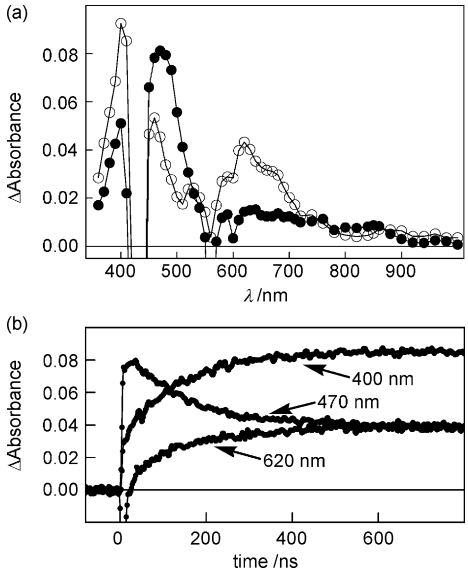


Figure 7. (a) Nanosecond transient absorption spectra of a mixture solution of **4** (5.0 μM) and $\mathbf{HV}^{2+}$ (3.0 mM) in Ar satd PhCN–THF (1/1, v/v) at 50 ns (●) and 500 ns (○) after the 558 nm-laser irradiation. (b) The absorption-time profiles monitored at 400, 470 and 620 nm.

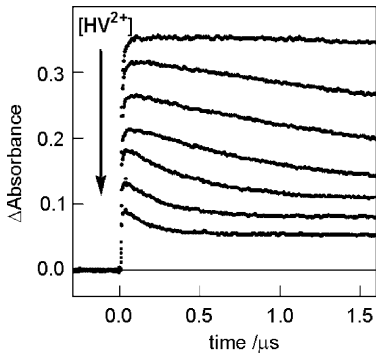


Figure 8. Decay dynamics of the triplet–triplet absorption due to $^3\mathbf{4}^*$ at 460 nm in Ar saturated PhCN–THF (1/1, v/v) upon addition of $\mathbf{HV}^{2+}$. [**4**]=5.0 μM, [$\mathbf{HV}^{2+}$]=0, 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 mM.

3. Conclusions

The zinc porphyrinic receptors bearing diarylurea sidearms at the *meso* positions were newly synthesized, and their complexation behavior with $\mathbf{HV}^{2+}$ was investigated in detail. From the electronic absorption and ^{1}H NMR spectroscopic studies, the receptors bound $\mathbf{HV}^{2+}$ in an induced-fit manner, employing multiple dipole-cation interaction between the diarylurea sidearms and the viologen backbone. The energetic contribution of one dipole-cation interaction to the complexation was estimated as -6.28 kJ/mol. The interaction between the porphyrin platform and the viologen backbone (-11.1 kJ/mol) was also found to be essential to formation of the stable complex. The steady-state fluorescence titration study revealed that the increase in stability of the receptor–$\mathbf{HV}^{2+}$ complex brought about the increase in the efficiency of photoinduced electron transfer from the porphyrinic receptor to $\mathbf{HV}^{2+}$. From the investigation of the photophysics of the **4**–$\mathbf{HV}^{2+}$ system, the formation of the donor–acceptor complex significantly facilitated the electron transfer from the singlet excited state of **4** to $\mathbf{HV}^{2+}$ ($k_{CS}=2.7\times10^9\ s^{-1}$, $\Phi_{CS}=0.84$). In the supramolecular electron transfer system, relatively slow charge recombination was implied, which should be due to dissociation of the redox products caused by electrostatic repulsion. The results obtained in the present study should offer significant insights into construction of supramolecular photoinduced electron transfer systems.

4. Experimental

4.1. General methods

^{1}H NMR and ^{1}H–^{1}H COSY spectra were measured on a JEOL JNM-A500 (500 MHz) or a JEOL JNM-LA400 (400 MHz) spectrometer, using tetramethylsilane (0.00 ppm) and residual DMSO (2.49 ppm) as internal standards for $CDCl_3$ and DMSO-d_6, respectively. FAB mass spectra were recorded on a Finnigan MAT TSQ-70 mass spectrometer using 3-nitrobenzyl alcohol as a matrix. IR spectra were measured on a Shimadzu FTIR-8400S spectrometer using KBr pellets.

Electronic absorption spectra were measured on a Shimadzu Multispec-1500 spectrometer, and fluorescence emission spectra were recorded on a Shimadzu RF-5000 or a JASCO FP-6600 spectrophotometer. Solvents used for electronic absorption and fluorescence emission spectra were of spectroscopic grade. Just before acquisition of the spectra, the sample solutions were subjected to N_2 bubbling through a syringe needle for 10 min.

The time-resolved fluorescence spectra were measured by a single-photon counting method using a second harmonic generation (SHG, 410 nm) of a Ti:sapphire laser (Spectra-Physics, Tunami 3950-L2S, fwhm 1.5 ps) as an excitation source and using a streakscope (Hamamatsu Photonics, C4334-01) equipped with a polychromator as a detector.

Nanosecond transient absorption measurements were carried out using a SHG (532 nm) of the Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. For measurements in the visible region and near-IR region (400–1000 nm), a monitoring light from a pulsed Xe lamp was detected with a Si–PIN photodiode (Hamamatsu Photonics, S1722-02). All the sample solutions in a quartz cell (1×1 cm) were deaerated by bubbling Ar gas through the solutions for 15 min.

4.2. Preparation of materials

All water-sensitive reactions were carried out under N_2 atmosphere, using dried solvent. Dichloromethane was dried over CaH_2 and distilled just prior to use. The preparation of 4-methyl-3-nitrobenzaldehyde **6** was previously reported in Ref. 8. 4-Methylbenzaldehyde, 4-bromobenzaldehyde and 1-octyne were commercially available. 4-Octylbenzaldehyde was prepared by the different method from those reported.[19] Size exclusion column chromatography was performed using BioRad Bio-Beads SX-1 with distilled THF as eluent.

4.3. Synthesis

4.3.1. Synthesis of 5,10-bis(3-amino-4-methylphenyl)-15,20-bis(4-methylphenyl)porphyrin (9a) and 5,15-bis(3-amino-4-methylphenyl)-10,20-bis(4-methylphenyl)porphyrin (9b). To a solution of chloranil (2.77 g, 11.3 mmol) in dry CH_2Cl_2 (500 mL) were added 4-methyl-3-nitrobenzaldehyde **6** (1.24 g, 7.51 mmol), 4-methylbenzaldehyde 7 (0.901 g, 7.50 mmol) and pyrrole **8** (1.01 g, 15.1 mmol) under N_2. After the mixture was stirred for a few minutes at ambient temperature under darkness, $BF_3\cdot OEt_2$ (0.95 mL, 7.56 mmol) was added, and then, the mixture was stirred for 1 h at the same temperature. The mixture was directly poured onto the top of an alumina column and allowed to pass through using CH_2Cl_2 as eluent. The resultant solution was concentrated to ca. 200 mL on a rotary evaporator, and then, washed with satd $NaHCO_3$ (100 mL$\times$3). The solution was dried over anhydrous Na_2SO_4, and the solvent was removed on a rotary evaporator. The residual dark purple solid was roughly purified by silica gel column chromatography (eluent; $CHCl_3$/hexane, 4:1, v/v) to obtain a fraction of a mixture of 5-(4-methyl-3-nitrophenyl)-10,15,20-tris(4-methylphenyl)porphyrin, 5,10-bis(4-methyl-3-nitrophenyl)-15,20-bis(4-methylphenyl)porphyrin, 5,15-bis(4-methyl-3-nitrophenyl)-10,20-bis(4-methylphenyl)-porphyrin. After removal of the solvent on a rotary evaporator, the residual dark purple solid was added to hot concd HCl (50 mL, 65 °C), followed by addition of $SnCl_2\cdot2H_2O$ (1.34 g, 5.94 mmol), and then, the reaction mixture was stirred at the same temperature for 2 h. After cooling, to the mixture was carefully added 27% aqueous NH_3 (70 mL) on an ice bath, and then, $CHCl_3$ (100 mL) was added. The mixture was stirred vigorously at ambient temperature for 2 h. The mixture was allowed to pass through a paper filter with Celite® mounted. The filtrate was washed with satd $NaHCO_3$ (100 mL), satd brine (100 mL), and water (100 mL). After dried over anhydrous Na_2SO_4, the solvent was removed by evaporation. Purification of the resultant mixture by silica gel column chromatography (eluent; $CHCl_3$/ethyl acetate, 5:1, v/v) yielded **9a** (142 mg, 0.203 mmol, 5%) and **9b** (83.7 mg, 0.119 mmol, 3%), both of which were dark purple solids. Porphyrins **9a** and

9b were discriminated from the ^{1}H NMR spectral patterns of the pyrrole β-Hs: two singlets and two coupled doublets were observed for the β-H signals of **9a**, while just two coupled doublets were observed for those of **9b**.[20]

4.3.2. 5,10-Bis(3-amino-4-methylphenyl)-15,20-bis(4-methylphenyl)porphyrin (9a). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.79 (br, 2H, inner-N*H*), 2.51 (s, 6H, 5,10-Ar-CH_3), 2.70 (s, 6H, 15,20-Ar-CH_3), 3.87 (br, 4H, –NH_2), 7.39 (d, J=7.3 Hz, 2H, 5,10-Ar-*H*), 7.54–7.56 (m, 8H, 4H of 5,10-Ar-*H* and 4H of 15,20-Ar-*H*), 8.09 (d, J=7.6 Hz, 4H, 15,20-Ar-*H*), 8.83 (d, J=4.9 Hz, 2H, pyrrole β-*H*), 8.84 (s, 2H, pyrrole β-*H*), 8.92 (s, 2H, pyrrole β-*H*), 8.94 (d, J=4.9 Hz, 2H, pyrrole β-*H*); TLC (silica gel, eluent; $CHCl_3$/ethyl acetate, 5:1, v/v) R_f=0.41; IR (KBr) 1620, 3318, 3367, 3460 cm^{-1}; FAB MS *m/z* 700 (M^+). Anal. Calcd for $C_{48}H_{40}N_6$: C, 82.26; H, 5.75; N, 11.99. Found: C, 82.04; H, 5.92; N, 11.68.

4.3.3. 5,15-Bis(3-amino-4-methylphenyl)-10,20-bis(4-methylphenyl)porphyrin (9b). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.80 (br, 2H, inner-N*H*), 2.50 (s, 6H, 5,15-Ar-CH_3), 2.70 (s, 6H, 10,20-Ar-CH_3), 3.85 (br, 4H, –NH_2), 7.39 (d, J=7.8 Hz, 2H, 5,15-Ar-*H*), 7.53–7.56 (m, 8H, 4H of 5,15-Ar-*H* and 4H of 10,20-Ar-*H*), 8.09 (d, J=7.8 Hz, 4H, 10,20-Ar-*H*), 8.83 (d, J=4.6 Hz, 4H, pyrrole β-*H*), 8.93 (d, J=4.6 Hz, 4H, pyrrole β-*H*); TLC (silica gel, eluent; $CHCl_3$/ethyl acetate, 5:1, v/v) R_f=0.67; IR (KBr) 1620, 3311, 3367, 3451 cm^{-1}; FAB MS *m/z* 700 (M^+). Anal. Calcd for $C_{48}H_{40}N_6\cdot H_2O$: C, 81.21; H, 5.82; N, 11.84. Found: C, 81.13; H, 5.67 N, 11.78.

4.3.4. {15,20-Bis(4-methylphenyl)-5,10-bis[4-methyl-3-(3-phenylureylen-1-yl)phenyl]porphyrinato}zinc(II) (2a). To a solution of **9a** (50.0 mg, 0.0713 mmol) in dry CH_2Cl_2 (30 mL) was added phenylisocyanate (41.0 , 0.344 mmol) under N_2, and the mixture was stirred for 3 h before another portion of phenylisocyanate (41.0 mg, 0.344 mmol) was added. After the reaction mixture was stirred at ambient temperature for 12 h, the solvent was removed on a rotary evaporator. The residue was dissolved in THF and filtered to remove insoluble materials. After removal of the solvent on a rotary evaporator, the residual dark purple solid was dissolved in $CHCl_3$ (20 mL), followed by addition of a saturated ethanolic solution of $Zn(OAc)_2$ (50 mL). The mixture was stirred at 50 °C for 1 h, and the solvent was removed by evaporation. The residue was dissolved in THF (20 mL) and filtered to remove insoluble materials. Purification of the resultant mixture by size-exclusion column chromatography (THF as eluent) and recrystallization from THF–hexane yielded **2a** as a purple solid (42.1 mg, 0.0420 mmol, 59%): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.59 (s, 6H, 5,10-Ar-CH_3), 2.66 (s, 6H, 15,20-Ar-CH_3), 6.85–6.90 (m, 2H, Ph-*H*), 7.14–7.20 (m, 4H, Ph-*H*), 7.37–7.40 (m, 4H, Ph-*H*), 7.56–7.60 (m, 6H, 2H of 5,10-Ar-*H* and 4H of 15,20-Ar-*H*), 7.73–7.77 (m, 2H, 5,10-Ar-*H*), 8.04–8.07 (m, 4H, 15,20-Ar-*H*), 8.27 (br, 2H, –N*H*), 8.76–8.79 (m, 6H, 4H of pyrrole β-*H* and 2H of 5,10-Ar-*H*), 8.86–8.88 (m, 4H, pyrrole β-*H*), 9.17–9.20 (br, 2H, –N*H*); IR (KBr) 1663, 3366 cm^{-1}; FAB MS *m/z* 1000 ($[M]^+$), 1001 ($[M+1]^+$), 1002 ($[M+2]^+$), 1003 ($[M+3]^+$). Anal. Calcd for $C_{62}H_{48}N_8O_2Zn\cdot H_2O$: C, 72.97; H, 4.94; N, 10.98. Found: C, 72.62; H, 4.64; N, 11.05.

4.3.5. {5,15-Bis(4-methylphenyl)-10,20-bis[4-methyl-3-(3-phenylureylen-1-yl)phenyl]porphyrinato}zinc(II) (2b). To a solution of **9b** (50.0 mg, 0.0713 mmol) in dry CH_2Cl_2 (30 mL) was added phenylisocyanate (41.6 mg, 0.349 mmol) under N_2, and the mixture was stirred for 3 h before another portion of phenylisocyanate (41.6 mg, 0.349 mmol) was added. After the reaction mixture was stirred at ambient temperature for 15 h, the solvent was removed on a rotary evaporator, and the residue was dissolved in THF and filtrated to remove insoluble materials. After removal of the solvent on a rotary evaporator, the residual dark purple solid was added to $CHCl_3$ (30 mL) followed by addition of a saturated ethanolic solution of $Zn(OAc)_2$ (50 mL). The mixture was stirred at 50 °C for 1 h, and the solvent was removed by evaporation. Purification of the resultant mixture by silica gel chromatography (eluent; $CHCl_3$/methanol, 50:1, v/v) followed by size-exclusion column chromatography (THF as eluent) and recrystallization from THF–hexane yielded **2b** as a purple solid (40.5 mg, 0.0404 mmol, 57%): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.59 (s, 6H, 5,15-Ar-CH_3), 2.65 (s, 6H, 10,20-Ar-CH_3), 6.88 (t, J=7.6 Hz, 2H, Ph-*H*), 7.18 (t, J=7.6 Hz, 4H, Ph-*H*), 7.39 (d, J=7.6 Hz, 4H, Ph-*H*), 7.56–7.60 (m, 6H, 2H of 5,15-Ar-*H* and 4H of 10,20-Ar-*H*), 7.74 (dd, J=1.5, 7.6 Hz, 2H, 5,15-Ar-*H*), 8.06 (d, J=7.6 Hz, 4H, 10,20-Ar-*H*), 8.29 (br, 2H, –N*H*), 8.76–8.79 (m, 6H, 4H of pyrrole β-*H* and 2H of 5,15-Ar-*H*), 8.86–8.88 (d, J=4.6 Hz, 4H, pyrrole β-*H*), 9.20 (br, 2H, –N*H*); IR (KBr) 1653, 3362 cm^{-1}; FAB MS *m/z* 1000 (M^+), 1001 ($[M+1]^+$), 1002 ($[M+2]^+$), 1003 ($[M+3]^+$). Anal. Calcd for $C_{62}H_{48}N_8O_2Zn\cdot H_2O$: C, 72.97; H, 4.94; N, 10.98. Found: C, 72.90; H, 4.65; N, 10.92.

4.3.6. Synthesis of 5,10,15-tris(3-amino-4-methylphenyl)-20-(4-methylphenyl)porphyrin (10) and 5,10,15,20-tetrakis(3-amino-4-methylphenyl)porphyrin (11). To a solution of chloranil (2.77 g, 11.3 mmol) in dry CH_2Cl_2 (500 mL) were added 4-methyl-3-nitrobenzaldehyde **6** (1.24 g, 7.51 mmol), 4-methylbenzaldehyde **7** (0.901 g, 7.50 mmol), and pyrrole **8** (1.01 g, 15.1 mmol) under N_2. After the mixture was stirred for a few minutes at ambient temperature under darkness, $BF_3\cdot OEt_2$ (0.95 mL, 7.56 mmol) was added, and then, the mixture was stirred for 1 h at the same temperature. The mixture was directly poured onto the top of an alumina column, and allowed to pass through using CH_2Cl_2 as eluent. The resultant solution was concentrated to ca. 200 mL on a rotary evaporator, and then, washed with satd $NaHCO_3$ (100 mL×3). The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed on a rotary evaporator. The residual dark purple solid was roughly purified by silica gel column chromatography (eluent; $CHCl_3$/hexane, 4:1, v/v) to obtain a fraction of a mixture of 10,15,20-tris(4-methyl-3-nitrophenyl)-5-(4-methylphenyl)porphyrin and 5,10,15,20-tetrakis(4-methyl-3-nitrophenyl)porphyrin. After removal of the solvent on a rotary evaporator, the residual dark purple solid was added to hot concd HCl (50 mL, 65 °C), followed by addition of $SnCl_2\cdot 2H_2O$ (1.34 g, 5.94 mmol), and then, the reaction mixture was stirred at the same temperature for 2 h. After cooling, to the mixture was carefully added 27% aqueous NH_3 (70 mL) on an ice bath, and then, $CHCl_3$ (100 mL) was added. The mixture was stirred vigorously at ambient temperature for 2 h. The

mixture was allowed to pass through a paper filter with Celite® mounted. The filtrate was washed with satd $NaHCO_3$ (100 mL), satd brine (100 mL) and water (100 mL). After dried over anhydrous Na_2SO_4, the solvent was removed by evaporation. Purification of a resultant mixture by silica gel column chromatography (eluent; $CHCl_3$/ethyl acetate, 4:1, v/v) yielded **10** (162 mg, 0.226 mmol, 6%) and **11** (112 mg, 0.150 mmol, 4%) as dark purple solids, respectively.

4.3.7. 5,10,15-Tris(3-amino-4-methylphenyl)-20-(4-methylphenyl)porphyrin (10). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.81 (br, 2H, inner-N*H*), 2.46 (s, 9H, 5,10,15-Ar-CH_3), 2.69 (s, 3H, 20-Ar-CH_3), 3.78 (br, 6H, –NH_2), 7.36 (d, J=7.3 Hz, 3H, 5,10,15-Ar-*H*), 7.49–7.56 (m, 8H, 6H of 5,10,15-Ar-*H* and 2H of 20-Ar-*H*), 8.08 (d, J=7.5 Hz, 2H, 20-Ar-*H*), 8.82 (d, J=4.6 Hz, 2H, pyrrole β-*H*), 8.90–8.93 (m, 6H, pyrrole β-*H*); TLC (silica gel, eluent; $CHCl_3$/ethyl acetate, 5:1, v/v), R_f=0.15; IR (KBr) 1616, 3312, 3367, 3451 cm^{-1}; FAB MS *m/z* 715 (M^+). Anal. Calcd for $C_{48}H_{41}N_7 \cdot H_2O$: C, 78.55; H, 5.91; N, 13.36. Found: C, 78.79; H, 5.58; N, 13.36.

4.3.8. 5,10,15,20-Tetrakis(3-amino-4-methylphenyl)porphyrin (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.82 (br, 2H, inner-N*H*), 2.51 (s, 12H, Ar-CH_3), 3.86 (br, 8H, –NH_2), 7.39 (d, J=7.6 Hz, 4H, Ar-*H*), 7.53–7.57 (m, 8H, Ar-*H*), 8.91 (s, 8H, pyrrole β-*H*); TLC (silica gel, eluent; $CHCl_3$/ethyl acetate, 5:1, v/v), R_f=0.05; IR (KBr) 1620, 3312, 3358, 3451 cm^{-1}; FAB MS *m/z* 730 (M^+). Anal. Calcd for $C_{48}H_{42}N_8 \cdot H_2O$: C, 76.98; H, 5.92; N, 14.96. Found: C, 77.20; H, 5.58 N, 14.84.

4.3.9. {20-(4-Methylphenyl)-5,10,15-tris[4-methyl-3-(3-phenylureylen-1-yl)phenyl]porphyrinato}zinc(II) (3). To a solution of **10** (50.0 mg, 0.0698 mmol) in dry CH_2Cl_2 (30 mL) was added phenylisocyanate (28.0 mg, 0.235 mmol) under N_2. After the reaction mixture was stirred at ambient temperature for 15 h, the solvent was removed on a rotary evaporator. $CHCl_3$ (50 mL) was poured to the residual dark purple solid, followed by addition of a saturated ethanolic solution of $Zn(OAc)_2$ (50 mL). The mixture was stirred at 50 °C for 1 h, and then, the solvent was removed by evaporation. The residue was dissolved in THF (20 mL) and filtered to remove insoluble materials. The resultant mixture was purified by size exclusion chromatography (THF as eluent). Further purification of the obtained solid by reprecipitation from THF into hexane yielded **3** as a purple solid (37.9 mg, 0.033 mmol, 48%): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.59 (s, 9H, 5,10,15-Ar-CH_3), 2.66 (s, 3H, 20-Ar-CH_3), 6.85–6.90 (m, 3H, Ph-*H*), 7.14–7.21 (m, 6H, Ph-*H*), 7.37–7.41 (m, 6H, Ph-*H*), 7.56–7.60 (m, 5H, 3H of 5,10,15-Ar-*H* and 2H of 20-Ar-*H*), 7.73–7.77 (m, 3H, 5,10,15-Ar-*H*), 8.06–8.08 (m, 2H, 20-Ar-*H*), 8.27 (m, 3H, –N*H*), 8.76–8.78 (m, 5H, 2H of pyrrole β-*H* and 3H of 5,10,15-Ar-*H*), 8.87–8.88 (m, 6H, pyrrole β-*H*), 9.16–9.20 (br, 3H, –N*H*); IR (KBr) 1663, 3369 cm^{-1}; FAB MS *m/z* 1134 (M^+), 1135 ([M+1]$^+$), 1136 ([M+2]$^+$), 1137 ([M+3]$^+$). Anal. Calcd for $C_{69}H_{54}N_{10}O_3Zn \cdot H_2O$: C; 71.78, H; 4.89, N; 12.13. Found: C, 71.73; H, 4.68; N, 12.04.

4.3.10. {5,10,15,20-Tetrakis[4-methyl-3-(3-phenylureylen-1-yl)phenyl]porphyrinato}zinc(II) (4). To a solution of **11** (50.0 mg, 0.0684 mmol) in dry CH_2Cl_2 (50 mL) was added phenylisocyanate (35.0 mg, 0.294 mmol) under N_2. After the reaction mixture was stirred at ambient temperature for 4 h, the solvent was removed on a rotary evaporator. $CHCl_3$ (50 mL) was poured to the residue, followed by addition of a saturated ethanolic solution of $Zn(OAc)_2$ (50 mL). The mixture was stirred at 50 °C for 1 h, and then, the solvent was removed by evaporation. The residue was dissolved in THF (20 mL) and filtered to remove insoluble materials. The resultant mixture was purified by size exclusion chromatography (THF as a eluent). The reside was thoroughly purified by reprecipitation from THF into hexane to afford **4** as a purple solid (45.0 mg, 0.0354 mmol, 52%): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.59 (s, 12H, 5,10,15,20-Ar-CH_3), 6.85–6.90 (m, 4H, Ph-*H*), 7.14–7.21 (m, 8H, Ph-*H*), 7.35–7.41 (m, 8H, Ph-*H*), 7.57 (m, 4H, 5,10,15,20-Ar-*H*), 7.75–7.77 (m, 4H, 5,10,15,20-Ar-*H*), 8.28 (br, 4H, –N*H*), 8.78–8.80 (m, 4H, 5,10,15,20-Ar-*H*), 8.88 (s, 8H, pyrrole β-*H*,), 9.16–9.20 (m, 4H, –N*H*); IR (KBr) 1662, 3363 cm^{-1}; FAB MS *m/z* 1268 (M^+), 1269 ([M+1]$^+$), 1270 ([M+2]$^+$), 1271 ([M+3]$^+$). Anal. Calcd for $C_{76}H_{60}N_{12}O_4Zn \cdot 2H_2O$: C, 69.85; H, 4.94; N, 12.86. Found: C, 69.96; H, 4.61; N, 12.62.

4.3.11. 4-(1-Octyn-1-yl)benzaldehyde (12). To a mixture of 4-bromobenzaldehyde (27.8 g, 150 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.12 g, 1.60 mmol) and 1-octyne (18.8 g, 171 mmol) in Et_3N (200 mL) were added cupper(I) iodide (0.609 g, 3.20 mol). The mixture was stirred at 50 °C for 12 h under N_2. Insoluble materials were removed by filtration, and the filtrate was washed with satd brine (100 mL×3) and water (100 mL). Purification by flash chromatography (silica gel, hexane as eluent) afforded **12** (31.5 g, 147 mmol, 98%), which was used in the next reaction without further purification due to instability under air. The spectroscopic data was identical to the reported data:[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.90 (t, J=7.1 Hz, 3H, –CH_3), 1.28–1.64 (m, 8H, –CH_2–), 2.44 (t, J=7.1 Hz, 2H, –C≡C–CH_2–), 7.53 (d, J=8.3 Hz, 2H, Ar-*H*), 7.80 (d, J=8.3 Hz, 2H, Ar-*H*), 9.99 (s, 1H, –C*H*O); IR (KBr) 1704, 2225, 2855, 2929, 2955 cm^{-1}; FAB MS *m/z* 214 (M^+).

4.3.12. 4-Octylbenzaldehyde (13). H_2 gas was introduced into a vigorously stirred solution of **12** (31.5 g, 147 mmol) in ethyl acetate (200 mL) for 5 min via a syringe needle. To the solution was added a suspension of palladium/activated carbon (Pd 10%) (1.50 g) in ethyl acetate (30 mL). The mixture was stirred for 6 h under H_2, and then, allowed to pass through a filter with Celite® mounted. The Celite® was thoroughly washed with hexane (200 mL). The filtrate was combined with the washing, and the solvent was removed on a rotary evaporator to yield a dark yellow oil. Purification of the resultant oil by silica gel column chromatography (eluent; hexane/ethyl acetate, 20:1, v/v) yielded 4-octylbenzaldehyde **13** (26.8 g, 122 mmol, 83%), which was used in the next reaction without further purification due to instability under air: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.88 (t, J=7.1 Hz, 3H, –CH_3), 1.26–1.32 (m, 10H, –CH_2–), 1.61–1.67 (m, 2H, –CH_2–), 2.69 (t, J=7.1 Hz, 2H, Ar-CH_2–), 7.34 (d, J=7.8 Hz, 2H, Ar-*H*), 7.80 (d, J=7.8 Hz, 2H, Ar-*H*), 9.97 (s, 1H, –C*H*O); IR (KBr) 1704, 2856, 2924, 2955 cm^{-1}; FAB MS *m/z* 218 (M^+).

4.3.13. 3-Nitro-4-octylbenzaldehyde (14). To a mixture of fuming HNO_3 (1.7 mL) and concd sulfuric acid (12.4 mL) was added **13** (4.36 g, 20.0 mmol) dropwise on an ice bath with vigorous stirring under N_2. After completion of the addition of the aldehyde, the ice bath was removed, and the reaction mixture was stirred for 15 min. The mixture was poured onto ice, and then, the product was extracted into Et_2O. The organic phase was washed with satd $NaHCO_3$ (100 mL×3) and water (100 mL). After dried over anhydrous Na_2SO_4, the solvent was removed by evaporation. Purification of the residual mixture by silica gel column chromatography (eluent; hexane/$CHCl_3$, 10:1, v/v) yielded **14** (3.35 g, 12.7 mol, 64%), which was used in the next reaction without further purification due to instability under air: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.88 (t, J=7.1 Hz, 3H, –C*H*$_3$), 1.21–1.51 (m, 10H, –C*H*$_2$–), 1.57–1.63 (m, 2H, –C*H*$_2$–), 2.95 (t, J=7.1 Hz, 2H, Ar-C*H*$_2$–), 7.54 (d, J=7.8 Hz, 2H, Ar-*H*), 8.02 (d, J=7.8 Hz, 2H, Ar-*H*), 10.03 (s, 1H, –C*H*O); IR (KBr) 1348, 1529, 1701, 2853, 2922, 2955 cm^{-1}; FAB MS *m*/*z* 263 (M^+), 264 ($[M+1]^+$).

4.3.14. 5,10,15,20-Tetrakis(3-nitro-4-octylphenyl)porphyrin (15). In dry CH_2Cl_2 (500 mL) were dissolved **14** (2.23 g, 8.47 mmol) and pyrrole **8** (568 mg, 8.47 mmol), and the mixture was stirred for 15 min under N_2. $BF_3\cdot OEt_2$ (0.170 mL, 1.35 mmol) was added under darkness, and the mixture was stirred for 1 h. *p*-Chloranil (1.56 g, 6.34 mmol) was added at one portion, and the mixture was stirred for 1 h at the same temperature. Then, the resultant mixture was put on the top of an alumina column and allowed to pass through using CH_2Cl_2 as eluent. The solvent was removed on a rotary evaporator to yield a dark brown solid, which was purified by silica gel column chromatography (eluent; CH_2Cl_2/hexane, 3:2, v/v) to yield **15** as a dark purple solid (750 mg, 0.603 mmol, 28%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.87 (br, 2H, inner-N*H*), 0.94 (t, J=7.1 Hz, 12H, –C*H*$_3$), 1.36–1.65 (m, 40H, –C*H*$_2$–), 1.93–2.01 (m, J=7.8 Hz, 8H, Ar-CH$_2$C*H*$_2$–), 3.24 (t, J=7.1 Hz, 8H, Ar-C*H*$_2$–), 7.78 (d, J=6.4 Hz, 4H, Ar-*H*), 8.36 (d, J=6.4 Hz, 4H, Ar-*H*), 8.72 (s, 4H, Ar-*H*), 8.87 (s, 8H, pyrrole β-*H*); IR (KBr) 1344, 1529, 2853, 2926, 2953 cm^{-1}; FAB MS *m*/*z* 1243 (M^+), 1244 ($[M+1]^+$). Anal. Calcd for $C_{76}H_{90}N_8O_8$: C, 73.40, H, 7.29, N, 9.01. Found: C, 73.49; H, 7.53; N, 8.99.

4.3.15. 5,10,15,20-Tetrakis(3-amino-4-octyl-phenyl)porphyrin (16). To a stirred hot concd HCl (90 mL, 65 °C) was added **15** (500 mg, 0.402 mmol) and $CHCl_3$ (20 mL), followed by addition of $SnCl_2\cdot 2H_2O$ (1.90 g, 8.41 mmol). The reaction mixture was stirred at the same temperature for 2 h before another portion of $SnCl_2\cdot 2H_2O$ (2.01 g, 8.91 mmol) and $CHCl_3$ (20 mL) was added. The same process was repeated again ($CHCl_3$, 20 mL; $SnCl_2\cdot 2H_2O$, 1.83 g, 8.11 mmol), and then, the reaction mixture was stirred at the same temperature for 1 h. After cooling, to the mixture was carefully added 27% aqueous NH_3 (100 mL) on an ice bath, and then, $CHCl_3$ (100 mL) was added. The mixture was stirred vigorously at ambient temperature for 2 h and allowed to pass through a paper filter with Celite® mounted. The filtrate was washed with water (100 mL) three times. After dried over anhydrous $MgSO_4$, the solvent was removed by evaporation. Purification of the resultant solid by silica gel column chromatography (eluent; hexane/ethyl acetate, 20:1, v/v) yielded **16** as a purple solid (391 mg, 0.348 mmol, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) −2.81 (br, 2H, inner-N*H*), 0.94 (t, J=7.3 Hz, 12H, –C*H*$_3$), 1.34–1.65 (m, 40H, –C*H*$_2$–), 1.88–1.96 (m, 8H, Ar-CH$_2$C*H*$_2$–), 2.81 (t, J=7.3 Hz, 8H, Ar-C*H*$_2$–), 3.87 (br, 8H, –N*H*$_2$), 7.38 (d, J=7.3 Hz, 4H, Ar-*H*), 7.54 (s, 4H, Ar-*H*), 7.58 (d, J=7.3 Hz, 4H, Ar-*H*), 8.92 (s, 8H, pyrrole β-*H*); IR (KBr) 1618, 2854, 2924, 2953, 3321, 3362, 3441 cm^{-1}; FAB MS *m*/*z* 1123 (M^+), 1124 ($[M+1]^+$). Anal. Calcd for $C_{76}H_{98}N_8$: C, 81.24; H, 8.79; N, 9.97. Found: C, 81.11; H, 8.94; N, 10.01.

4.3.16. {5,10,15,20-Tetrakis[4-octyl-3-(3-phenylureylen-1-yl)phenyl]porphyrin (the precursor of 5). To a solution of **16** (200 mg, 0.178 mmol) in dry CH_2Cl_2 (20 mL) was added phenylisocyanate (170 mg, 1.43 mmol) under N_2. After the reaction mixture was stirred at ambient temperature for 15 h, the solvent was removed on a rotary evaporator. The residue was dissolved in THF (40 mL) and filtered to remove insoluble materials. The resultant mixture was purified by size exclusion column chromatography (THF as eluent). Reprecipitation of the obtained material from THF into hexane yielded {5,10,15,20-tetrakis[4-octyl-3-(3-phenylureylen-1-yl)phenyl]porphyrin as a purple solid (182 mg, 0.114 mmol, 64%), which was used in the next step without further purification: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) −2.90 (br, 2H, inner-N*H*), 0.86–0.90 (t, J=7.0 Hz, 12H, –C*H*$_3$), 1.30–1.58 (m, 40H, –C*H*$_2$–), 1.82–1.87 (m, 8H, Ar-CH$_2$–C*H*$_2$–), 2.90–2.95 (t, J=7.0 Hz, 8H, Ar-C*H*$_2$–), 6.85–6.89 (m, 4H, Ph-*H*), 7.12–7.21 (m, 8H, Ph-*H*), 7.39–7.42 (m, 8H, Ph-*H*), 7.55–7.58 (m, 4H, 5,10,15,20-Ar-*H*), 7.80–7.82 (m, 4H, 5,10,15,20-Ar-*H*), 8.24 (br, 4H, –N*H*), 8.70–8.71 (m, 4H, 5,10,15,20-Ar-*H*), 8.90 (s, 8H, pyrrole β-*H*), 9.14–9.16 (m, 4H, –N*H*); IR (KBr) 1653, 2856, 2926, 2953, 3320 cm^{-1}; FAB MS *m*/*z* 1599 (M^+), 1600 ($[M+1]^+$), 1601 ($[M+2]^+$).

4.3.17. {5,10,15,20-Tetrakis[4-(1-octyl)-3-(3-phenylureylen-1-yl)phenyl]porphyrinato}zinc(II) (5). {5,10,15,20-Tetrakis[4-(1-octyl)-3-(3-phenylureylen-1-yl)phenyl]porphyrin (100 mg, 0.0625 mmol) was dissolved in DMSO (10 mL), followed by addition of a saturated ethanolic solution of $Zn(OAc)_2$ (100 mL). The mixture was stirred at reflux for 1 h, and then, the ethanol was removed by evaporation. To the resultant mixture was added water (100 mL) followed by filtration to yield a purple solid. The solid was dried in vacuo, and then, dissolved in THF (50 mL) to remove insoluble materials by filtration. The filtrate was evaporated, and the residue was purified by size exclusion column chromatography (THF as eluent, two times). Further purification of the obtained solid by reprecipitation from THF into hexane yielded **5** as a purple solid (98.0 mg, 0.0589 mmol, 94%): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 0.86 (m, 12H, –C*H*$_3$), 1.30–1.59 (m, 40H, –C*H*$_2$–), 1.85–1.89 (m, 8H, Ar-CH$_2$–C*H*$_2$–), 2.91–2.95 (m, 8H, Ar-C*H*$_2$–), 6.86–6.89 (m, 4H, Ph-*H*), 7.14–7.21 (m, 8H, Ph-*H*), 7.39–7.42 (m, 8H, Ph-*H*), 7.55–7.58 (m, 4H, 5,10,15,20-Ar-*H*), 7.79–7.82 (m, 4H, 5,10,15,20-Ar-*H*), 8.24 (br, 4H, –N*H*), 8.69–8.71 (m, 4H, 5,10,15,20-Ar-*H*), 8.90 (s, 8H, pyrrole β-*H*), 9.14–9.16 (m, 4H, –N*H*); IR (KBr) 1660, 2854, 2926, 2953, 3302 cm^{-1}; FAB MS *m*/*z* 1661 (M^+), 1662 ($[M+1]^+$), 1663 ($[M+2]^+$). Anal. Calcd for $C_{104}H_{116}N_{12}O_4Zn\cdot H_2O$: C, 74.28; H, 7.07; N, 10.00. Found: C, 74.08; H, 7.30; N, 9.90.

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