Porphyrins

Heteroleptic Tetrapyrrole-Fused Dimeric and Trimeric Skeletons with Unusual Non-Frustrated Fluorescence

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Abstract: Phthalocyanine (Pc) and porphyrin (Por) chromophores have been fused through the benzo[α]pyrazine moiety, resulting in unprecedented heteroleptic tetrapyrrolefused dimers and trimers. The heteroleptic tetrapyrrole nature has been clearly revealed based on single-crystal Xray diffraction analysis of the zinc dimer. Electrochemical analysis, theoretical calculations, and time-resolved spectroscopic results disclose that the two/three-tetrapyrrole-fused skeletons behave as one totally π -conjugated system as

Introduction

Porphyrins (Por) and phthalocyanines (Pc), with delocalized π electron systems and versatile physical and chemical properties, are promising molecular materials with a wide variety of applications.^[1] When these tetrapyrrole macrocycles are fused into further extended aromatic skeletons, individual Pc/Por π systems conjugate together to result in characteristic optical and redox features for this new class of compounds, rendering them useful in various disciplines ranging from photosynthetic antenna models to photodynamic therapy (PDT). However, attention in this direction seems to focus just on the homo-tetrapyrrole conjugated systems including various kinds of homo-Por-fused oligomers^[2,3] and homo-Pc-fused dimers and trimers.^[4] Heteroleptic tetrapyrrole oligomers that are constructed by simultaneously fusing the Pc and Por skeletons together have been rarely studied, with the very few preliminary reports limited to the synthesis and some spectroscopic characterizations of only three Pc-Por dimers fused through the benzene,^[5] pyrazine,^[6] or naphthalene^[7] units (Scheme S1 in the Supporting Information).

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[b]	J. Oh, ⁺ K. H. Park, Prof. Dr. D. Kim Spectroscopy Laboratory for Functional π -Electronic Systems and Department of Chemistry, Yonsei University, Seoul 120-749 (Korea) E-mail: dongho@yonsei.ac.kr	Results and Dis
(†) 💻	These authors contributed equally to this work. Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504837.	The key precursor for mers H_4 -1 and H_6 -2.

a result of the strong conjugative interaction between/ among the tetrapyrrole chromophores. In particular, the effectively extended π -electron system through the fusedbridge induced strong electronic communication between the Pc and Por moieties and large transition dipole moments in the Pc-Por-fused systems, providing high fluorescence quantum yields (>0.13) and relatively long excited state lifetimes (>1.3 ns) in comparison with their homo-tetrapyrrolefused analogues.

In this regard, fusing individual Por and Pc chromophores into heteroleptic tetrapyrrole conjugated systems is a fascinating approach to produce new functional molecules. The heteroleptic nature leads to unique optical and electrochemical properties in the new compounds. Moreover, their efficiently extended π -conjugated systems can induce intriguing behaviors such as near-infrared (NIR) absorption, emission, and nonlinear optical properties, which provide the potential for use in applications such as molecular sensors, NIR dyes, and PDT materials.

Towards developing novel tetrapyrrole-based advanced molecular materials with diverse application potentials, in the present case, we report the synthesis and characterization of unprecedented heteroleptic tetrapyrrole-fused dimeric and trimeric skeletons, {[H₂/ZnBDAPc(OC₈H₉)₆][(H₂/ZnTMP)]} (H_4-1/Zn_2-1) and $\{[(H_2/ZnTMP)][cis-H_2/Zn(BDA)_2Pc(OC_8H_9)_4][(H_2/2n_2)]$ ZnTMP)]} $(H_6 - 2/Zn_3 - 2)$ $[BDAPc(OC_8H_9)_6 = dianion$ of 2,3,9,10,16,17-hexakis(2,6-dimethylphenoxy)-benzo-22,25-diazaphthalocyanine, cis-(BDA)₂Pc(OC₈H₉)₄ = dianion of 2,3,9,10-tetrakis(2,6-dimethylphenoxy)-15,18,22,25-bis(benzodiaza)phthalocyanine, TMP = dianion of 5,10,15,20-tetrakis(2,4,6-trimethylphenyl) porphyrin] (Scheme 1). Moreover, we have explored in state and excited-state behavior of the and trimers by steady-state and time-res and electrochemical analysis in combinacalculations.

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Scheme 1. Molecular structures of Pc–Por-fused dimers 1 and trimers 2 involved in the present work together with their monomeric phthalocyanine and porphyrin references 3 and 4.

2',3'-di-cyanopyrazino[2,3- β]porphyrin (5), was prepared by heating at reflux in trichlorobenzene with metal-free 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin (H₂TMP; H₂-4) and 2,3-bis(bromomethyl)pyrazine as the starting materials according to the literature procedure to give 5 in approximately 10.0% yield.^[8] It is worth noting that for the purpose of enhancing the solubility and impeding the aggregation of the target Pc-Por-fused oligomeric compounds, 4,5-bis(2,6-dimethylphenoxy)phthalonitrile with two bulky substituents was chosen as the second precursor. As a result, mixed cyclic tetramerization of 5 and 4,5-bis(2,6-dimethylphenoxy)phthalonitrile in a 1:10 molar ratio in the presence of lithium pentanolate in *n*-pentanol heated at reflux followed by treatment with acetic acid led to the isolation of the target metal-free Pc-Por-fused dimer H_4 -1 (9.8%) and the first Pc–Por-fused trimer H_6 -2 (2.6%) with quite good solubility in common organic solvents in addition to a large quantity of metal-free 2,3,9,10,16,17,23,24octakis(2,6-dimethylphenoxy)phthalocyanine $H_2Pc(OC_8H_9)_8$ (Scheme 2). For reference, unsymmetrical metal-free 2,3,9,10,16,17-hexakis(2,6-dimethylphenoxy)-22,25-diaza-phthalocyanine H₂-3 was also synthesized and isolated according to the literature procedure.^[9] Further reaction of the metal-free tetrapyrrole species, including the dimer H_4 -1, trimer H_6 -2, and monomer H₂-3, with Zn(OAc)₂·2H₂O in DMF at 90 °C led to the isolation of the zinc complexes Zn_2 -1, Zn_3 -2, and Zn-3.

All these newly prepared compounds gave satisfactory elemental analysis data (Table S1 in the Supporting Information). Their MALDI-TOF mass spectra clearly show intense signals for the corresponding molecular ion $[M]^+$. The isotopic pattern closely resembles the simulated one, as exemplified by the spectrum of the Pc–Por-fused dimer H₄-1 (Figure S1 in the Supporting Information). Nevertheless, these compounds were fur-



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Scheme 2. Synthesis of Pc–Por-fused dimers (H₄-1 and Zn₂-1) and trimers (H₆-2 and Zn₃-2) as well as the reference phthalocyanines (H₂-3 and Zn-3). (I) Li, *n*-C₅H₁₁OH, reflux, 2 h; CH₃COOH, CH₃OH, 1 h. (II) Zn(OAc)₂·2H₂O, DMF, 90 °C, 4 h.

ther characterized with a range of spectroscopic techniques including NMR, IR, electronic absorption, and fluorescence spectroscopy.

Satisfactory ¹H NMR spectra were obtained for the dimer H_4 -1 in CDCl₃ (Figure S2 in the Supporting Information). With the help of the ¹H-¹H COSY spectrum (Figure S3 in the Supporting Information), all the signals could be unambiguously assigned with the results detailed in Table S2 (in the Supporting Information). The ¹H NMR spectrum of H₄-1 exhibited three singlets at $\delta =$ 8.92, 8.51, and 8.42 ppm from the Pc α protons and one singlet at $\delta = 8.06$ ppm from the protons on the ben $zo[\alpha]$ pyrazine moiety owing to the C_{2v} molecular symmetry. The two doublets at $\delta = 8.72$ and 8.58 ppm, which were correlated with each other in the ¹H-¹H COSY spectrum, were assigned to the two kinds of β protons on the Por moiety. The other β proton signal on the Por moiety was observed at $\delta\!=$ 8.92 ppm, which is overlapped by one Pc α proton singlet. The two singlets observed at $\delta =$ 7.56 and 7.30 ppm were attributed to the protons of the meso-attached aryl groups on the Por moiety. Signals for the aromatic protons of 2,6-dimethylphenoxyl substituents exhibited one singlet at $\delta =$ 7.50 ppm and multiplets at $\delta =$ 7.44–7.37 ppm with an integral ratio of 1:2. Also, on the basis of the analysis of the ¹H-¹H COSY spectrum of this compound, the aliphatic proton signals can be unambiguously assigned, with the signals appearing at $\delta = 2.95$, 2.65, and 1.92 ppm, which are correlated with the singlets at δ = 7.56 and 7.30 ppm, belonging to the methyl protons on the Por moiety. The signals appearing at $\delta = 2.54$, 2.48, and 2.46 ppm, correlated with the signals for the aromatic protons of the 2,6-dimethylphenoxyl substituents, were assigned to the



methyl protons on the Pc moiety. In addition, the two singlets at $\delta = -0.51$ and -2.17 ppm were assigned to the inner isoindole/pyrrole protons. As can be expected, except for the absence of the inner isoindole/pyrrole proton signals, the zinc complex Zn₂-1 gives similar signals in its NMR spectrum, which are therefore assigned in a similar manner (Figure S4 in the Supporting Information). This was also true for the two analogous trimers H₆-2 and Zn₃-2 (Figures S5–S7 in the Supporting Information).

It is noteworthy that two possible structural isomers with cis- and trans-configuration might exist for the Pc-Por-fused trimer H₆-2. However, cis-H₆-2 was revealed as the sole isomer isolated from the reaction mixture on the basis of the NMR spectroscopic results. All efforts thus far have failed to afford the trans-isomer of the Pc-Por-fused trimer. This seems strange at first glance, but can be easily rationalized on the basis of the theoretical analysis of the phthalocyanine formation mechanism with the half-phthalocyanine as the key intermediate.^[10,11] Nevertheless, this is also in good agreement with the previous isolation of the cis-isomer, rather than the transisomer, of pyrene-fused unsymmetrical phthalocyanine derivative Zn[Pc(Pz-pyrene)₂(OC₈H₉)₄].^[9] As exhibited in Figure S5 (in the Supporting Information), observation of the two Pc α proton singlets at $\delta = 9.34$ and 9.03 ppm, and two singlets for the protons on the benzo[α]pyrazine rings at $\delta = 8.78$ and 8.30 ppm in the ¹H NMR spectrum of H_6 -2 clearly reveals the C_{2v} molecular symmetry of this trimer with a *cis*-configuration rather than D_{2h} symmetry with a trans-configuration. This was further supported by the observation of four signals resulting from the β protons on the Por moieties at $\delta =$ 8.74, 8.64, 8.61, and 8.53 ppm. Signals for the protons in the meso-attached aryl moieties on the Por side appear at $\delta\!=\!7.82$, 7.62, and 7.32 ppm, whereas the aromatic protons of the 2,6-dimethylphenoxyl substituents exhibit one singlet at $\delta =$ 7.51 ppm and multiplets at $\delta =$ 7.48–7.41 ppm. According to the ¹H-¹H COSY spectrum (Figure S6 in the Supporting Information), the aliphatic proton signals in the NMR spectrum of trimer H₆-2 can also be unambiguously assigned in a similar way to the dimer H₄-1 as tabulated in Table S1 (in the Supporting Information). The singlets at $\delta = 0.44$ and -2.07 ppm with an integral ratio of 1:2 can be assigned to the inner isoindole and pyrrole protons, respectively.

The IR spectra of H_4 -1 and H_6 -2 as well as Zn_2 -1 and Zn_3 -2 are shown in Figure S8 (in the Supporting Information). In addition to the bands associated with the aromatic Pc and Por moieties, such as the C—H wagging and torsion vibrations, and the isoindole ring and the C=N aza group stretching vibrations,^[12] the bands at 2966–2972, 2918–2920, and 2848– 2850 cm⁻¹ are assigned to the asymmetric and symmetric C—H stretching vibrations of the -CH₃ groups, whereas those at 1263–1284 and 1093–1095 cm⁻¹ are ascribed to the asymmetric and symmetric C—O—C stretching vibrations of the 2,6-dimethylphenoxy groups in the Pc moiety.^[13] In the IR spectra of H₄-1 and H₆-2, two weak bands from the asymmetric N—H stretching vibrations of the isoindole and pyrrole moieties were observed at approximately 3300 cm⁻¹,^[14] which disappear in the IR spectra of the zinc complexes Zn_2 -1 and Zn_3 -2.

Structural study

Single crystals of the zinc complex Zn₂-1 suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into the CHCl₃ solution of this compound with the help of 1,4diazabicyclo[2.2.2]octane (DABCO). Zn2-1 crystallizes in the triclinic space group P1 with two dimeric molecules and two DABCO molecules per unit cell. The crystal structure of Zn₂-1 unambiguously reveals its planar structure (Table S3 and Figure S9 in the Supporting Information). However, despite great efforts thus far, repeated trials still failed to afford single crystals of the Pc-Por-fused trimer 2 suitable for X-ray diffraction analysis. The geometrical optimizations of H₄-1, H₆-2, Zn₂-1, and Zn₃-2 have been carried out based on the crystal structure of Zn₂-1 (Figure S10 in the Supporting Information). The optimized structure of Zn₂-1 adopts an almost coplanar molecular structure with a dihedral angle between the mean planes of the 25-atom ZnPor moiety and 41-atom ZnPc moiety as small as 2.15°. Similarly, H₄-1, H₆-2, and Zn₃-2 displayed coplanar geometries with the dihedral angles of 5.64°, 18.34°, and 17.90°, respectively. These features indicate the efficiently π conjugated heteroleptic tetrapyrrole nature, which extends over the whole Pc-Por-fused dimer or trimer through their benzo[α]pyrazine bridges.

Electrochemical properties

The electrochemical behavior of H_4 -1 and H_6 -2 as well as their zinc complexes Zn₂-1 and Zn₃-2 was investigated by differential pulse voltammetry (DPV) in CH₂Cl₂ and the half-wave redox potentials versus saturated calomel electrode (SCE) are tabulated in Table S4 (in the Supporting Information). For a comparative study, the electrochemistry of reference compounds H₂-3 and H₂-4 as well as Zn-3 and Zn-4 was also studied. Figure S11 (in the Supporting Information) shows the differential pulse voltammograms of compounds H₄-1, H₆-2, H₂-3, and H₂-4. As can be seen, the Pc-Por-fused dimer H₄-1 displayed four reduction potentials at -0.61, -0.93, -1.30, and -1.55 V, and three oxidation potentials at +1.18, +1.04, and +0.84 V. Observation of three oxidation processes at +0.84, +1.04, and +1.18 V for the Pc–Por-fused dimer H₄-1, which cannot be simply assigned to those of the individual moieties (at +1.02and $\,+\,1.35\,V$ for $H_2\text{--}\textbf{3}$ and $\,+\,0.97$ and $\,+\,1.38\,V$ for $H_2\text{--}\textbf{4})\text{,}$ indicates the strong electronic communication between the HOMOs of the two constituents in the fused dimer system, H₄-1. Moreover, H₄-1 showed a small potential difference between the first oxidation and reduction processes ($\Delta E^{o}_{1/2} =$ + 1.45 V) in comparison with + 1.59 V for H₂-3 and + 2.22 V for H₂-4. These results support the effective conjugation interaction through the benzo[α]pyrazine unit in the Pc–Por-fused system. In the reduction processes, the first and second reduction processes of H₄-1 can be said to occur mainly on the Pc moiety owing to the very close reduction potentials of the reference Pc compound, H_2 -3, at -0.57 and -0.91 V, whereas the third and fourth reduction processes of H₄-1 seem to mainly correspond to the Por moiety owing to the reduction processes with similar potentials at -1.25 and -1.68 V for the refer-



ence Por compound, H₂-**4**. These results can be ascribed to the large energy gap between the LUMOs of the Pc and Por moieties compared with that of the HOMOs, which results in less effective electronic communication between the Pc and Por moieties, leading to the different features between the oxidation and reduction processes of H₄-1 (see below). Similar features were observed for the dimeric zinc complex Zn_2 -1.

For the trimer, H₆-**2**, six reduction (at -0.39, -0.57, -0.86, -1.02, -1.31, and -1.73 V) and three oxidation (at +0.85, +1.05, and +1.22 V) processes were revealed in the voltammogram. In addition, the $\Delta E^{o}_{1/2}$ of +1.24 V was estimated for H₆-**2**, which is smaller than that for H₄-**1**. In the comparative analysis with H₄-**1**, H₂-**3**, and H₂-**4**, these results indicate that the expansion of the fused system intensifies the electronic communication over the three tetrapyrrole chromophores in H₆-**2**. The zinc complex analog, Zn₃-**2**, showed similar features in the voltammograms.

Electronic structures

To gain insight into the electronic structures of the heteroleptic tetrapyrrole-fused dimer and trimer, density functional theory (DFT) calculations were carried out at the B3LYP/LANL2DZ level. Despite the slightly overestimated vertical transition energies, the simulated electronic absorption spectra of H₄-1, H₆-2, H₂-3, and H₂-4 together with their zinc complexes Zn₂-1, Zn₃-2, Zn-3, and Zn-4 are in good agreement with the experimental results (details in the Supporting Information, and see below). Figure 1 compares the molecular orbital distribution and energy levels of H₄-1 with monomeric references H₂-3 and H₂-4 to clarify the interactions between the two tetrapyrrole cores in the Pc–Por-fused dimer H₄-1.

Along with the electrochemical results, the delocalized molecular orbital over the entire molecule in the HOMO of H_4 -1 clearly describes the strong conjugative interaction between the Pc and Por moieties through the benzo[*a*]pyrazine-



Figure 1. Frontier molecular orbitals of H_{4} -1 with the corresponding orbitals of Por (H_2 -4) and Pc (H_2 -3). The HOMOs and LUMOs are represented as H and L, respectively.

fused bridge (Figure 1), suggesting that the fused dimeric compound H₄-1 behaves as a single, totally π -conjugated molecular system. In the LUMO/LUMO+1 and LUMO+2/LUMO+3, the molecular orbitals were partially delocalized over the Pc and Por moieties, respectively. This feature is in accordance with the electrochemical analysis of H₄-1, which result from the large energy gap between the LUMOs of the Pc and Por moieties. This is also true for the Pc–Por-fused trimer H₆-2 and the zinc complexes Zn₂-1 and Zn₃-2 (Figures S12–S14 in the Supporting Information). Here, in the effectively π -conjugated systems, these partially delocalized molecular orbital distributions allude to the intramolecular charge-transfer (CT) character in the Pc–Por-fused systems.

Optical properties

The electronic absorption spectra of H_4 -1 and H_6 -2 as well as their zinc complexes Zn_2 -1 and Zn_3 -2 were recorded in toluene and toluene/pyridine (100:1), respectively. The data are summarized in Table S5 (in the Supporting Information). Figure 2 compares the electronic absorption spectra of H_4 -1 and H_6 -2 with those of the individual tetrapyrrole reference compounds, H_2 -3 and H_2 -4. In the electronic absorption spectra, H_2 -3 shows



Figure 2. Electronic absorption (black line) and fluorescence spectra (blue line) of H₂-4, H₂-3, H₄-1, and H₆-2 in toluene.

an intense B (or Soret) band at 356 nm, an $n-\pi^*$ band associated with the lone electron pairs on the oxygen atoms at 430 nm,^[15] and two intense Q bands at 662 and 683 nm, whereas H₂-4 displays a strong Soret band at 420 nm and four weak Q bands at 515, 547, 592, and 648 nm.^[16] The Pc–Porfused dimer H₄-1 shows two Soret-like bands at 361 and 420 nm, together with the split Q-like bands at 701 and 726 nm with two shoulders at 633 and 668 nm. In comparison with the reference compounds H₂-3 and H₂-4, significant broadening and redshift take place in the absorption bands of H₄-1, indicating the effective π -conjugation extension between the fused Pc and Por chromophores. These features are also

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observed in the Pc–Por-fused systems, H_6 -2, Zn_2 -1, and Zn_3 -2 in Figure 2 and Figure S15 (in the Supporting Information).

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The fluorescence spectra of H₄-1, H₆-2, Zn₂-1, and Zn₃-2 as well as their reference monomeric compounds were measured in toluene and toluene/pyridine (100:1) at room temperature. The maxima for the fluorescence bands were observed at 735, 780, 744, and 776 nm for H₄-1, H₆-2, Zn₂-1, and Zn₃-2, respectively, which were clearly redshifted compared with those of references H₂-3, H₂-4, Zn-3, and Zn-4. The fluorescence quantum yields were estimated as 0.41 for H₄-1, 0.27 for H₆-2, 0.15 for Zn₂-1, and 0.13 for Zn₃-2 (Table 1). Moreover, the fluorescence

Table 1. Fluorescence data, quantum yields (Φ_{i}) and lifetimes (τ_{i}), and radiative (k_{r}) and nonradiative (k_{n}) decay rates for the metal-free and the corresponding zinc compounds for 1–4. ^[a]								
Compound	λ_{\max} [nm]	$\Phi_{\rm f}$	$ au_{\rm f}$ [ns]	$k_{\rm r}^{\rm [b]} [10^7 {\rm s}^{-1}]$	$k_{\rm nr}^{\rm [b]} [10^7 {\rm s}^{-1}]$			
H ₄ -1	735	0.41	5.3	7.7	11.2			
H ₆ -2	780	0.27	2.5	10.8	29.2			
H ₂ - 3	688	0.54	6.0	9.0	7.6			
H ₂ - 4	651	0.06	10.8	0.6	8.7			
Zn ₂ -1	744	0.15	1.9	7.9	44.7			
Zn₃- 2	776	0.13	1.3	10.0	66.9			
Zn- 3	685	0.24	2.6	9.2	29.2			
Zn- 4	645	0.045	2.4	1.9	39.8			
[a] The metal-free compounds for 1–4 were measured in toluene and the zinc compounds for 1–4 were measured in toluene/pyridine(v/v = 100:1). [b] Radiative and nonradiative decay rates can be calculated by using the observed fluorescence quantum yields and fluorescence lifetimes based on the equations: $\Phi_t = k_t/(k_t + k_{nt})$ and $\tau_t = 1/(k_t + k_{nt})$.								

cence decay profiles were fitted with the time constants of 5.3, 2.5, 1.9, and 1.3 ns for H₄-**1**, H₆-**2**, Zn₂-**1**, and Zn₃-**2**, respectively, as shown in Figure 3. Here, the expansion of the fused system, from H₂-**3** to H₄-**1** and H₆-**2**, induced a decrease in fluorescence quantum yield, from 0.54 to 0.27, and lifetime, from 6.0 to 2.5 ns (Figure S16 in the Supporting Information), indicating the acceleration of the nonradiative decay rate along with the extension of the π -electron system.^[4a,17] A similar tendency was observed for Zn-**3**, Zn₂-**1**, and Zn₃-**2**. In accordance with their



Figure 3. Nanosecond time-resolved fluorescence decay profiles for (a) H_4 -1 and (b) H_6 -2 in toluene and (c) Zn_2 -1 and (d) Zn_3 -2 in toluene/pyridine (100:1).

absorption spectral features, these results suggest that either the Pc or Por subunit in the Pc–Por-fused oligomers cannot act as an independent chromophore as in non-conjugated Pc–Por oligomers.^[18]

To further clarify the nature of the excited-state dynamics of the Pc–Por-fused systems, femtosecond transient absorption (fs-TA) measurements were carried out. For comparative studies, the TA spectra were recorded with photoexcitation at 530/720 and 530/760 nm for H₄-1 and H₆-2 and at 550/720 and 550/760 nm for Zn₂-1, and Zn₃-2, respectively (Figure 4 and Figure S17 in the Supporting Information). The TA spectra of



Figure 4. Femtosecond transient absorption spectra and decay profiles (inset) of (a) H₄-1 with $\lambda_{pump} = 530$ nm and (b) H₆-2 with $\lambda_{pump} = 530$ nm in toluene, and (c) Zn₂-1 with $\lambda_{pump} = 550$ nm and (d) Zn₃-2 with $\lambda_{pump} = 550$ nm in toluene/pyridine (100:1) at room temperature.

H₄-1 displayed intense ground-state bleaching for the Q-like band in the range 615-750 nm and broad excited-state absorption bands in the range 450-610 nm. The TA decay profile of H₄-1 was fitted with the time constant of 5.3 ns, which is well-matched with its fluorescence decay. Similar features were observed in the TA spectra and decay profiles of H_6 -2, Zn_2 -1, and Zn₃-2. Here, even with the investigation for the fast excited-state dynamics in the range of approximately 2 ps (Figures S17–S20 in the Supporting Information), no significant spectral features for energy flow from the Por moiety to Pc moiety was observed. Along with the calculation results and electrochemical analysis of H₄-1, H₆-2, Zn₂-1, and Zn₃-2, these TA data strongly suggest that the effective conjugative interaction through the benzo[α]pyrazine-fused bridge induces the Pc-Por-fused oligomers to behave as one-quantum molecular systems.

Fusion of either the Por or Pc moieties into the homo-tetrapyrrole dimers and trimers provides them with distinct physicochemical and optical features induced by the extended conjugated electronic structures, such as extremely redshifted absorption bands to the NIR region. This feature in turn results from the decreased HOMO–LUMO energy gap and the more extended vibrational level structures, which lead to the acceleration of the nonradiative decay rate.^[4a, 19] As a result, the homo-Pc-fused systems typically show extremely low fluorescence yield and short excited-state lifetimes in comparison with their monomers,^[3,4] as exemplified by the significantly decreased fluorescence quantum yield and lifetime of homo-bi-

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nuclear/trinuclear Pcs (0.04/0.8 ns and 0.02/0.4 ns, respectively) in comparison with 0.33/6.2 ns for the Pc monomer.^[4a] In the case of homo-Por-fused systems, although such extension of the π -conjugation decreases the S₁-state lifetime, the perturbation of the electronic structure of Por increases the oscillator strength of the forbidden Q-band transitions, leading to an enhancement of fluorescence quantum yield.[19-20] Interestingly, the Pc-Por-fused dimers and trimers still exhibit quite high fluorescence quantum yield (>0.13) and long excited-state lifetimes (>1.3 ns) in comparison with the homo-tetrapyrrolefused dimers and trimers. Such intense fluorescence in the NIR region for the Pc-Por-fused systems can be attributable to the effective conjugative interaction between the Pc and Por moieties through the benzo[α]pyrazine-fused bridge. In the molecular orbitals of the Pc-Por-fused dimers and trimers, the strong electronic interaction between the HOMOs of the Pc and Por moieties results in the delocalization of the HOMO over the entire molecular skeleton. With their large extinction coefficient at Q-like bands, these results reflect the fact that the effective delocalization of the π -electron density along the long axis of the fused systems induces large transition dipole moments, leading to the high radiative decay rate and increased fluorescence quantum yield upon expansion of the fused systems (Table 1).^[19-20] Moreover, the effective electronic communication through the benzo[α]pyrazine-fused bridge induces the perturbation of electronic structures of the Pc and Por moieties. For homo-Por-fused systems, it is expected that the perturbation intensifies the transition to the lowest excited state, resulting in the enhancement of fluorescence quantum yield.^[19-20] Therefore, the perturbation should also be responsible for the quite high fluorescence quantum yield for the Pc-Por-fused systems.

Motivated by the localized LUMO and LUMO + 1 of H_4 -1, H₆-2, Zn₂-1, and Zn₃-2, we measured the electronic absorption and fluorescence spectra for the two dimers and two trimers in a highly polar solvent, benzonitrile. In benzonitrile, although the absorption spectral features were similar to those in toluene, weak fluorescence spectra were also observed (Figure S21 and Table S6 in the Supporting Information). Furthermore, the TA results displayed that their singlet-excited-state lifetimes were significantly decreased to 160, 60, 100, and 40 ps for H₄-1, H₆-2, Zn₂-1, and Zn₃-2, respectively, where the slow decay components with the time constant longer than 10 ns were assigned to their triplet states (Figure S22 in the Supporting Information). As seen in the molecular orbital structures of H₄-1, H₆-2, Zn₂-1, and Zn₃-2, these results demonstrate the intramolecular CT character of the Pc-Por-fused systems. Whereas the nonpolar environment in toluene frustrates the localization of electron density on the Pc moiety, the strong dipole moment of the polar solvent induces a stable charge-separated state involving the localized electron density on the Pc moiety, resulting in the fast decay in the excited-state dynamics (Scheme S2 in the Supporting Information). Here, the formation of the charge-separated state in all compounds was not observed even in the few ps range for the investigation of the fast dynamics. In conjunction with the TA results in toluene, this result suggests that the effectively extended π -conjugation

through the benzo[a]pyrazine-fused bridge leads to very fast charge separation and recombination processes in the CT state in these systems.

Conclusion

The Pc–Por-fused skeleton has been extended into the trimer. In particular, compared with homo-tetrapyrrole-fused analogs, both Pc–Por-fused dimers and trimers exhibit high fluorescence quantum yields (> 0.13) and relatively long excited-state lifetimes (> 1.3 ns) mainly as a result of the large transition dipole moments originating from the effective π -conjugation extension in the Pc–Por-fused systems. These results will be helpful for the design and synthesis of tetrapyrrole-fused oligomeric skeletons and even corresponding two-dimensional nanostructures with well-defined compositions, rich with nitrogen atoms, and tunable metal ions and, therefore, with a wide range of potential applications ranging from photonic and electronic nanodevices to catalysis.

Experimental Section

General remarks

1,2,4-Trichlorobenzene (TCB) was freshly distilled from CaH₂ under nitrogen. *n*-Pentanol was distilled from sodium. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70–230 mesh) and biobead (BIORAD S-X1, 200–400 mesh) columns with the indicated eluents. All other reagents and solvents were used as received. The compounds 4,5-bis(2,6-dimethylphenoxy)phthalonitrile,^[21] 2,3-di-cyanopyrazine,^[22] H₂TMP (H₂-4),^[23] ZnTMP (Zn-4),^[24] 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-2',3'-di-cyanopyrazino[2,3- β]porphyrin^[25] were prepared according to the published procedures.

Preparation of Pc-Por-fused dimer H₄-1 and trimer H₆-2

A mixture of 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (220.8 mg, 0.60 mmol), 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-2',3'-dicyanopyrazino[2,3- β]porphyrin **5** (56.1 mg, 0.060 mmol), and lithium(10.5 mg, 1.5 mmol) in *n*-pentanol (3.0 mL) was heated to reflux under nitrogen for 2 h. After cooling to room temperature, the resulting green solution was poured into methanol (300 mL) containing 3.0 mL of CH₃COOH. The precipitate was collected by filtration and purified by chromatography on a silica gel column using CH₂Cl₂ as the eluent. The target products were further purified by biobead column chromatography with CHCl₃ as the eluent, giving the trimer complex H₆-2 as the first fraction, followed by the dimer complex H₄-1. Repeated chromatography followed by recrystallization from CHCl₃ and CH₃OH gave both H₄-1 (12.0 mg, 9.8%) and H₆-2 (4.0 mg, 2.6%) as green powders.

H₄-1: ¹H NMR (CDCl₃, 400 MHz): δ =8.92 (br, 4H), 8.72 (d, 2H, *J*= 4.00 Hz), 8.58 (d, 2H, *J*=4.00 Hz), 8.51 (s, 2H), 8.42 (s, 2H), 8.06 (s, 2H), 7.56 (s, 4H), 7.50 (s, 6H), 7.44–7.37 (m, 12H), 7.30 (s, 4H), 2.95 (s, 6H), 2.65 (s, 6H), 2.54 (s, 12H), 2.48 (s, 12H), 2.46 (s, 12H), 1.92 (s, 24H), -0.51 (s, 2H), -2.17 ppm (s, 2H); UV/Vis (toluene): λ_{max} (log ε)=361 (4.82), 420 (5.21), 633 (4.61), 668 (4.65), 701 (5.15), 726 nm (5.13); MALDI-TOF MS: an isotopic cluster peaking at *m/z*= 2042.0 (calcd for C₁₃₆H₁₁₆N₁₄O₆ [*M*]⁺=2041.9); elemental analysis calcd (%) for C₁₃₆H₁₁₆N₁₄O₆ 1.5 CHCl₃·2.5 CH₃OH: C 73.06, H 5.58, N 8.51; found: C 73.41, H 5.97, N 8.48.



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H₆-2: ¹H NMR (CDCl₃, 400 MHz): δ = 9.34 (s, 2H), 9.03 (s, 2H), 8.78 (s, 2H), 8.74 (br, 4H), 8.64 (d, 2H, *J*=8.00 Hz), 8.61 (d, 2H, *J*= 8.00 Hz), 8.53 (s, 4H), 8.30 (s, 2H), 7.82 (s, 4H), 7.62 (s, 4H), 7.32 (s, 8H), 7.48–7.41 (m, 6H), 7.51 (s, 6H), 3.21 (s, 6H), 2.98 (s, 6H), 2.66 (s, 12H), 2.07 (s, 12H), 1.96 (s, 36H), 2.57 (s, 12H), 2.51 (s, 12H), -2.07 ppm (s, 4H); UV/Vis (toluene): λ_{max} (log ε) = 426 (5.61), 758 nm (5.48); MALDI-TOF MS: an isotopic cluster peaking at *m/z* = 2608.2 (calcd for C₁₇₆H₁₅₀N₂₀O₄·1.75 CHCl₃·3 CH₃OH·2H₂O: C 73.61, H 6.12, N 9.53; found: C 73.58, H 5.73, N 9.50.

Preparation of dimeric zinc complex Zn₂-1

A mixture of H_4 -1 (8.0 mg, 0.004 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (5.15 mg, 0.024 mmol) in DMF (1 mL) was heated at 90 °C for 4 h under nitrogen. After cooling to room temperature, the mixture was evaporated under reduced pressure and the residue was purified by chromatography on a silica gel column using CHCl₃ as the eluent. The first pale-green band containing the target compound Zn₂-1 was collected. Repeated chromatography followed by recrystallization from CHCl₃ and *n*-hexane gave Zn₂-1 as a green powder (6.0 mg, 70.4% yield). ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.05$ (s, 2 H), 8.78 (s, 2 H), 8.65 (d, 2 H, J=4.00 Hz), 8.50 (d, 2 H, J=4.00 Hz), 8.46 (s, 2H), 8.27 (s, 2H), 8.15 (s, 2H), 7.50 (s, 4H), 7.44 (s, 6H), 7.35 (br, 16H), 2.91 (s, 6H), 2.52 (s, 18H), 2.45 (s, 12H), 2.43 (s, 12H), 1.84 ppm (s, 24H); UV/Vis (toluene/pyridine = 100:1): λ_{max} (log $\epsilon) =$ 369 (5.07), 422 (5.35), 718 nm (5.36); MALDI-TOF MS: an isotopic cluster peaking at m/z = 2168.8 (calcd for $C_{136}H_{112}N_{14}O_6Zn_2$ [*M*]⁺ = 2168.7); elemental analysis calcd (%) for C₁₃₆H₁₁₂N₁₄O₆Zn₂•1.75 CHCl₃: C 69.57, H 4.82, N 8.25; found: C 69.84, H 4.86, N 8.30.

Preparation of trimeric zinc complex Zn₃-2

By employing the procedure for the preparation for Zn₂-1 with H₆-**2** instead of H₄-1 as the starting material, Zn₃-2 was isolated in 58.1% yield. ¹H NMR (CDCl₃, 400 MHz): δ = 9.56 (s, 2H), 9.25 (s, 2H), 8.81 (s, 2H), 8.75 (br, 4H), 7.52–7.41 (m, 12H), 8.61–8.56 (m, 8H), 8.30 (s, 2H), 7.82 (s, 4H), 7.60 (s, 4H), 7.31 (s, 8H), 3.23 (s, 6H), 2.97 (s, 6H), 2.66 (s, 12H), 2.58 (s, 12H), 2.52 (s, 12H), 2.07 (s, 12H), 1.95 ppm (s, 36H); UV/Vis (toluene/pyridine = 100:1): λ_{max} (log ε) = 423 (5.61), 567 (4.95), 765 nm (5.45); MALDI-TOF MS: an isotopic cluster peaking at m/z=2799.1 (calcd for C₁₇₆H₁₄₄N₂₀O₄Zn₃·3 CHCl₃: C 68.09, H 4.69, N 8.87; found: C 67.96, H 4.64, N 9.23.

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