Comparative Photophysical Properties of Free-Base, Bis-Zn(II), Bis-Cu(II), and Bis-Co(II) Doubly N-Confused Hexaphyrins(1.1.1.1.1)

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We have comparatively investigated the photophysics of a series of bis-metal doubly N-confused hexaphyrins-(1.1.1.1.1) using time-resolved fluorescence, femtosecond transient absorption, two-photon absorption measurements, and geometry-optimized ab initio calculations. Bis-Zn(II) and free-base doubly N-confused hexaphyrins exhibit well-resolved and red-shifted B- and Q-like absorption bands compared with porphyrins. Their allowed transitions are (π,π^*) transitions of the hexaphyrin ring, as confirmed by the HOMO and LUMO frontier orbitals based on ab initio calculations at the B3LYP/6-31G level. On the other hand, the absorption spectra of bis-Cu(II) and bis-Co(II) doubly N-confused hexaphyrins are relatively broad, presumably due to large couplings between the metal d-orbitals and π -electrons of the hexaphyrin ring. Owing to these couplings, bis-Cu(II) and bis-Co(II) doubly N-confused hexaphyrins have much shorter excited-state lifetimes of 9.4 ± 0.3 ps and 670 fs, respectively, than those (267 ± 16 and 62.4 ± 1.2 ps, respectively) of bis-Zn(II) and free-base doubly N-confused hexaphyrins. The two-photon absorption cross section ($\sigma^{(2)}$) values, which are believed to depend strongly on the ring planarity (π -conjugation), are in line with the excited-state lifetimes trends.

Introduction

During the last decade expanded porphyrins, possessing more than four pyrrole rings to form a π -conjugated macrocyclic ring, have attracted much attention due to their rich chemistry such as versatile ways of connecting pyrrole rings to produce a variety of expanded porphyrins, anion or neutral receptors, organic nonlinear optical materials, and new IR dyes and the interplay between aromaticity and antiaromaticity.¹⁻⁵ Another important aspect as aromatic ligands in porphyrins is the chelation of various transition metals in central cores formed by the framework of four pyrrole rings.⁶ While only one metal site is available for the relatively small size cavity of porphyrins, bismetal coordination can be envisaged for expanded porphyrins due to their expanded inner cavities. In this regard, representative expanded porphyrins, hexaphyrins, can be promising candidates for bis-metal complexation due to their planar conformation as well as rectangular cavity framework. Sessler et al. reported that [24]hexaphyrin(1.0.0.1.0.0), amethyrin, could accommodate two metal ions with six inward pointing pyrrole nitrogens.^{7,8} In contrast, normal [26]hexaphyrin(1.1.1.1.1)^{5,9-12} does not form a bis-metal complex^{13,14} except a bis-Au(III) complex,¹⁵ despite its planar conformation, because it requires the involvement of inner CH of the N₂C₂ core in the coordination with the metal

(Scheme 1). Thus if one or more carbon atoms in the cavity is replaced by nitrogens, the metal coordination seems to be plausible. This idea has led to the synthesis of doubly N-confused hexaphyrins(1.1.1.1.1) where two confused pyrroles are introduced into the core of normal hexaphyrin. Doubly N-confused hexaphyrins were initially prepared via a stepwise route¹⁶ and were synthesized via an unexpected double pyrrolic rearrangement route in improved yields.¹⁷ It is notable that these doubly N-confused hexaphyrins accommodate two metal ions within their flat rectangular coordination site quite smoothly, in sharp contrast to normal hexaphyrins(1.1.1.1.1).

In metalloporphyrins, it has been well established that the central metals play an important role in photophysical, electrochemical, catalytic, and electronic properties. In this context, it is relevant to investigate the bis-metal doubly N-confused hexaphyrins such as bis-Zn(II), bis-Cu(II), and bis-Co(II) complexes to explore the electronic interactions between the metal and hexaphyrin ring and to compare their photophysical properties with free-base doubly N-confused hexaphyrins (Scheme 1). The choice of filled d-orbital Zn(II) and unfilled d-orbital Cu(II) and Co(II) as central metals in bis-metal doubly N-confused hexaphyrins is expected to provide a rationale to distinguish (d,d), LMCT (π ,d), MLCT (d, π^*), and ring (π , π^*) states in the deactivation processes of photoexcited bis-metal doubly N-confused hexaphyrins.

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SCHEME 1: Molecular Structures of Free-Base, Bis-Zn(II), Bis-Cu(II), and Bis-Co(II) Doubly N-Confused Hexaphyrins(1.1.1.1.1) (top) and *meso*-Hexakis(pentafluorophenyl) [26]Hexaphyrin(1.1.1.1.1) (bottom)



In this work, we have explored the photophysical properties of 1, 2, 3, and 4 including excited singlet- and triplet-state dynamics by various time-resolved spectroscopic techniques and quantum mechanical calculations on HOMO–LUMO transitions based on the B3LYP/6-31G level. Much different photophysical properties of 3 and 4 compared with 1 and 2 demonstrate the involvement of metal d-electrons in the formation of low-lying quenching states below the normally emissive ring (π , π^*) states of 1 and 2. Since our work is the first attempt to explore the fundamental photophysical properties of bis-metal complexes of expanded porphyrins, we believe that our results will provide a firm basis for the characterization of multimetal-chelated expanded porphyrins.

Experimental Section

Sample Preparation. The details of the synthesis of 1-4 are described elsewhere¹⁷ and in the Supporting Information. Under aerobic conditions, to a solution of meso-hexakis-(pentafluorophenyl) [26]hexaphyrin (5) (400 mg) in pyridine (100 mL) was added CuCl (2 g), and the resulting mixture was stirred for 3 h. TLC analysis of the reaction mixture revealed the appearance of a pale blue band faster than 5. After usual workup followed by chromatographic separation through a silica gel column, reddish solids (104 mg) were isolated as the sole major product 3. Positive-mode high-resolution electrospray ionization mass spectroscopy (HR-ESI-TOF-MS) exhibited the parent ion peak at m/z = 1616.9052 (M + H) (cald for $C_{66}H_{11}F_{30}N_6O_2Cu_2$, 1616.9050), thus demonstrating that two oxygen atoms had been incorporated in addition to two copper ions. The structure of this complex has been revealed by singlecrystal X-ray diffraction analysis to be bis-Cu(II) doubly N-confused hexaphyrin 3, where the two Cu atoms are each bound to three pyrrolic nitrogen atoms and a carbonyl oxygen atom with a Cu-Cu distance of 4.896(1) Å in a planar macrocycle with the mean plane deviation of only 0.079 Å and small displacements of the Cu ions (0.059 Å). Bond distances are Cu-N_A (2.043(4) Å), Cu-N_B (1.961(4) Å), Cu-N_C (2.052-(4) Å), and Cu-O (1,932(3) Å), respectively. Remarkably, both the inverted pyrrole rings of 5 underwent simultaneous rearrangements to form N-confused pyrroles with concomitant oxygenation at the internal pyrrolic α -position in 3. Complex 3

was demetalated to give its free base 2 quantitatively upon treatment with trifluoroacetic acid.

General Comments. Absorption spectra were acquired with a UV-vis spectrometer (Shimadzu, UV-3101PC). Solvents of HPLC grade were purchased from Aldrich and used without further purification. All measurements were carried out at room temperature (23 ± 2 °C).

Near-IR Fluorescence Spectrum and Lifetime Measurements. The fluorescence emission was detected using a near-IR photomultiplier (Hamamatsu, H9170-75) and a lock-in amplifier (EG&G, 5210) combined with a chopper after laser excitation at 442 nm from a CW He-Cd laser (Melles Griot, Omnichrome 74). Time-resolved fluorescence was detected using a time-correlated single-photon-counting (TCSPC) technique.¹⁸ As an excitation light source, we used a homemade cavity-dumped Ti:Sapphire oscillator, which provides a high repetition rate (200-400 kHz) of ultrashort pulses (100 fs at full width at half-maximum (fwhm)) pumped by a CW Nd-YVO₄ laser (Spectra-Physics, Millennia V). The output pulses of the oscillator were frequency-doubled with a second-harmonic crystal. The TCSPC detection system consisted of a near-IR photomultiplier (Hamamatsu, H9170-75), a TAC (EG&G Ortec, 457), two discriminators (EG&G Ortec, 584 (signal) and Canberra, 2126 (trigger)), and two wideband amplifiers (Philip Scientific (signal) and Mini Circuit (trigger)). A personal computer with a multichannel analyzer (Canberra, PCA3) was used for data storage and signal processing. The overall instrumental response function by an IR dye (Aldrich, IR1100) was about 350 ps (fwhm). For the deconvolution procedure, the IRF function was obtained by detecting emission from a IR dye molecule (Aldrich, IR1100) with a known lifetime of ~ 6 ps.

Femtosecond Transient Absorption Measurements The dual-beam femtosecond time-resolved transient absorption spectrometer consisted of two independently tunable homemade noncollinear optical parametric amplifiers (NOPA) pumped by a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X) operating at 5 kHz repetition rate and an optical detection system.¹⁹ The NOPA systems were based on noncollinearly phase-matching geometry and easily color-tuned by controlling a delay between white light continnum and pump pulses. The generated visible NOPA pulses had a pulse width of \sim 35 fs and an average power of 10 mW at 5 kHz repetition rate in the range 500-700 nm. The probe beam was split into two parts. One part of the probe beam was overlapped with the pump beam at the sample to monitor the transient (signal), while the other part of the probe beam was passed through the sample without overlapping the pump beam to compensate the fluctuation of the probe beam (reference). The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). To obtain the time-resolved transient absorption difference signal at a specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 47 Hz, the modulated probe pulses as well as the reference pulses were detected by two separate photodiodes. The modulated signals of the probe pulses were measured by a gated-integrator (SRS, SR250) and a lock-in amplifier (EG&G, DSP7265) and stored in a personal computer for further signal processing. The polarization angle between pump and probe beam was set at the magic angle (54.7°) in order to prevent polarization-dependent signals.

Nanosecond Flash Photolysis Measurements. The nanosecond transient absorption spectra were obtained by nanosecond

flash photolysis techniques.²⁰ An excitation pulse of 532 nm was generated from the second-harmonic output of a Q-switched Nd:YAG laser (Continuum, Surelite). The time duration of the excitation pulse was ca. 6 ns, and the pulse energy was ca. 2 mJ/pulse. A CW Xe lamp (150 W) was used as a probe light source for transient absorption measurement. The probe light was collimated on the sample cell and then spectrally resolved by using a 15 cm monochromator (Acton Research, SP150) equipped with a 600 grooves/mm grating after passing the sample. The spectral resolution was about 3 nm for the transient absorption experiment. The light signal was detected by using photomultiplier tubes (Hamamatsu, R928 and R5108). The output signal from the PMT was recorded with a 500 MHz digital storage oscilloscope (Tektronix, TDS3052) for the temporal profile measurement. Since the triplet-state dynamics of molecules in solution is strongly dependent on the concentration of oxygen molecules dissolved in solution, we tried to remove oxygen rigorously by repeated freeze-pump-thaw cycles. To ensure our data, we first examined the triplet-state dynamics of Zn(II)TPP in toluene at room temperature, which gives the lifetime of 1 ms by our flash photolysis setup. Since the intrinsic triplet-state lifetime of Zn(II)TPP is 25 ms at 77 K, the triplet-state lifetime of 1 ms at room temperature is limited by collisional quenching.²¹ Since the concentration of molecules also affects significantly the excited triplet-state lifetime due to triplet-triplet annihilation processes, we kept the concentration at 10^{-5} M with relatively low photoexcitation density at 532 nm produced by the second-harmonic output of a Q-switched Nd:YAG laser.

Quantum Mechanical Calculation. Quantum mechanical calculations were performed with the Gaussian 98 program suite.²² All calculations were carried out by the density functional theory (DFT) method employing the B3LYP functional as 6-31G basis set. The X-ray crystal structures were used as initial geometry for geometry optimization. The excited-state calculations were performed with the time-dependent density functional theory (TD-DFT) method using the same functional and basis set as those used for geometry optimizations.

Measurement of Two-Photon Absorption Cross-section $(\sigma^{(2)})$. The TPA spectra were measured at 1200 nm by using the open-aperture Z-scan method²³ with \sim 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Ge-PIN photodiode (New Focus) as intensity reference, and the other was used for transmittance measurement. After passing through an f = 10 cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell was 1 mm. The transmitted laser beam from the sample cell was then detected by the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0 , ranged from 40 to 60 GW cm⁻². Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}$$
(1)

where α_0 is the linear absorption coefficient, *l* the sample length, and z_0 the diffraction length of the incident beam.



Figure 1. Absorption (solid line) and fluorescence (dashed line) spectra of 1 (a) and 2 (b) in toluene. Inset shows the fluorescence decay profile of 1 at 1045 nm with photoexcitation at 400 nm.

After obtaining the nonlinear absorption coefficient β , the TPA cross-section $\sigma^{(2)}$ of one solute molecule (in units of 1 GM = 10^{-50} cm⁴·s/photon·molecule) can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_{\rm A} d \times 10^{-3}}{h\nu} \tag{2}$$

where N_A is the Avogadro constant, *d* is the concentration of the TPA compound in solution, *h* is the Planck constant, and ν is the frequency of the incident laser beam.

We obtained the TPA cross-section $\sigma^{(2)}$ values of hexaphyrins at 1200 nm, where linear absorption is negligible, to satisfy the condition of $\alpha_0 l \ll 1$ in retrieving the pure TPA $\sigma^{(2)}$ values in the simulation procedure. We also measured the TPA crosssection value of AF-50 as a reference compound, which is 50 GM at 800 nm.

Results and Discussion

Photophysical Properties of 1 and 2. The crystal structures of doubly N-confused hexaphyrins(1.1.1.1.1) 1-4 were reported to have a relatively flat rectangular shape with two inverted pyrrole rings, where the two metal atoms are each bound to three pyrrolic nitrogen atoms and a carbonyl oxygen atom with a metal-metal distance of 4.9 Å in a planar macrocycle (Supporting Information, Figure S1). The doubly N-confused hexaphyrins exhibit aromaticity due to 26π -electrons around the hexaphyrin ring, as judged from their strong diatropic ring currents.^{16,17} The absorption spectrum of **1** exhibits a strong B-like absorption band at 608 nm and rather weak



Figure 2. Frontier orbitals of 1 (a) and 2 (b) by ab initio calculations at the B3LYP/6-31G level.

Q-like ones at 779, 883, 912, and 1042 nm (Figure 1a). Overall, the absorption bands are red-shifted compared with those of porphyrins mainly due to the enhanced π -conjugation pathway. The absorption spectrum of 2 has a B-like band at 571 nm and several weak Q-like ones at 727, 798, 910, and 1051 nm (Figure 1b). Interestingly, the bathochromic B-like and the hypsochromic Q-like (0,0) bands of 1 relative to 2 are similar to those of metalloporphyrins relative to free-base porphyrins.⁶ The fluorescence spectra of 1 and 2 show peaks at 1044 and 1058 nm and weak vibronic bands at around 1250 nm, respectively. Considering the absorption edge, the Stokes shift of 1 was estimated to be $\sim 30 \text{ cm}^{-1}$, which implies negligible structural changes between ground and excited states. The larger Stokes shift of $\sim 80 \text{ cm}^{-1}$ of **2** than that of **1** indicates that the molecular structure of 1 is more planar and rigid than that of 2 due to the anchoring of a flexible hexaphyrin ring by bis-Zn(II) coordination.

Given the crystal structures as initial input geometries, ab initio calculations on the B3LYP/6-31G level were performed to calculate the molecular orbitals of 1 and 2. The HOMO and LUMO frontier orbitals of 1 and 2 show large electron densities around their pyrrole rings, which matches well with the e_g and a_{2u} orbitals of porphyrins (Figure 2), and the S₁ states can be assigned to (π,π^*) transitions. While the frontier orbitals of 1 have a slight electron density on the central Zn(II) metals, the frontier orbitals of 1 and 2 exhibit high aromaticity and ring planarity.

The fluorescence lifetime of **1** was measured by the timecorrelated single-photon-counting (TCSPC) technique, which gave a lifetime of ~ 255 ps at 1045 nm with excitation at 400



Figure 3. Transient absorption decay profiles of 1-4 (a) and 1 on a longer time scale (b) in toluene pumped and probed at the corresponding absorption maxima.

nm (inset of Figure 1a). It is noteworthy that this is much shorter than that of Zn(II)TPP (~2.54 ns). Since the IRF function of our TCSPC setup in the IR region was estimated to be ca. 350 ps, we could not resolve the fluorescence decay of **2**. According to the energy gap law,²⁴ the reduced HOMO–LUMO gap mainly due to the enhanced π -conjugation of the 26 π -electron system seems to accelerate the internal conversion rate, yielding a much shorter lifetime than that of porphyrins with 18 π -electrons.^{6,25}

To explore the excited-state dynamics of 1 and 2, we have measured the transient absorption decay profiles (Figure 3a). The bleaching recovery time of 267 ± 16 ps for **1** matches well with its fluorescence lifetime of ~255 ps. In addition, the longlived component (>10 ns) of 1 observed as a tail in the transient absorption decay can be assigned as the decay of the triplet state (Figure 3b). Interestingly, the shorter excited singlet-state lifetime²⁶ of 62.4 \pm 1.2 ps of **2** than that of **1** was observed in the transient absorption decay profile. Since Zn(II) metal enhances the intersystem crossing rate due to spin-orbit coupling as observed in the fluorescence lifetimes of 2.54 ns for Zn(II)TPP and 13.6 ns for H₂TPP, the longer singlet excitedstate lifetime and smaller Stokes shift of 1 compared with 2 are ascribed to the higher planarity of 1 than 2, leading to the deceleration of nonradiative decay channels despite its enhanced intersystem crossing from the S_1 to T_1 state.

To examine the excited triplet-state dynamics, we have carried out nanosecond flash photolysis for 1 and 2 in argon-saturated toluene solutions with nanosecond pulse excitation at 532 nm. The weak and broad T-T absorption spectra of 1 and 2 with



Figure 4. Nanosecond flash photolysis spectra of **1** (a) and **2** (b) in argon-saturated toluene. The pump source at 532 nm is a frequency-doubled Nd:YAG laser.

apparent bleaching signals at the indicated delays are shown in Figure 4. The triplet-state lifetime and quantum yield of **1** were found to be $2.3 \pm 0.1 \,\mu s$ and 0.2, respectively. Although a longer triplet-state lifetime of $9.5 \pm 1.2 \,\mu s$ was observed for **2**, the triplet-state quantum yield was estimated to be less than 0.01. The relatively short excited triplet-state lifetime and high triplet quantum yield of **1** compared with **2** are attributable to the enhanced spin—orbit coupling by the two central Zn(II) metals.

Photophysical Properties of 3 and 4. The absorption spectra of 3 and 4 are similar to those of 1 and 2 but exhibit relatively broad features (Figure 5). The B-like bands of 3 and 4 are located at 619 and 616 nm, and their lowest Q-like bands are observed at 1048 and 1043 nm, respectively. Importantly, the smeared absorption spectra of 3 and 4 presumably arise from strong interactions between unoccupied d-orbitals of central bismetals and hexaphyrin ring π -electrons. To examine the metal contribution to the excited-state formation, we have investigated the frontier orbitals of 3 and 4 by using ab initio calculations on the B3LYP/6-31G level. Contrary to the frontier orbitals of 1 and 2, those of 3 and 4 exhibit large contributions by the central metal ions, indicating that the metal d-orbitals are heavily involved in the formation of excited states of 3 and 4 (Figure 6). It is noteworthy that the HOMO-1 and LUMO+1 of 3 and 4 have an energy gap similar to the HOMO and LUMO of 1 and 2. It should also be mentioned that the contributions by metal d-orbitals to the HOMO and LUMO of 3 and 4 are significantly enhanced compared with those of 1 and 2.



Figure 5. Absorption spectra of 3 (a) and 4 (b) in toluene.



Figure 6. Frontier orbitals of 3 (a) and 4 (b) by ab initio calculations at the B3LYP/6-31G level.

Furthermore, we have calculated the electronic transitions of 1-4 using the time-dependent density functional theory (TD-DFT) method. In the cases of 1 and 2, we observed the strong B- and weak Q-like absorption bands, which is largely in accordance with their absorption spectra. For 3 and 4, however, the calculated absorption spectra exhibit several weak transitions

 TABLE 1: Excited-State Lifetimes, Fluorescence Quantum

 Yields, and Triplet-State Quantum Yields of a Series of

 Doubly N-Confused Hexaphyrins

sample	$ au_1/\mathrm{ps}$	$ au_2/\mathrm{ps}$	$\Phi_{\mathrm{fl}}{}^a$	$ au_{\mathrm{T}}/\mu\mathrm{s}$	Φ_{T}
1	267 ± 16 (85%)	>10 000 (15%)	5.46	2.3	0.2
2	62.4 ± 1.2		0.61	9.5	< 0.01
3	9.4 ± 0.3 (59%)	29.2 ± 0.9 (41%)	b	С	С
4	0.67 ± 0.02		b	С	С

^{*a*} The relative fluorescence quantum yields were estimated by that of *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin(1.1.1.1.1) as unity. ^{*b*} No fluorescence was observed. ^{*c*} No signal was observed in nanosecond flash photolysis.

around B- and Q-like bands in addition to strong B- and weak Q-like bands. Moreover, several low-lying states with weak oscillator strength were clearly observed (Supporting Information, Table S1). Possible explanations are that the HOMO and LUMO produce low-lying excited states between the allowed ring (π,π^*) transitions, which are responsible for the quenching process of the singlet excited (π,π^*) states.

No fluorescence emission was detected near the absorption edge of 3 and 4, implying that the quenching states are involved in their relaxation processes from the normally emissive ring (π,π^*) states. From the femtosecond transient absorption decay profiles, the excited states of 3 and 4 were observed to have lifetimes of 9.4 \pm 0.3 (59%) with 29.2 \pm 0.9 ps (41%) and 0.67 ± 0.02 ps, respectively (Figure 3 and Table 1). The population of the excited triplet state seems to be inefficient, since no signal of 3 and 4 in the nanosecond flash photolysis measurement was observed. It was reported for Cu(II)TPP that the unpaired metal electron in the d⁹ complex split the ${}^{3}(\pi,\pi^{*})$ into a triple doublet ${}^{2}T(\pi,\pi^{*})$ and a quartet ${}^{4}T(\pi,\pi^{*})$, which are responsible for fast ${}^{2}S_{1}(\pi,\pi^{*})$ state dynamics. The spinmultiplet states seem to be produced in hexaphyrin rings through electronic mixing between the odd electron in the d_{7^2} orbital of the Cu(II) d⁹ system and the normal singlet and triplet hexaphyrin ring (π,π^*) states, which can be inferred from the photophysics of Cu(II) porphyrin. It should be noted that the two Cu(II) ions in the hexaphyrin ring should be involved simultaneously in the electronic mixing with the hexaphyrin ring (π,π^*) states in bis-Cu(II) doubly N-confused hexaphyrin. Accordingly, in a manner similar to the case of Cu(II)TPP, the double-exponential decays of 3 with the time constants 9.4 \pm 0.3 (59%) and 29.2 \pm 0.9 ps (41%) can be assigned as the formation of triple multiplet $({}^{3}T/{}^{5}T(\pi,\pi^{*}))$ excited states from the initially populated single triplet ${}^{3}S_{1}(\pi,\pi^{*})$ state and a subsequent relaxation to the ground state, respectively.^{6,27-29}

While the HOMOs (HOMO, HOMO-1, and HOMO-2) of **4** reveal large metal contributions, the LUMOs (LUMO, LUMO+1, and LUMO+2) of **4** are characterized by negligible metal contributions, leading to the possibility of metal-to-ligand (MLCT) (d, π^*) charge transfer (CT) transitions between the allowed (π , π^*) transitions. Thus the low-lying MLCT (d, π^*) state is suggested to be responsible for the quenching of fluorescence emission from the ring (π , π^*) state in **4**.

To confirm our interpretations of the quenching states of **3** and **4**, we have investigated the transient absorption decay profiles of **3** and **4** in benzonitrile (Figure 7). The best fitted curves of **3** in benzonitrile exhibit double-exponential decay with time constants of 6.1 ± 0.1 (55%) and 25.4 ± 0.5 ps (45%), yielding the weight-averaged time constant of 14.6 ± 0.3 ps, which is comparable to that $(17.6 \pm 0.4 \text{ ps})$ in toluene. However, the transient absorption decay profile of **4** in benzonitrile gives double-exponential decay with time constants of 0.91 ± 0.02



Figure 7. Transient absorption decay profiles of 3 and 4 in toluene and benzonitrile pumped and probed at the absorption maxima.

(93%) and 18.5 \pm 0.4 ps (7%), which are apparently longer than 0.67 \pm 0.02 ps in toluene (Figure 7).

Since the initially excited ${}^{3}S_{1}(\pi,\pi^{*})$ state of **3** is followed by a rapid equilibrium between triple triplet ${}^{3}T(\pi,\pi^{*})$ and triple quintet ⁵T(π,π^*) states and a subsequent relaxation to the ground state, the overall energy relaxation dynamics should be insensitive to the polarity of the solvent. On the other hand, the slower relaxation processes of 4 observed in benzonitrile are regarded to be associated with the MLCT (d,π^*) state, which is consistent with the theoretical calculations of the HOMO and LUMO of 4. But there still exists a possibility for the involvement of the LMCT (π,d) state in the relaxation process of 4, because the stabilization of this state is also sensitive to the solvent polarity. Thus, on the basis of our theoretical and spectroscopic investigations we can suggest that the central metals in bis-metal doubly N-confused hexaphyrins play an important role in the energy relaxation processes, as observed in metalloporphyrins. On the basis of our theoretical and spectroscopic investigations, we can propose the schematic diagrams for energy relaxation processes of a series of bis-metal and free-base doubly Nconfused hexaphyrins(1.1.1.1.1) as shown in Figure 8.

Two-Photon Absorption Behaviors of 1, 2, 3, and 4. There have been numerous research activities to search for new optical nonlinear materials with large two-photon absorption (TPA) cross sections ($\sigma^{(2)}$) due to potential applications in a variety of fields including photodynamic therapy, three-dimensional microfabrication and optical data storage, and optical limiting. Recently, expanded porphyrins containing more than four pyrrole rings have received much attention due to their high TPA values contributed by a large number of π -electrons. For enhanced TPA values of expanded porphyrins, it is relevant to



Figure 8. Schematic energy relaxation diagrams of 1 and 2 (a), 3 (b), and 4 (c).

consider various factors to affect the TPA values such as the π -conjugation pathway, the number of π -electrons (Hückel's [4n+2] rule vs aromaticty/antiaromaticity), ring planarity, and the central metals. In this regard, we have examined the TPA properties of 1, 2, 3, and 4 by an open-aperture Z-scan method with \sim 130 fs pulses. Because of the structural rigidity due to the coordination with central Zn(II) metals in 1, the relatively high TPA cross-section value of 3450 GM was obtained at 1200 nm. The faster ${}^{1}S(\pi,\pi^{*})$ state decay with the time constant of 62 ps and smaller TPA value of 2250 GM at 1150 nm of 2 were measured as compared with 1. This feature is probably attributable to the flexible hexaphyrin ring without coordination with bis-Zn(II) metals in 2. In the cases of 3 and 4, however, relatively low TPA values of <100 GM were observed presumably due to short-lived excited states contributed by d-orbitals in the formation of their excited electronic states, although the absorption spectra of **3** and **4** are quite similar to those of 1.

Conclusion

We have comparatively explored the photophysical properties of a series of bis-metal doubly N-confused hexaphyrins-(1.1.1.1.1). As for bis-Zn(II) and free-base doubly N-confused hexaphyrins, the allowed transitions are $\pi - \pi^*$ transitions around a hexaphyrin ring, which is confirmed by ab initio calculations at the B3LYP/6-31G level. The two Zn(II) metals of **1** enhance the intersystem crossing rate to give the high triplet quantum yield of 0.2. Furthermore, the coordination by the two Zn(II) metal ions leads to the rigid planarity of the hexaphyrin ring, resulting in a longer singlet excited-state lifetime (267 ± 16 ps) than that (62.4 ± 1.2 ps) of **2** and a high two-photon absorption cross-section ($\sigma^{(2)}$) value of 3450 GM. On the other hand, bis-Cu(II) and bis-Co(II) doubly N-confused hexaphyrins exhibit much shorter excited-state lifetimes of 9.4 \pm 0.3 with 29.2 \pm 0.9 ps and 670 \pm 20 fs, respectively. The ultrafast relaxation processes for photoexcited **3** and **4** are ascribed to the formation of triple multiplet states (${}^{3}T(\pi,\pi^{*})$ and ${}^{5}T(\pi,\pi^{*})$) and the LMCT(d, π^{*}) states, respectively, both of which are located energetically below their band-gaps.

Overall, our comprehensive comparative spectroscopic investigations of various bis-metal doubly N-confused hexaphyrins(1.1.1.1.1) will serve as platforms for the further understanding of electronic structures of expanded porphyrins, which also will be useful in future applications in photodynamic therapy, anion sensing, drug delivery, optical nonlinear materials, and so on.

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Supporting Information Available: X-ray crystallographic structures, Z-scan trace, and TD-DFT calculations of electronic transitions are available free of charge via the Internet at http:// pubs.acs.org.

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