An Electron-Deficient Porphyrin Tape

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Abstract: Hexakis(pentafluorophenyl)substituted *meso-meso-*linked Zn^{II} -diporphyrin (9), which was prepared by the acid-catalyzed cross-condensation of 1,1,2,2-tetrapyrroethane (5) with dipyrromethane dicarbinol (6), was converted into *meso-meso*, β - β , β - β triply linked Zn^{II} -diporphyrin 3 by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and $Sc(OTf)_3$. Beside the red-shifted absorption spectrum and split first oxidation potential that are common to the triply-linked Zn^{II} -di-

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porphyrins, diporphyrin **3** exhibited considerably improved chemical stability owing to a lowered HOMO and good solubility in common organic solvents. The two-photon absorption (TPA) cross-section and S_1 -state lifetime of compound **3** were 1700 GM and 3.3 ps, respectively.

Introduction

Extensive efforts have been devoted to the exploration of π conjugated porphyrins owing to their potential use in various applications, such as organic semiconductors, photodynamic therapy (PDT), nonlinear optics (NLO), and photovoltaics.^[1-3] Among these, we have developed *meso-meso*.β- $\beta,\beta-\beta$ triply linked porphyrin arrays (porphyrin tapes) that exhibited exceptionally red-shifted absorption bands as a consequence of extensive π -conjugation.^[4] Several variants of these porphyrin tapes have also been created with unique attributes, such as 2D-extended L- and T-shaped tapes,^[5] self-organized amphiphilic columnar liquid crystals,^[6] covalently linked C60-conjugates,[7] C60-binding hosts,[8] and a square-shaped porphyrin sheet.^[9] Despite these developments, porphyrin tapes still face serious drawbacks, such as poor solubility and facile oxidative degradation. The former arises from their flat molecular shapes whilst the latter is

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 $Ar^{1} \qquad N \qquad Ar^{2} \qquad Dbp = \qquad Bu$ $Ar^{1} \qquad N \qquad Zn \qquad N$ $Ar^{1} \qquad N \qquad Ar^{2} \qquad Pfp = \qquad F$ $I (Ar^{1} = Dbp, Ar^{2} = Dbp)$ $2 (Ar^{1} = Dbp, Ar^{2} = Pfp)$

due to their high-lying HOMOs. Recently, by combining electron-rich- and electron-poor porphyrins, we have devel-

oped hybrid porphyrin tapes with improved solubility and chemical stability compared with their parent porphyrin

tapes.^[10] As an extension of this strategy, herein we report

the synthesis and characterization of an electron-deficient

triply linked porphyrin tape (3) that consists of only penta-

fluorophenyl-substituted Zn^{II}-porphyrin units (Scheme 1).

This structure was used to examine the influence of the elec-

tron-deficient substituents on the stability, solubility, and

electronic properties of porphyrin tapes.

2 (Ar¹ = Dbp, Ar² = Pfp) **3** (Ar¹ = Pfp, Ar² = Pfp)

Scheme 1. Structures of *meso--meso*, β - β , β - β triply linked diporphyrins 1–3.

Results and Discussion

Typically, *meso-meso-*linked porphyrin precursors have been prepared by Ag¹-promoted oxidative-coupling reactions.^[11] Because this oxidative coupling should be unfavorable for electron-deficient pentafluorophenyl-substituted porphyrin substrates, we adopted a different approach to *mesomeso-*linked diporphyrin **8**, that is, the cross-condensation of 1,1,2,2-tetrapyrroethane (**5**) with dipyrromethane dicarbinol (**6**, Scheme 2). The formation of compound **5** was originally



Scheme 2. Synthesis of diporphyrin 8.

reported by Dolphin and co-workers as a byproduct in the reductive synthesis of meso-unsubstituted dipyrromethane^[12] but has not been used for the synthesis of porphyrin macrocycles.^[13] After an extensive investigation, we found that the trifluoroacetic acid (TFA)-catalyzed condensation of 1,4-dioxane-2,3-diol (4) with pyrrole afforded compound 5 in 13% yield. This reaction was carried out at low temperature because compound 5 underwent facile scrambling into tripyrromethane at ambient temperature. Then, the synthesis of diporphyrin 8 was attempted by the acid-catalyzed crosscondensation of compound 5 with dipyrromethane dicarbinol (6).^[14] The use of TFA or methanesulfonic acid led to complete scrambling of compound 5, thereby giving porphyrin monomer 7 as the major product with trace amounts of compound 8. The scrambling was suppressed by the use of p-toluenesulfonic acid monohydrate. Under these conditions, the condensation of compounds 5 and 6 gave compound 8 (3.7% yield), along with compound 7 (8.1% yield). The structure of compound 8 was determined by X-ray diffraction (Figure 1). The asymmetric unit contained two dimers in which two porphyrins were held with a C_{meso} - C_{meso} bond distance of 1.494 and 1.514 Å, and a dihedral angle of



Figure 1. X-ray crystal structure of diporphyrin **8**; only one of the two dimer molecules is shown. Thermal ellipsoids are set at 30% probability. Solvent molecules are omitted for clarity.

75.5 and 77.9°, respectively. With porphyrin **7** in hand, we examined the oxidative coupling of its Zn^{II} complex (**7-Zn**) under various conditions. As expected, the inertness of complex **7-Zn** toward oxidative coupling was confirmed by the recovery of the monomer, even after oxidations with AgPF₆ or DDQ and Sc(OTf)₃ under forcing conditions.

Diporphyrin 8 was metalated with $Zn(OAc)_2$ in MeOH to quantitatively afford Zn^{II} -diporphyrin 9, which was then oxidized with DDQ and Sc(OTf)₃ to furnish triply linked diporphyrin 3 in 66% yield (Scheme 3). The ¹H NMR spec-



Scheme 3. Synthesis of porphyrin tape 3.

trum of compound **3** showed two doublets at $\delta = 7.71$ and 7.67 ppm owing to the outer peripheral β -protons and a singlet at $\delta = 7.09$ ppm that was due to the bay-area β -protons. To our delight, compound 3 was quite soluble in common organic solvents and highly stable as a solution in air. Crystals of compound 3 that were suitable for XRD were obtained from the slow diffusion of MeOH into a solution in chlorobenzene. Figure 2 shows the solid-state structure of compound 3 in which the porphyrin core was almost coplanar with a relatively small mean plane deviation (0.036 Å). The $C_{\text{meso}}\text{-}C_{\text{meso}}$ and two $C_{\beta}\text{-}C_{\beta}$ bond lengths were 1.49 and 1.44 Å, respectively, and the Zn--Zn distance was 8.44 Å. These structural features were similar to those of previously reported compounds 1^[15] and 2,^[10] but the crystal-packing structure was unique, in that diporphyrins 3 were stacked with an interporphyrin separation of about 6.83 Å without meaningful offset (see the Supporting Information).

Figure 3 shows the UV/Vis/NIR absorption spectra of compounds 9, 1, and 3, along with hexakis(3,5-di-*tert*-butylphenyl) *meso-meso*-linked Zn-diporphyrin 10 in CHCl₃. The absorption spectrum of compound 9 was similar to that of compound 10, thereby exhibiting split Soret bands at 418 and 456 nm. The absorption features of compound 3 were also similar to those of compounds 1 or 2, with three main bands: a Soret-like band at 414 nm, a red-shifted Soret band

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Figure 2. X-ray crystal structure of **3**. Thermal ellipsoids are set at 30 % probability. Solvent molecules are omitted for clarity.



Figure 3. UV/Vis/NIR absorption (solid) and fluorescence spectra (dashed) of a) compounds 9 and 10, and b) compounds 1 and 3 in CHCl₃.

at 559 nm, and extensively red-shifted Q-band-like bands at 945 and 1077 nm.

Extensive studies were carried out to elucidate the molecular-structure–TPA-property relationship.^[4b] The most important factor for the enhancement of TPA was presumably the extension of π -electron conjugation. Another effective factor that was proposed to enhance TPA was charge-transfer interactions.^[16] In this context, *meso--meso*, β - β , β - β triply linked diporphyrins **1–3**, which could be regarded as D-D, D-A, and A-A (D: a 3,5-di-*tert*-butylphenyl-substituted donor-type porphyrin, and A: a pentafluorophenyl-substituted acceptor-type porphyrin), respectively, were used to examine the effects of charge-transfer interactions on TPA property.^[10] A wavelength-scanning open-aperture Z-scan method was used to determine TPA, with the NIR pulses generated from an NIR optical parametric amplifier that was pumped by a femtosecond Ti:sapphire regenerative amplifier system with a 130 fs pulse-width. We measured the TPA values by photoexcitation in the wavelength range of 850–1150 nm (**9**) and 1400–2100 nm (**3**), at which the one-photon absorption contribution was negligible (Figure 4).



Figure 4. One- (OPA) and two-photon absorption (TPA) spectra of compounds 9 (top) and 3 (bottom) in CH₂Cl₂. TPA spectra are plotted at $\lambda_{ex}/2$.

The highest TPA values and excited-state lifetimes are listed in Table 1. In compounds **9** and **3**, the maximum TPA crosssections were 240 and 1700 GM, respectively; the TPA value per porphyrin units (σ^2/N) of compound **3** was about seven

Table 1. TPA cross-section (σ^2) values and excited-state lifetimes of compounds **1**, **2**, **3**, and **9**.

	σ^2 [GM]	$\sigma^2 / N[GM]^{[a]}$	$\lambda_{ex}[nm]$	$\tau_{\rm s}[{\rm ps}]$
1	1900	950	1700	4.5
2	2200	1100	1650	3.7
3	1700	850	1700	3.3
9	240	120	1050	1.6×10^{3}

[a] TPA cross-section per porphyrin unit.

times larger than that of compound 9, thus showing that the TPA values were strongly associated with effective π -conjugation. Compared with dimer 1 (D-D) and dimer 2 (D-A), the TPA values of dimer 3 were relatively small. Seemingly, the D-D and D-A structures were more effective at enhancing TPA than the A-A system and charge-transfer interaction played some role in TPA enhancement.^[17]

To explore the excited-state dynamics of triply linked porphyrin dimers 1–3, femtosecond transient absorption (TA) measurements were carried out (for compound 3, see Figure 5; for compounds 1 and 2, see the Supporting Information). In the TA spectrum of compound 3, sharp and in-

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Figure 5. Transient absorption spectra of triply linked porphyrin dimer **3**; inset shows the decay profiles. $\lambda_{punp} = 1050 \text{ nm}$; $\lambda_{probe} = 560 \text{ and } 680 \text{ nm}$.

tense ground-state bleach (GSB) signals were observed in the range of 500–650 nm, which were accompanied by an excited-state absorption (ESA) band in the region of 650– 750 nm. These dynamic spectroscopic features of compound **3** were similar to those of compounds **1** and **2**. The temporal profile of compound **3** was governed by a fast recovery process (τ_s =3.3 ps), which was much faster than that of singly linked dimer **9** (τ_s =1.6 ns, see the Supporting Information). It was possible to explain the ultrafast internal conversion in terms of the energy-gap law, which meant that there was a strong correlation between the ordering of the S₁-state energies and lifetimes.^[4,17]

The electrochemical potentials of these electron-deficient diporphyrins were measured by cyclic voltammetry in CH₂Cl₂. The CV of meso-meso-linked diporphyrin 9 showed reversible oxidation and reduction waves (0.72, -1.48, and -1.60 V) that were positively shifted from those of the parent diporphyrin (0.43, 0.32, and -1.89 V; see the Supporting Information) by about 0.40 V. The CVs of compounds 1 and 3 are shown in Figure 6. As in compound 1, the first oxidation potential of compound 3 was split ($\Delta E =$ 0.28 V), owing to the electronic communication between the two porphyrins, which was comparable to that of compound 1 (0.31 V). More importantly, the first oxidation potential of compound 3 (0.41 V) was positively shifted from that of compound 1 by 0.44 V, and the first and second reduction potentials were reversible waves at -0.79 and -1.01 V. The higher first oxidation potential of compound 3 was consistent with its chemical stability towards oxidative degradation. On the basis of these electrochemical data, the electrochemical HOMO-LUMO gaps were 1.10 and 1.20 eV for compounds 1 and 3, respectively.

Conclusions

Triply linked electron-deficient diporphyrin 3 was prepared by the cross-condensation of 1,1,2,2-tetrapyrroethane (5) with dipyrromethane dicarbinol (6), followed by oxidation



Figure 6. CVs of a) compound **1** and b) compound **3** in CH_2Cl_2 with 0.1 M Bu₄NPF₆ as an electrolyte (*V* versus ferrocene/ferrocenium ion pair; reference electrode: Ag/AgClO₄; working electrode: Pt electrode; counter electrode: Pt wire electrode; scan rate: 0.05 V s⁻¹).

with DDQ and $Sc(OTf)_3$. Dimer **3** exhibited red-shifted absorption bands and a split first oxidation potential, which are common for electron-rich porphyrin tapes. The TPA value of compound **3** was 1700 GM, much larger than that of the singly linked dimer **9** but slightly smaller than those of D-D- and D-A-type tapes **1** and **2**. The S₁-state lifetime of compound **3** was 3.3 ps. Dimer **3** displayed better solubility and improved chemical stability owing to its positively shifted HOMO, which encouraged its incorporation into more-elaborate molecular systems; work on the development of such systems is underway in our laboratory.

Experimental Section

General

¹H NMR and ¹⁹F NMR spectra were recorded on a JEOL ECA-600 spectrometer (600 MHz for ¹H and 565 MHz for ¹⁹F nuclei). Chemical shifts (δ) are reported in ppm relative to the residual solvent as the internal reference for the ¹H NMR spectra (δ =7.260 ppm) and hexafluorobenzene as an external reference for the ¹⁹F NMR spectra (δ =-162.9 ppm). UV/Vis/NIR spectra were recorded on a Shimadzu UV-3100PC spectrometer. HRMS (ESI-TOF) of samples in MeCN were recorded on a BRUKER microTOF instrument in positive- or negative-ion modes. X-ray data were recorded on a Rigaku-Raxis imaging plate system. Unless otherwise noted, materials that were obtained from commercial suppliers were used without further purification. Column chromatography on silica gel was performed on Wakogel C-300 and C-400. Thin-layer chromatography (TLC) was carried out on Al sheets coated with silica gel 60 F₂₅₄ (Merck 5554).

1,1,2,2-Tetrapyrroethane (5)

TFA (160 μ L, 2.1 mmol, 5 mol%) was added to a solution of 1,4-dioxane-2,3-diol (**4**, 5.0 g, 42 mmol) in pyrrole (58 mL, 840 mmol, 20 equiv) and the resulting solution was stirred under a N₂ atmosphere at 0°C. After 2 h, the reaction was quenched by the addition of triethylamine and unreacted pyrrole was removed by distillation under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ CH₂Cl₂, 1:1). Recrystallization from CH₂Cl₂/*n*-hexane gave the product as a white powder (1.6 g, 5.5 mmol, 13% yield). The spectroscopic data were the same as those reported previously.^[12]

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meso-meso-Linked Diporphyrin (8)

To a solution of tetrapyrroethane (5, 500 mg, 1.72 mmol) and dicarbinol $6^{[14b]}$ (2.65 g, 3.79 mmol, 2.2 equiv) in dry CH₂Cl₂ (100 mL) was added *p*-toluenesulfonic acid monohydrate (372 mg, 1.89 mmol, 1.1 equiv), and the resulting solution was stirred under a N₂ atmosphere at ambient temperature for 1 h. After the addition of DDQ (2.35 g, 10.3 mmol, 6.0 equiv), the solution was stirred for a further 1 h and then passed through a short alumina column to remove any tar. The reaction mixture was purified by GPC and column chromatography on silica gel to afford porphyrin **7** (225 mg, 278 µmol, 8.1% yield) and diporphyrin **8** (104 mg, 64 µmol, 3.7% yield). The spectroscopic data of compound **7** were the same as those reported previously.^[18]

8: ¹H NMR (600 MHz, CDCl₃, 298 K): δ =9.00 (m, 8H; β-H), 8.61 (d, *J*= 4.6 Hz, 4H; β-H), 8.15 (d, *J*=4.6 Hz, 4H; β-H), -2.31 ppm (brs, 4H; inner NH); ¹⁹F NMR (565 MHz, CDCl₃, 298 K): δ =-126.44 (m, 12 F; *o*-F), -151.15 (t, *J*=22.0 Hz, 2F; *p*-F), -151.27 (t, *J*=22.0 Hz, 4F; *p*-F), -161.19 (dt, ¹*J*=6.1 Hz, ²*J*=23.0 Hz, 4F; *m*-F), -161.39 ppm (dt, ¹*J*=6.1 Hz, ²*J*=23.0 Hz, 4F; *m*-F), -161.39 ppm (dt, ¹*J*=6.1 Hz, ²*J*=23.0 Hz, 4F; *m*-F), -161.39 ppm (dt, ¹*J*=6.1 Hz, ²*J*=23.0 Hz, 8F; *m*-F); UV/Vis (CHCl₃): λ_{max} (ε)=410 (209000), 447 (215000), 518 (61000), 591 (18000), 647 (3500), 664 nm (4000 mol⁻¹dm³cm⁻¹); HRMS (ESI-TOF, positive-ion mode): *m*/*z* calcd for C₇₆H₂₁N₈F₃₀: 1615.1405; found: 1615.1384 [*M*+H]⁺.

Crystal data: $C_{76}H_{20}F_{30}N_8 \cdot 2.5 C_2H_4Cl_2$; $M_w = 1862.38$; triclinic; space group: P-1 (No. 2); a = 18.5492(3), b = 21.5458(4), c = 22.1560(4) Å; a = 68.6717(9), $\beta = 89.6696(9)$, $\gamma = 64.5465(8)^\circ$; V = 7327.5(2) Å³; Z = 4; $\rho_{calcd} = 1.688 \text{ g cm}^{-3}$; T = 93(2) K; $R_1 = 0.1051$ [$I > 2\sigma(I)$]; $R_w = 0.3173$ (all data); GOF = 1.069. Crystals were grown from 1,2-dichloroethane/ MeOH.

meso-meso-Linked Zn^{II}-Diporphyrin (9)

To a solution of compound **8** (83.5 mg, 51.7 µmol) in MeOH (100 mL) was added Zn(OAc)₂·2 H₂O (190 mg, 1.1 mmol, 20 equiv) and the resulting solution was stirred under a N₂ atmosphere at ambient temperature. After 12 h, the reaction mixture was washed with water, dried over Na₂SO₄, and the solvent was removed under reduced pressure to afford the product as a red solid (86.2 mg, 49.5 µmol, 96 % yield). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 9.08 (m, 8 H; β-H), 8.67 (d, *J* = 4.6 Hz, 4H; β-H), 8.18 ppm (d, *J* = 4.6 Hz, 4H; β-H); ¹⁹F NMR (565 MHz, CDCl₃, 298 K): δ = -136.70 (m, 12F; o-F), -151.86 (t, *J* = 2.0 Hz, 2F; p-F), -151.98 (t, *J* = 22.0 Hz, 4F; p-F), -161.74 (dt, ¹*J* = 5.9 Hz, ²*J* = 23.5 Hz, 4F; m-F); uV/ Vis (CHCl₃): λ_{max} (ϵ) = 320 (37000), 418 (203000), 456 (21000), 563 (51000), 602 nm (14000 mol⁻¹dm³ cm⁻¹); fluorescence (CHCl₃, λ_{ex} = 418 nm): λ_{max} = 597, 652 nm; HRMS (ESI-TOF, negative-ion mode): *m*/z calcd for C₇₆H₁₆N₈F₃₀Zn₂Cl: 1776.9244; found: 1776.9220 [*M*+Cl]⁻.

meso-meso, β - β , β - β Triply Linked Zn^{II}-Diporphyrin (3)

To a solution of compound $9~(55.0~\text{mg},\,31.6~\mu\text{mol})$ in dry toluene (80 mL) was added Sc(OTf)₃ (77.9 mg, 158 µmol, 5.0 equiv) and DDQ (35.9 mg, 158 $\mu mol,\, 5.0$ equiv) and the resulting solution was stirred under a N_2 atmosphere at 110°C for 6 h. After cooling to RT, THF was added to the reaction mixture and the resulting solution was passed through an alumina column with THF as an eluent. The solution was evaporated and recrystallization from CH₂Cl₂/MeOH gave the product as violet crystals (36.4 mg, 20.9 μ mol, 66 % yield). ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta =$ 7.71 (d, J=4.6 Hz, 4H; β-H), 7.67 (d, J=4.6 Hz, 4H; β-H), 7.09 ppm (s, 4H; bay-area); ¹⁹F NMR (565 MHz, CDCl₃, 298 K): $\delta = -137.17$ (dd, ¹J = 7.3 Hz, ${}^{2}J = 25.7$ Hz, 8F; *o*-F), -137.43 (dd, ${}^{1}J = 7.3$ Hz, ${}^{2}J = 25.7$ Hz, 4F; o-F), -151.88 (m, 6F; p-F), -161.14 ppm (m, 12F; m-F); UV/Vis $(CH_2Cl_2): \lambda_{max}(\varepsilon) = 414 \ (137\ 000), \ 523 \ (54\ 600), \ 559 \ (128\ 000), \ 601 \ (91\ 400),$ 661 (35000), 945 (13300), 1077 nm (13600 mol⁻¹ dm³ cm⁻¹); fluorescence (CHCl₃, λ_{ex} =414 nm): λ_{max} =1101, 1272 nm; HRMS (ESI-TOF, negativeion mode): m/z calcd for C₇₆H₁₂N₈F₃₀Zn₂Cl: 1772.8931; found: 1772.8920 $[M+C1]^-$.

Crystal data: $C_{76}H_{18}F_{30}N_8Zn_2 \cdot 5$ MeOH·2 PhCl; $M_w = 2088.93$; monoclinic; space group: $P2_1/c$ (No. 14); a = 21.6317(7), b = 6.9196(2), c = 28.9465(6) Å; $\beta = 104.2737(14)^{\circ}$; V = 4199.0(2) Å³; Z = 2; $\rho_{calcd} = 28.9465(6)$

1.652 g cm⁻³; T=93(2) K; $R_1=0.0753$ [$I>2\sigma(I)$]; $R_w=0.2214$ (all data); GOF=1.012; crystals were grown from PhCl/MeOH.

Crystallographyic Data

CCDC 871954 (**3**) and CCDC 871954 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Two-photon-Absorption Experiments

The TPA spectrum was measured in the NIR region by using the openaperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a repetition rate of 3 kHz that was generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). After passing through a 10 cm focal length lens, the laser beam was focused and passed through a 1 mm quartz cell. Because the position of the sample cell could be controlled along the laser beam direction (z axis) by using the motorcontrolled delay stage, the local power density within the sample cell could be simply controlled under constant laser intensity. The transmitted laser beam from the sample cell was then detected by using the same photodiode as that used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point (I_0) was in the range of 40-60 GW cm⁻². For a Gaussian beam profile, the nonlinear absorption coefficient can be obtained by curve fitting of the observed open-aperture traces T(z) to Equation (1), where a_0 is the linear absorption coefficient, l is the sample length, and z_0 is the diffraction length of the incident beam.

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

After the nonlinear absorption coefficient has been obtained, the TPA cross-section $\sigma^{(2)}$ of one solute molecule (in GM, where $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ sphoton}^{-1} \text{ molecule}^{-1}$) can be determined by using Equation (2), where N_A is the Avogadro constant, *d* is the concentration of the compound in solution, *h* is the Planck constant, and ν is the frequency of the incident laser beam.

$$\beta = \frac{10^{-3} \sigma^{(2)} N_A d}{h\nu}$$
(2)

Transient Absorption Experiments

The femtosecond time-resolved transient absorption (TA) spectrometer used for this study consisted of a femtosecond optical parametric amplifier (Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical-detection system. The generated OPA pulses had a pulse width of about 100 fs and an average power of 1 mW in the range of 450-800 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated with a sapphire window (2 mm thick) by focusing a small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between the pump and probe beam was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). The intensities of the spectroscopically dispersed WLC probe pulses were monitored by a miniature spectrograph (OceanOptics, USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption-spectra intensities were saved alternately with or without pump pulses. Typically, 6000 pulses were used to excite the samples and to obtain the TA spectra at a particular delay time. The polarization angle between the pump and the probe beam was set at the magic angle (54.7°) by using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation

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full-width at half-maximum (fwhm) in the pump-probe experiments was less than 200 fs and the chirp of WLC probe pulses was 800 fs in the range of 400–800 nm. To minimize chirp, all of the reflection optics were used in the path of the probe beam and a quartz cell of 2 mm path length was used. After completing each set of fluorescence and TA experiments, the absorption spectra of all of the compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

Time-Resolved Fluorescence-Lifetime Experiments

Time-resolved fluorescence-lifetime experiments were performed by using the time-correlated single-photon-counting (TCSPC) technique. As an excitation light source, we used a home-made cavity-dumped Ti:sapphire oscillator, which provided a high repetition rate (200-400 kHz) of ultrashort pulses (100 fs at fwhm) pumped by a continuous wave (cw) Nd-YVO4 laser (Coherent, Verdi). The output pulse of the oscillator was frequency-doubled by a 1 mm thickness of a second harmonic crystal (barium borate, BBO, CASIX). The fluorescence was collected by using a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) that was connected to a TCSPC board (Becker&Hickel SPC-130). The overall instrumental response function was about 25 ps (fwhm). A vertically polarized pump pulse by a Glan-laser polarizer irradiated the samples and a sheet polarizer, which was set at complementary angle to the magic angle (54.7°), was placed in the fluorescence-collection path to obtain polarization-independent fluorescence decays.

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Mix tape: A hexakis(pentafluorophenyl)-substituted *meso-meso*, β - β , β - β triply linked Zn^{II}-diporphyrin exhibited considerably improved chemical stability, owing to a lowered HOMO, and good solubility in common organic solvents.

Porphyrinoids

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An Electron-Deficient Porphyrin Tape 💻

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