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Electronic Supplementary Information

Tetrakis(4-tert-butylphenyl) Substituted and Fused Quinoidal **Porphyrins**

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1. Experimental Section

1.1 General

All reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous toluene and dichloromethane (DCM) was distilled under a nitrogen atmosphere over sodium and calcium hydride, respectively. 5,15-2-(4-*tert*-butylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane,² Bismesitylporphyrin,¹ were prepared according to the literatures. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). All NMR spectra were recorded on the Bruker DPX300 or AMX500 spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Electron ionization mass spectrometry (EI MS) was performed on a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. MALDI-TOF mass spectra were measured on a Bruker Autoflex MALDI-TOF instrument using tetracyanoquinodimethane (TCNQ) as a matrix. UV-vis absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Cyclic voltammetry and differential pulse voltammetry measurements were performed in dry DCM on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1 M Bu₄NPF₆ as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. The potential was externally calibrated against the ferrocene/ferrocenium couple.

The femtosecond time-resolved transient absorption 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 ~100 fs and an average power of 1 mW in the range 450 to 800 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm thick) by focusing of 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 pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by 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 pulse. Typically, 6000 pulses were used excite samples and to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation fwhm in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all 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.

The two-photon absorption spectrum was measured in the NIR region 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 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. Since the position of the sample cell could be controlled along the laser beam direction (*z* axis) 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 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. For a Gaussian beam profile, the nonlinear absorption coefficient can be obtained by curve fitting of the observed open-aperture traces T(z) with the following equation:

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

where α_0 is the linear absorption coefficient, l is the sample length, and z_0 is the diffraction length of the incident beam. After the nonlinear absorption coefficient has been obtained, the TPA cross section $\sigma^{(2)}$ of one solute molecule (in units of GM, where 1 GM = 10^{-50} cm⁴ s photon⁻¹ molecule⁻¹) can be determined by using the following relationship:

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

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

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1.2 Synthetic procedure and characterization data



Following a literature procedure,³ a solution of thallium(III) trifluoroacetate (TTFA, 22.7 g, 41 mmol) in TFA (60 mL) was added dropwise over 5 min to a solution of 5,15bismesitylporphyrin (3) (1.240 g, 2.27 mmol) and TFA (60.00 mL, 0.78 mol) in DCM (320 mL). The mixture turned from blue to green and then slowly to yellow-green. After 20 min, the solution was poured into H₂O (2 L). The organic layer was washed by H₂O (250 mL), dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The brown thallium (III) complex was demetalated immediately by stirring in TFA (50 mL) for 1 h and then the resulting yellow solution was poured into water. The mixture was extracted by DCM (500 mL) and the organic layer was washed with several portions of H₂O and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by column chromatography (silica, hexane/DCM = 1/5) to afford the desired product 5,15dioxoporphodimethene **4** (550 mg) in 42% yield. ¹H NMR (CDCl₃, 500 MHz): δ ppm 14.08 (s, 2H, NH), 7.15 (d, 2H, J = 3.7 Hz, pyrrole), 6.95 (s, 4H, mesilyl), 6.39 (br, 4H, pyrrole), 2.37 (s, 6H), 2.14 (s, 12H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm 175.83, 147.36, 138.33, 136.14, 133.54, 128.12, 21.06 19.72. HR MS (EI): calcd. for C₂₈H₃₆N₄O₂: 576.2525; found: m/z = 576.2531 (error = 0.91 ppm).



To a 250 mL two-necked round-bottomed flask was added CBr₄ (422 mg, 1.27 mmol), PPh₃

(650.0 mg, 2.48 mmol) and anhydrous toluene (50 mL). The mixture was stirred at room temperature for 5 minutes. Then compound **4** was added at once and the mixture was heated at 80 °C for 12 hrs. After cooling to the room temperature, the precipitate was removed by filtration and washed with toluene. The solvent was removed under vacuum the residue was purified by column chromatography (silica gel, hexane/DCM = 1/5) to give the desired product **5** (358.5 mg) in 55% yield. ¹H NMR (CDCl₃, 500 MHz): δ ppm 13.18 (s, 2H, NH), 6.91 (s, 4H), 6.66 (d, 4H, *J* = 4.4 Hz), 6.29 (d, 4H, *J* = 4.4 Hz), 2.35 (s, 6H), 2.14 (s, 12H). HR MS (EI): calcd. for C₄₀H₃₂Br₄N₄: 883.9360 ; found: *m*/*z* = 883.9365 (error = 0.56 ppm).



A mixture of compound **5** (108 mg, 0.122 mmol), 2-(4-*tert*-Butylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (316 mg, 1.22 mmol), toluene (100 mL), and Na₂CO₃ aqueous solution (2 M, 13 mL) was degassed by bubbling through nitrogen stream for 30 min. Pd(PPh₃)₄ (28.18 mg, 0.0244 mmol) was added and the mixture was further degassed by three freeze-pump-thaw cycles. The reaction was heated at 120 °C for 48 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic layer was washed by water and dried over anhydrous MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 1/3) to afford the desired product **1-H2** (93 mg) in 68% yield. ¹H NMR (CDCl₃, 500 MHz): δ ppm 12.80 (s, 2H, NH), 7.26 (m, 16H), 6.86 (s, 4H), 6.04 (m, 4H), 5.67 (m, 4H), 2.31 (s, 6H), 2.11 (s, 12H), 1.30 (m, 36H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm 150.54, 146.79, 139.84, 137.85, 137.22, 135.03, 129.50, 127.60, 126.36, 124.92, 34.52, 31.32, 29.69, 21.04, 20.07. HR MS (MALDI-TOF): calcd. for C₃₂H₂₀O₂: 1100.6696, found: *m/z* = 1100.6683 (error = -1.2 ppm).

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Compound **1-H2** (93 mg, 0.084 mmol) was dissolved in toluene (30 mL) and nickel (II) acetylacetonate (43.3 mg, 0.168 mmol) was added. The mixture was heated at 100 °C for 24 h. The solvent was removed and the residue was purified by column chromatography (silica gel, hexane/DCM = 1/2) to give the nickel complex **1** (96 mg) in 99% yield. ¹H NMR (CDCl₃, 500 MHz): δ ppm 7.36 (d, 8H, *J* = 7.55 Hz), 7.29 (d, 8H, *J* = 7.55 Hz), 6.86 (s, 2H), 6.81 (s, 2H), 6.06 (d, 4H, *J* = 4.4 Hz), 5.70 (d, 4H, *J* = 4.4 Hz), 2.30 (m, 12H), 1.86 (s, 6H), 1.30 (m, 36H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm 155.10, 150.39, 145.29, 140.10, 139.76, 137.16, 136.91, 136.71, 135.67, 134.01, 129.55, 128.72, 127.84, 127.47, 124.78, 121.03, 34.53, 31.35, 29.70, 21.03, 20.43, 19.28. HR MS (MALDI-TOF): calcd. for C₈₀H₈₂N₄Ni: 1156.5893; found: *m/z* = 1156.5852 (error = 3.5 ppm).



Compound **1** (50 mg, 0.043 mmol) was dissolved in DCM (5 mL) and methane sulfonic acid (1 mL) was added slowly. The mixture was stirred for 5 min at room temperature, then DDQ

(39 mg, 0.173 mmol) was added. The reaction was quenched by water after stirring for 15 minutes under nitrogen atmosphere and extracted with DCM. The organic layer was washed by water and dried over anhydrous MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM = 1/4) to afford the desired product compound **2** (38 mg) in 80% yield. ¹H NMR (CDCl₃, 500 MHz): δ ppm 8.20 (d, *J* = 8.88 Hz, 4H), 7.60 (s, 4H), 7.30 (d, *J* = 8.88 Hz, 4H), 7.07 (s, 4H), 6.83 (s, 4H), 2.50 (s, 6H), 2.26 (s, 12H), 1.37-1.26 (m, 36H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm 151.04, 148.45, 142.58, 141.37, 137.57, 137.24, 136.42, 134.75, 130.74, 129.87, 129.55, 127.93, 127.67, 123.32, 122.78, 120.29, 114.37, 114.07, 34.82, 31.19, 29.71, 22.70, 21.40, 20.27. HR MS (MALDI-TOF): calcd. for C₃₂H₂₀O₂: 1148.5267; found: *m/z* = 1148.5302 (error = 3 ppm).

2. TDDFT caculations of 1 and 2.

Time-dependent DFT (TDDFT) calculations have been performed at the B3LYP/6-31G* level of theory,⁴⁻⁸ as implemented in the *Gaussian 09* program package.⁹ The geometry of **1** and **2** was fully optimized in gas phase using the default convergence criteria without any constraints and confirmed by frequency calculations. UV-vis-NIR absorption spectra were generated assuming an average UV-vis width of 4000 cm⁻¹ at half-height using the SWizard program.¹⁰

Calcd. (nm)	f	Composition (H=HOMO, L= LUMO, L+1 = LUMO+1, etc.)
628.3	0.1051	H-1->L+0(+55%) H-0->L+0(+41%)
605.4	0.2162	H-0->L+0(+49%) H-1->L+0(43%)
419.2	0.8364	H-1->L+1(+74%) H-0->L+0(7%)
366.9	0.1259	H-0->L+2(+56%) H-12->L+0(25%) H-0->L+4(+5%)

Table S1. Calculated absorption data	for 1	1.
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Figure S1. Calculated absorption spectrum for compound 1.

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Calcd. (nm)	f	Composition(H=HOMO, L= LUMO, $L+1 = LUMO+1$, etc.)
770.5	0.3950	H-0->L+0(+81%) H-2->L+0(+11%) H-1->L+1(8%)
629.0	0.1818	H-2->L+0(+87%) H-0->L+0(8%)
476.0	0.2140	H-20->L+2(31%) H-2->L+1(+30%)
		H-1->L+1(+12%) H-22->L+2(5%)
474.6	1.3032	H-1->L+1(+71%) H-20->L+2(+9%) H-0->L+0(+9%)

Table S2. Calculated absorption data for 2.



Figure S2. Calculated electronic absorption spectrum of 2.

3. Photophysical and electrochemical data of compounds 1 and 2

CO.	λ_{abs}	$\varepsilon_{\rm max}$	$E_{ m ox}^{1/2}$	$E_{\rm red}^{1/2}$	$E_{\rm ox}^{\rm onset}$	$E_{\rm red}^{\rm onset}$	НОМО	LUMO	$E_{\rm g}^{\rm EC}$	$E_{\rm g}^{\rm Opt}$
	(nm)	$(M^{-1}cm^{-1})$	(V)	(V)			(eV)	(eV)	(eV)	(eV)
1	451, 634	53 900	0.21 0.95	-1.55 -1.82	0.13	-1.20	-4.93	-3.60	1.33	1.69
2	534, 669, 781	54 700	0.35, 0.85	-1.08 -1.50	0.26	-0.94	-5.06	-3.86	1.20	1.33

 Table S3. Photophysical and electrochemical properties of 1 and 2

 ε_{max} : molar extinction coefficient at the absorption maximum. $E_{\text{ox}}^{1/2}$ and $E_{\text{red}}^{1/2}$ are half-wave potentials of the oxidative and reductive waves, respectively. $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ are the onset potentials of the first oxidative and reductive redox wave, respectively, with potentials *versus* Fc/Fc⁺ couple. HOMO and LUMO energy levels were calculated according to equations: HOMO = - (4.8 + $E_{\text{ox}}^{\text{onset}}$) and LUMO = - (4.8 + $E_{\text{red}}^{\text{onset}}$). E_{g}^{EC} : electrochemical energy gap derived from LUMO-HOMO. E_{g}^{Opt} : optical energy gap derived from lowest energy absorption onset in the absorption spectra.



Figure S3. Differential pulse voltammograms of **1** and **2** in CH_2Cl_2 with 0.1M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode and Pt wire as counter electrode. Fc⁺/Fc was used as external reference.

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4. Transient absorption spectra and Z-scan curves for 1 and 2

Figure S4. Femtosecond transient absorption spectra of **1** in dichloromethane measured at room temperature (296 K). Excitation wavelength is 450 nm.



Figure S5. Femtosecond transient absorption spectra of **2** in dichloromethane measured at room temperature (296 K). Excitation wavelength is 780 nm.

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Figure S6. Z-scan curves of **1** and **2** in dichloromethane by photoexcitation in the range from 1200 to 1600 nm.

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6. Additional NMR spectra and HR mass spectra



Figure S7. ¹H NMR spectrum of compound 4 (500 MHz, CDCl₃, rt).



Figure S8. ¹³C NMR spectrum of compound 4 (125 MHz, CDCl₃, rt).



Figure S9. ¹H NMR spectrum of compound **5** (500 MHz, CDCl₃, rt).



Figure S10. ¹H NMR spectrum of compound 1-H2 (500 MHz, CDCl₃, rt).



Figure S11. ¹³C NMR spectrum of compound 1-H2 (125 MHz, CDCl₃, rt).



Figure S12. ¹H NMR spectrum of compound **1** (500 MHz, CDCl₃, rt).







Figure S14. ¹H NMR spectrum of compound 2 (500 MHz, CDCl₃, rt).



Figure S15. ¹³C NMR spectrum of compound 2 (125 MHz, CDCl₃, rt).



Figure S16. HR mass spectrum (MALDI-TOF) of the compound 2.



Figure S17. HR mass spectrum (MALDI-TOF) of compound 1.



Figure S18. HR mass spectrum (MALDI-TOF) of compound 1-H2.



 Mass
 (ppm)
 equiv.

 576.2531
 2070398.0
 100.00
 576.2525
 0.91
 25.0
 C 38 H 32 O 2 N 4

Figure S19. HR mass spectrum (EI) of compound 4.



Figure S20. HR mass spectrum (EI) of compound 5