# **Electronic Supplementary Information**

# Intramolecular electron transfer reactions in *meso-*(4nitrophenyl)-substituted subporphyrins

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## **1. Experimental Protocols**

## Instrumentations and materials.

All reagents and solvents were of commercial reagent grade and were used without further purification unless where noted. Preparative separations were performed by silica gel column chromatography (Wako gel C-300). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the  $\delta$  scale in ppm relative to the internal standards CHCl<sub>3</sub> ( $\delta$  = 7.26 ppm for <sup>1</sup>H,  $\delta$  = 77.16 ppm for <sup>13</sup>C). BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta$  = 0.00 ppm for <sup>11</sup>B) was used as external standard for <sup>11</sup>B NMR measurements. CDCl<sub>3</sub> was purified by passing through a short aluminum oxide pad before use. HR-APCI-TOF-MS spectra were recorded on a Bruker Daltonics micrOTOF LC instrument. X-Ray crystallographic data was obtained by using a Rigaku XtaLAB P-200 system. The structures were solved by using SHELXL-98. CCDC number 1429320 (1) contains supplementary crystallographic data for this article. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

## **Steady-state Absorption and Emission Measurements**

Steady-state absorption spectra were obtained with an UV-VIS-NIR spectrometer (Varian, Cary5000) and steady-state fluorescence spectra were measured on a Hitachi model F-2500 fluorescence spectrophotometer and a Scinco model FS-2.

#### **Time-Resolved Fluorescence Decay Measurements**

A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay and fluorescence anisotropy decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides a ultrashort pulse (80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). This high repetition rate slows down to  $1M \sim 800$  kHz by using homemade pulse-picker. The pulse-picked output pulse was frequency-doubled by a 1 mm thickness of a BBO crystal (EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) 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 was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

#### **Femtosecond Transient Absorption Measurements**

The femtosecond time-resolved transient absorption (fs-TA) spectrometer consists of an optical parametric amplifier (OPA; Palitra, Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C, Quantronix) operating at 1 kHz repetition rate and an optical detection system. The generated OPA pulses have a pulse width of  $\sim 100$  fs and an average power of 1 mW in the range of 280-2700 nm, which are used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3 mm thick) by focusing a small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by a High Speed Spectrometer (Ultrafast Systems) for both visible and near-infrared measurements. To obtain the time-resolved transient absorption difference signal at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses excite the samples to obtain the fs-TA spectra at each 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 in order to prevent polarization-dependent signals. Cross-correlation fwhm in 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 region. To minimize chirp, all reflection optics in the probe beam path and a quartz cell of 2 mm path length were used. After fs-TA experiments, the absorption spectra of all compounds were carefully examined to detect if there were any changes due to degradation and photooxidation of samples.

#### **Computational Methods**

Quantum mechanical calculations were performed with the *Gaussian 09* program suite.<sup>S1</sup> All calculations were carried out by the density functional theory (DFT) method with Coulomb Attenuated Method-Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (CAM-B3LYP), employing the 6-31G(d,p) basis set. The X-ray crystallographic structure of **1** was used as the initial geometry for geometry optimizations of **1-4**.

#### Synthesis of compounds 1-4.



A 100 mL round-bottomed flask was charged with 4-nitrobenzoic acid (4.12 g, 24.65 mmol, 1 eq) and a magnetic stir bar. The flask was then equipped with standard distillation apparatus, to which a 100 mL collection flask was fitted. The entire set-up was then placed under an argon atmosphere. SOCl<sub>2</sub> (60 mL, 830 mmol) and a catalytic amount of DMF (2 drops) were added to the reaction flask, and the resulting reaction mixture was heated to just below refluxing temperature for 6 h. The SOCl<sub>2</sub> was then removed by distillation. The set-up was allowed to cool to room temperature. Anhydrous toluene (60 mL) was then added to the flask, followed by removal of the toluene by distillation to drive off any remaining SOCl<sub>2</sub>. This process was repeated three times. The distillation apparatus was carefully dismantled, and the resulting crude material was placed under vacuum. Upon cooling to room temperature, the crude material became a solid that was used in the next step without further purification.



To an argon purged solution of tripyrrane **ttol** (1 g, 2.47 mmol, 1 eq) in 1,2dichlorobenzene (100 mL) was added borane triethylamine complex (1.1 mL, 7.39 mmol, 3 eq), and the resulting mixture was heated to 150 °C for 2 h under argon. Gradually, the reaction mixture became a fluorescent green colour, indicating the successful formation of the triethylamine-tri-*N*-tripyrromethene-borane complex *in situ*. The solution was then diluted with 1,2-dichlorobenzene (200 mL), followed by the careful addition of a solution of 4nitrobenzoyl chloride (4.57 g, 24.65 mmol, 10 eq) in 1,2-dichlorobenzene (50 mL). Following addition of the acid chloride, the reaction temperature was maintained at 150 °C for 30 min. Then, the reaction mixture was quenched with pyridine ( $\approx$ 12 eq) and the resulting solution was heated to reflux in open air for 1 h. Following reflux, the reaction mixture was allowed to cool to room temperature, followed by the addition of ethylenediamine ( $\approx$ 12 eq). After stirring for 1 h at room temperature, the resulting black solution was poured on to a

silica gel pad (CH<sub>2</sub>Cl<sub>2</sub> eluent). CH<sub>2</sub>Cl<sub>2</sub> (1000 mL) was passed through the pad to remove the reaction solvent, unconsumed starting materials and unwanted by-products. Next, elution with MeOH/TFA (400 mL/40 mL) afforded a black fraction. The black fraction was neutralized by the careful addition of a saturated aqueous solution of NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $\approx$ 500 mL), washed with 1 M HCl ( $\approx$  500 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and then filtered. MeOH was then added to the filtered solution, followed by heating to 50°C with stirring for 30 min to enforce desired axial exchange to B-OMe. After 30 min, the solvent mixture was removed under reduced pressure. The resulting black tar was chromatographed on a silica gel column (loaded with neat CH<sub>2</sub>Cl<sub>2</sub>, eluent system ethyl acetate/ hexane 1/3). Both subporphyrin and subchlorin fractions were collected, including the latter axial OH fractions. The combined fractions were then oxidised with MnO<sub>2</sub> (stirring in CH<sub>2</sub>Cl<sub>2</sub> for 2 h) to convert all of the subchlorin to subporphyrin. Additional silica gel chromatography followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH yielded 1 (226 mg, 16%). Single crystals of 1 suitable for X-Ray diffraction analysis were obtained by vapour diffusion of pentane into a benzene solution of 1.



1: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.56 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 4.8 Hz, 2H), 8.14 (s, 2H), 8.07 (d, J = 4.8 Hz, 2H), 7.95 (d, J = 7.8 Hz, 4H), 7.52 (d, J = 7.8 Hz, 4H), 2.58 (s, 6H) and 0.83 (s, 3H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  –15.30 (s, 1B) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  147.48, 144.67, 141.45, 141.06, 140.90, 138.20, 134.14, 133.82, 133.26, 129.70, 123.97, 123.30, 122.77, 121.94, 121.49, 116.73, 116.73, 47.012, and 21.53 ppm; HRMS (APCI-TOF, positive mode): m/z = 575.2247, calcd for [C<sub>36</sub>H<sub>27</sub><sup>11</sup>BN<sub>4</sub>O<sub>3</sub>]<sup>+</sup> = 575.2255 [*M*+H]<sup>+</sup>; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup>cm<sup>-1</sup>]) = 378 (82,000), 464 (10900), and 493 nm (10300); Fluorescence (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{ex}$  = 378 nm);  $\lambda_{em}$  [nm] = 631,  $\Phi_{F}$  = 0.022.

For **2**, **3**, and **4**, 3-methyl-4-nitrobenzoic acid, 3,5-dimethyl-4-nitrobenzoic acid, and 2-methyl-4-nitrobenzoic acid were taken through the reaction sequence, respectively.



**2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.32 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 4.8 Hz, 2H), 8.13 (s, 2H), 8.08 (s with small unresolvable coupling, 1H), 8.07 (d, J = 4.8 Hz, 2H), 8.00 (dd,  $J_1$  = 1.2 Hz,  $J_2$  = 8.7 Hz, 1H), 7.95 (d, J = 7.8 Hz, 4H), 7.52 (d, J = 7.8 Hz, 4H), 2.85 (s, 3H), 2.58 (s, 6H) and 0.83 (s, 3H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -15.30 ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  148.53, 142.98, 141.42, 141.05, 140.94, 138.14, 137.38, 134.18, 133.26, 131.34, 129.67, 125.25, 123.13, 122.69, 121.74, 121.56, 116.93, 47.01, 21.53 and 21.20 ppm; HRMS (APCI-TOF, positive mode) : m/z = 589.2413, calcd for [C<sub>37</sub>H<sub>29</sub><sup>11</sup>BN<sub>4</sub>O<sub>3</sub>]<sup>+</sup> = 589.2412 [M+H]<sup>+</sup>; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup>cm<sup>-1</sup>]) = 379 (122,000), 464 (13400), and 493 nm (13500); Fluorescence (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{ex}$  = 379 nm);  $\lambda_{em}$  [nm] = 582,  $\Phi_{\rm F}$  = 0.040.



**3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.15 (d, J = 4.8 Hz, 2H), 8.12 (s, 2H), 8.06 (d, J = 4.8 Hz, 2H), 7.95 (d, J = 7.8 Hz, 4H), 7.81 (s, 2H), 7.52 (d, J = 7.8 Hz, 4H), 2.59 (s, 6H), 2.55 (s, 6H) and 0.83 (s, 3H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  –15.33 ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  151.47, 141.36, 141.06, 141.01, 139.68, 138.03, 134.28, 134.18, 133.50, 133.26, 130.12, 129.64, 122.84, 122.56, 121.67, 121.42, 117.63, 46.99, 21.53 and 18.07 ppm; HRMS (APCI-TOF, positive mode): m/z = 603.2561, calcd for [C<sub>38</sub>H<sub>31</sub><sup>11</sup>BN<sub>4</sub>O<sub>3</sub>]<sup>+</sup> = 603.2568 [*M*+H]<sup>+</sup>; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup>cm<sup>-1</sup>]) = 375 (155,000), 463 (13500), and 489 nm (11360); Fluorescence (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{ex} = 375$  nm);  $\lambda_{em}$  [nm] = 539,  $\Phi_{F} = 0.013$ .



4: Subporphyrin 4 exists in a 4:1 ratio of *exo:endo* atropisomers. DFT calculations carried out in previous work confirmed that chemical shifts corresponding to the *exo* atropisomer resonate lower down field.

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  147.78, 143.61, 141.78, 141.39, 141.31, 141.03, 137.98, 134.08, 133.90, 133.13, 129.53, 125.14, 122.77, 122.48, 121.66, 120.54, 120.48, 115.90, 47.03, 22.45 and 21.40 ppm; HRMS (APCI-TOF, positive mode): m/z = 589.2397, calcd for  $[C_{37}H_{29}^{11}BN_4O_3]^+ = 589.2412 [M+H]^+$ ; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup>cm<sup>-1</sup>]) = 372 (150,000), 460 (16250), and 485 nm (10980); Fluorescence (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{ex} = 372 \text{ nm}$ );  $\lambda_{em}$  [nm] = 538,  $\Phi_F = <0.001$ .

# 2. NMR spectra



**Figure S2-1.** <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub> at room temperature.



**Figure S2-2.** <sup>13</sup>C NMR spectrum of **1** in CDCl<sub>3</sub> at room temperature.



**Figure S2-3.** <sup>11</sup>B NMR spectrum of **1** in CDCl<sub>3</sub> at room temperature.



**Figure S2-4.** <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub> at room temperature.



**Figure S2-5.** <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub> at room temperature.



**Figure S2-6.** <sup>11</sup>B NMR spectrum of **2** in CDCl<sub>3</sub> at room temperature.



**Figure S2-7.** <sup>1</sup>H spectrum of **3** in CDCl<sub>3</sub> at room temperature.



Figure S2-8. <sup>13</sup>C spectrum of 3 in CDCl<sub>3</sub> at room temperature.



**Figure S2-9.** <sup>11</sup>B spectrum of **3** in CDCl<sub>3</sub> at room temperature.



**Figure S2-10.** <sup>1</sup>H spectrum of **4** in CDCl<sub>3</sub> at room temperature.



Figure S2-11. <sup>13</sup>C spectrum of 4 in CDCl<sub>3</sub> at room temperature.



**Figure S2-12.** <sup>11</sup>B NMR spectrum of **4** in CDCl<sub>3</sub> at room temperature.

#### **3 Mass Spectra**



Figure S3-1. HR-APCI-TOF MS spectrum of 1 (top: observed, bottom: simulated).



Figure S3-2. HR-APCI-TOF MS spectrum of 2 (top: observed, bottom: simulated).





Figure S3-3. HR-APCI-TOF MS spectrum of 3 (top: observed, bottom: simulated).

Figure S3-4. HR-APCI-TOF MS spectrum of 4 (top: observed, bottom: simulated).

# 4. X-Ray Crystallographic Analysis

 Table S4-1. Crystal data of 1

Compound	1
sum formula	$C_{90}H_{72}B_2N_8O_6$
formula weight /mol <sup>-1</sup>	1383.18
crystal dimensions /mm <sup>3</sup>	0.20×0.05×0.01
crystal description	orange
crystal system	triclinic
space group	P -1
a / Å	14.124(3)
<b>b</b> / Å	15.235(4)
<i>c</i> / Å	17.465(3)
lpha/°	87.755 (16)
<b>β</b> /°	69.970 (12)
$\gamma /^{\circ}$	89.95(2)
$V/\text{\AA}^3$	3527.8(14)
Ζ	2
$\rho_{\text{calcd.}} / \text{g cm}^{-3}$	1.302
$\mu/\mathrm{mm}^{-1}$	0.648
F(000)	1452.0
T / K	93
$\theta$ range	6.667-68.103
index ranges	-16 <h<16< th=""></h<16<>
5	-18 <k<18< th=""></k<18<>
	-20< <i>l</i> <21
reflections measured	45334
reflections independent	12443
reflections unique	7919
R <sub>int</sub>	0.1453
$R_1 [I > 2\sigma (I)]$	0.1084
$R_{\rm w}$ (all data)	0.2952
data/restrains/parameters	12443/0/972
GOF	1.084
CCDC	1429320

## 5. Cyclic Voltammetry



**Figure S5-1.** Cyclic voltammogram of **1** in  $CH_2Cl_2$  (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M  $nBu_4NPF_6$ , working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO<sub>4</sub>). Differential Pulse Voltammetry was used to confirm the reduction potentials.



**Figure S5-2.** Cyclic voltammogram of **2** in  $CH_2Cl_2$  (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>, working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO<sub>4</sub>).



**Figure S5-3.** Cyclic voltammogram of **3** in  $CH_2Cl_2$  (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M  $nBu_4NPF_6$ , working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO<sub>4</sub>).



**Figure S5-4.** Cyclic voltammogram of **4** in  $CH_2Cl_2$  (scan rate: 0.05 V/s, supporting electrolyte: 0.1 M  $nBu_4NPF_6$ , working electrode: Pt, counter electrode: Pt wire, reference electrode: Ag/0.01 M AgClO<sub>4</sub>).

### 6. NOSbF<sub>6</sub> titration



**Figure S6-1.** UV-Vis absorption spectra of triphenyl subporphyrin (A) in  $CH_2Cl_2/Acetonitrile 1:1$  with 0.1 M  $nBu_4NPF_6$  upon titration with a solution of NOSbF<sub>6</sub> in  $CH_2Cl_2/Acetonitrile 1:1$ . Black dashed line 0 eq, yellow dashed line 30 eq, blue dashed line 45 eq, red line 60 eq of NOSbF<sub>6</sub> added.

### 7. Absorption and Emission Spectra



Figure S7-1. UV-Vis absorption (left) and emission (right) spectra of 1-4 in toluene.



**Figure S7-2.** Femtosecond transient absorption spectra and decay profiles (inset) of (a) **1**, (b) **2**, (c) **3**, and (d) **4** in CH<sub>2</sub>Cl<sub>2</sub> for photoexcitation at 490 nm.



**Figure S7-3.** Fluorescence decay profile of (a) **1**, (b) **2** and (c) **3** in  $CH_2Cl_2$  for photoexcitation at 380 nm and monitoring at 720 nm for **1**, 700 nm for **2** and 650 nm for **3**.

# 8. DFT Calculation



Figure S8-1. Optimized molecular structures of (a) 1, (b) 2, (c) 3 and (d) 4.



Figure S8-2. Energy diagram and molecular orbital distribution of (a) 1, (b) 2, (c) 3 and (d) 4.

#### 9. Reference

S1 Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Pet ersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fuku da, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. H eyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. D aniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.