Supporting Information

Is the Special Pair Structure a Good Strategy for the Kinetics During the Last Step of the Energy Transfer With the Nearest Antenna?

A Chemical Model Approach.

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Table of Content

1. Experimental Section 2
2. References 7
3. NMR and High Resolution Mass Spectra 8
   1H NMR spectrum of 7 8
   MALDI-TOF spectrum of 7 9
   ESI HRMS spectrum of 7 10
   1H NMR spectrum of 8 11
   MALDI-TOF spectrum of 8 12
   ESI HRMS spectrum of 8 13
   1H NMR spectrum of 12 14
   MALDI-TOF spectrum of 12 16
   ESI HRMS spectrum of 12 16
   1H NMR spectrum of 13 17
   MALDI-TOF spectrum of 13 18
   ESI HRMS spectrum of 13 18
   1H NMR spectrum of 1 19
   MALDI-TOF spectrum of 1 21
   ESI HRMS spectrum of 1 21
4. Optical spectra 22
5. Computed energy barriers 24
6. Photophysical spectra and decays for 1, 8 and 13 25
1. Experimental Section

Materials. Zinc(II) 5-(8-bromobiphenylene-1-yl)-10,20-bis(nonyl)porphyrin 9,1 zinc(II) 5,15-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(nonyl)porphyrin 10,1 zinc (II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}]-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonyl-porphyrin 11,1 and zinc (II) 5-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-bis(3,5-di-tert-butylphenyl)porphyrin 62 were synthesised as previously described. The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. Dried toluene was obtained by passing through alumina under nitrogen in the solvent purification systems and then further dried over activated molecular sieves; extra dry DMF was purchased from Aldrich. Triethylamine, dichloromethane and 1,2-dichloroethane were distilled from CaH₂; THF and toluene were distilled from sodium benzophenone ketyl. Unless specified otherwise all other solvents were used as commercially supplied. Silica gel (Merck; 70-120 mm) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Size exclusion chromatography was carried out under gravity using cross-linked polystyrene Bio-Beads® SX-1 (200 – 400 mesh) in DCM. Reactions were monitored by thin-layer chromatography, UV-vis spectroscopy, and MALDI/TOF mass spectrometry.
Zinc(II) 5-(4-bromophenyl)-10,20-bis(3,5-di-tert-butyl-phenyl)-porphyrin 7

Under an inert atmosphere, a mixture of zinc (II) 5-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-bis(3,5-di-tert-butyl phenyl)porphyrin (155 mg, 0.18 mmol), 1-bromo,4-iodobenzene (76 mg, 0.27 mmol), cesium carbonate (91 mg, 0.28 mmol), Pd(PPh₃)₄ (21 mg, 0.0018 mmol) in 10 mL of anhydrous toluene and 5 mL of DMF was stirred at 100 °C overnight. The reaction was quenched with an aqueous saturated NH₄Cl solution (20 mL). The organic layer was separated, washed with a saturated NaHCO₃ solution (2x20 mL) and dried over MgSO₄. After evaporation until dryness, the residue was recrystallized in dichloromethane/methanol affording a microcrystalline violet powder (0.14 g, quant.).

UV-vis (THF) λmax (log ε)= 414 (5.73), 542 (4.31), 579 (3.30) nm.

ESI HRMS : m/z 902.2896 calced for C₅₄H₅₅BrN₄Zn, 902.2 (M⁺). ESI HRMS : m/z 902.2896 calced for C₅₄H₅₅BrN₄Zn, 902.2895 (M⁺). UV-vis (THF) λmax (log ε)= 414 (5.73), 542 (4.31), 579 (3.30) nm.

5-(4-bromophenyl)-10,20-bis(3,5-di-tert-butyl-phenyl)-porphyrin 8

20 mL of HCl aqueous solution (4M) was added onto a solution of zinc(II) 5-(4-bromophenyl)-10,20-bis(3,5-di-tert-butyl-phenyl)porphyrin (0.15 g, 0.166 mmol) in 50 mL of dichloromethane. The reaction mixture was vigourously stirred for 1 hour. The organic layer was separated, washed with a saturated NaHCO₃ aqueous solution (2x20 mL) and dried over magnesium sulfate. After evaporation until dryness, the residue was recrystallized in dichloromethane/methanol affording a microcrystalline violet powder (0.14 g, quant.).

1H NMR (300.16 MHz, CDCl₃): δ 10.23 (s, 1H, meso), 9.35 (d, 2H, J = 4.7 Hz, β), 9.07 (d, 2H, J = 4.6 Hz, β), 8.96 (d, 2H, J = 4.8 Hz, β), 8.84 (d, 2H, J = 4.8 Hz, β), 8.11 (m, 6H, C₆H₄+C₆H₃), 7.87 (d, 2H, J = 8.3 Hz, C₆H₄), 7.83 (m, 2H, C₆H₃), 1.56 (s, 36H, tBu) and -2.94 (s, 2H, NH) ppm. MALDI-TOF MS : m/z 840.3 calced for C₅₄H₅₅BrN₄, 840.3 (M⁺). ESI HRMS : m/z 841.3839 calced for C₅₄H₅₈BrN₄, 841.3844 (M+H⁺). UV-vis (THF) λmax (log ε)= 412 (5.43), 508 (4.09), 542 (3.69), 584 (3.59), 641 (3.29) nm.

5-{8-[10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonylporphyrin 12

3
10 mL of HCl aqueous solution (4M) was added onto a solution of zinc(II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonylporphyrin (58 mg, 0.038 mmol) in 15 mL of dichloromethane. The reaction mixture was vigourously stirred for 30 minutes. The acidic layer was removed and 10 mL of HCl aqueous solution (4M) was added again. After stirring for 30 minutes, the organic layer was separated, washed with a saturated NaHCO₃ aqueous solution (2x20 mL) and dried over magnesium sulfate. After evaporation until dryness, the residue was purified by silica gel (chloroform/petroleum ether 1/2) affording the title compound as a purple solid (33 mg, 62%). ¹H NMR (300.16 MHz, CD₂Cl₂): δ 9.34 (d, 2H, J = 4.6 Hz, β), 9.21 (s, 1H, meso), 8.77 (d, 2H, J = 4.9 Hz, β), 8.74 (d, 2H, J = 5.0 Hz, β), 8.66 (d, 2H, J = 4.7 Hz, β), 8.57 (br d, 2H, J = 4.9 Hz, β), 8.50 (d, 2H, J = 4.9 Hz, β), 8.47 (br d, 2H, J = 4.2 Hz, β), 8.37 (d, 2H, J = 4.8 Hz, β), 7.35-7.28 (m, 3H, DPB), 7.22-7.12 (m, 3H, DPB), 3.92 (m, 8H, CH₂), 2.13 (s, 12H, CH₃), 1.99 (m, 8H, CH₂), 1.62 (m, 8H, CH₂), 1.45 (m, 8H, CH₂), 1.32 (m, 32H, CH₂), 0.89 (t, 12H, J = 7.3 Hz, CH₃), -7.13 (s, 2H, NH) and -7.21 (s, 2H, NH) ppm. MALDI-TOF MS: m/z 1398.9 calcld for C₉₄H₁₁₄BN₃O₂, 1399.9 (M+H⁺). ESI HRMS: m/z 1399.9323 calcld for C₉₄H₁₁₆BN₃O₂, 1399.9263 (M+H⁺). UV-vis (THF) λmax (log ε) = 397 (5.54), 517 (4.13), 551 (3.81), 598 (3.68), 652 (3.43) nm.

Magnesium(II) 5-{8-[magnesium(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonylporphyrin 13

5-{8-[10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonylporphyrin (25 mg, 0.018 mmol) was dissolved in 10 mL of dichloromethane and 0.42 mL of NEt₃ (3 mmol) and 0.38 g of MgBr₂·OEt₂ (1.5 mmol) were successively added. The reaction mixture was stirred for 30 minutes. 10 mL of dichloromethane was added and the organic phase was washed by a diluted NaHCO₃ aqueous solution (2 x 20mL). The organic layer was dried over magnesium sulfate and evaporated until dryness. Chromatographic column on alumina eluting with CH₂Cl₂ and with acetone-CH₂Cl₂ (20%) afforded 3 as purple powder (20 mg, 80%). ¹H NMR (300.16 MHz, CD₂Cl₂): δ 9.33 (br s, 2H, β), 9.22(s, 1H, meso), 8.74 (m, 4H, β), 8.63 (br s, 2H, β), 8.54 (br s, 2H, β), 8.43 (br s, 2H, β), 8.30 (br s, 2H, β), 8.17 (br s, 2H, β), 7.30-7.23(m, 3H, DPB), 7.16-7.07 (m, 3H, DPB), 3.60 (br m, 8H, CH₂), 2.04 (s, 12H, CH₃), 1.95 (br m, 8H, CH₂), 1.62 (br m, 8H, CH₂), 1.49-1.21 (m, masked by heptane, CH₃), 0.91 (m, masked by heptane, CH₃) ppm. MALDI-TOF MS: m/z 1442.8 calcld for C₉₄H₁₁₁BMg₂N₃O₂, 1442.8 (M⁺). ESI HRMS: m/z 1443.8654 calcld for C₉₄H₁₁₁BMg₂N₃O₂, 1443.8746 (M+H⁺). UV-vis (THF) λmax (log ε)= 408 (5.58), 569 (4.04), 614 (3.85) nm.
Magnesium(II) 5-{8-[magnesium(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-[4-(10,20-bis-3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]phenyl-10,20-dinonylporphyrin 1

Under an inert atmosphere, a solution of Pd$_2$(dba)$_3$ (0.9 mg, 0.001 mmol) and S-PHOS (2.5 mg, 0.006 mmol) in 6 mL of freshly distilled toluene was added onto a mixture of magnesium(II) 5-{8-[magnesium(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2] dioxaborolan-2-yl)-10,20-dinonylporphyrin (15 mg, 0.010 mmol), 5-(4-bromophenyl)-10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin (13 mg, 0.015 mmol) and cesium carbonate (13 mg, 0.04 mmol). 3 mL of anhydrous DMF was added and the reaction mixture was stirred at 90 °C for 16 h. The reaction was quenched with 10 ml of water. The organic layer was separated, extracted from aqueous phase. The combined organic fractions were washed with brine (2 × 20 mL) and dried over MgSO$_4$. The solvents were removed under vacuum and the purple residue was purified over SEC chromatography affording the title compound as a dark purple solid (6 mg, 28%). $^1$H NMR (300.16 MHz, THF-d$_8$): δ 10.41 (s, 1H, meso), 9.83 (dd, 1H, $J$ = 7.0 Hz, $J$ = 1.7 Hz, C$_6$H$_2$), 9.56 (d, 2H, $J$ = 4.6 Hz, β), 9.50 (d, 2H, $J$ = 4.1 Hz, β), 9.39 (s, 1H, meso), 9.24 (d, 2H, $J$ = 4.4 Hz, β), 9.14 (d, 2H, $J$ = 4.2 Hz, β), 8.90 (d, 2H, $J$ = 3.9 Hz, β), 8.79 (d, 2H, $J$ = 3.9 Hz, β), 8.62 (d, 2H, $J$ = 4.7 Hz, β), 8.52 (d, 3H, $J$ = 4.0 Hz, β + C$_6$H$_3$), 8.46 (dd, 1H, $J$ = 7.0 Hz, $J$ = 1.9 Hz, C$_6$H$_4$), 8.39 (s, 2H, C$_6$H$_3$), 8.31 (s, 2H, C$_6$H$_3$), 8.24 (d, 2H, $J$ = 4.7 Hz, β), 8.03 (t, 2H, $J$ = 1.8 Hz, C$_6$H$_3$), 7.97 (d, 2H, $J$ = 5.4 Hz, β), 7.44 (d, 1H, $J$ = 7.2 Hz, DPB), 7.30 (d, 1H, $J$ = 6.6 Hz, DPB), 7.24 (dd, 1H, $J$ = 2.8 Hz, $J$ = 7.8 Hz, DPB), 7.21 (dd, 1H, $J$ = 2.1 Hz, $J$ = 8.1 Hz, DPB), 7.05 (m, 2H, DPB), 3.58 (masked by THF-d$_8$), 3.46 (m, 8H, CH$_2$), 2.01 (m, 8H, CH$_2$), 1.66 (s, 18H, tBu), 1.34 (m, masked by water and heptane, CH$_2$), 1.29 (s, 18H, tBu), 0.90 (m, masked by heptane, CH$_3$) and -2.60 (s, 2H, NH) ppm. MALDI-TOF MS : $m/z$ 2079.2 calecd for C$_{142}$H$_{156}$Mg$_2$N$_{12}$, 2079.2 (M$^+$). ESI HRMS : $m/z$ 2079.2318 calecd for C$_{142}$H$_{156}$Mg$_2$N$_{12}$, 2079.2344 (M$^+$). UV-vis (THF) $\lambda_{max}$ (log ε)= 417 (5.65), 509 (4.32), 544 (4.10), 572 (4.10), 583 (4.13), 615 (3.99), 640 (3.92) nm.

**Instruments.** $^1$H NMR spectra were recorded on a Bruker Avance II 300 (300 MHz) spectrometer at the “Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne (PACSMUB)”; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm), methylene chloride (5.30 ppm) or THF-d$_8$ (1.73 and 3.58 ppm). UV-vis spectra were recorded on a Varian Cary 1 spectrophotometer. Mass spectra and accurate
mass measurements (HR-MS) were obtained respectively on a Bruker Daltonics Ultraflex II spectrometer in the MALDI/TOF reflectron mode using dithranol as a matrix and on a Bruker MicroQTof instrument or on a Thermo LTQ Orbitrap XL mass spectrometer in the positive ESI mode. Both measurements were performed at the “Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne (PACSMUB)”. UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A and the emission spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. The fluorescence lifetimes were measured using a TimeMaster Model TM-3/2003 apparatus from PTI. The source was nitrogen laser with high-resolution dye laser (fwhm ~1600ps) and fluorescence lifetimes were obtained from deconvolution or distribution lifetimes analysis.

**Transient absorption spectroscopy.** The fs transient absorption spectra (at 1.5 nm of spectra resolution) along with the decay traces were acquired with a Helios spectrometer from Ultrafast Systems in the 450-800 nm range and 150 fs to 3.0 ns time window. This Helios instruments used an all-reflective supercontinuum generation setup resulting in a temporal chirp of the probe pulse of ~200 fs. Fiber optics were used to couple the multichannel spectrometer with a CMOS sensor with 1.5 nm intrinsic resolution. The instrument control and the data acquisition were made with a LabVIEW-based software. The data analysis was made with the Surface Xplorer™ software package. The laser excitation was performed using the Solstice (Spectra-Physics), a one box ultrafast regenerative Ti-sapphire amplifier. The system produced pulses centered at 795nm with bandwidth of ~15nm, energy of 3.75mJ, ~75 fs duration and 1 kHz repetition rate. The frequency was doubled with a second harmonic generator crystal (BBO) to obtain an excitation at 400 nm.

**Computations.** All density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations were performed with Gaussian 09\(^3\) at the Université de Sherbrooke with the Mammoth supercomputer supported by Le Réseau Québécois De Calculs Hautes Performances. The DFT geometry optimisations as well as TD-DFT calculations\(^4\)-\(^13\) were carried out using the B3LYP method. 6-31g* basis sets for all porphyrin macrocycles, the biphenylene linkage as well as the bridging benzene were used. 3-21g* basis sets for solubilising side groups\(^14\)-\(^18\) were employed. 6-31g* basis sets were used for magnesium atoms.\(^14\)-\(^19\)
Quantum yields. The fluorescence quantum yields were measured against H$_2$TPP tetraphenylporphyrin in 2MeTHF ($\Phi_F = 0.11$ in 2MeTHF at 296K). Each measurement was performed 3 times with fresh solutions.

2. References

3. NMR and High Resolution Mass Spectra

Figure S1. $^1$H NMR of zinc (II) 5-(4-bromophenyl)-10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin 7 (300 MHz, CDCl$_3$)
Figure S2. MALDI-TOF spectrum of 7 (positive mode)
Figure S3. ESI HRMS spectrum of 7 (positive mode)
Figure S4. $^1$H NMR of 5-(4-bromophenyl)-10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin 8 (300 MHz, CDCl$_3$).
Figure S5. MALDI-TOF spectrum of 8 (positive mode)
Figure S6. ESI HRMS spectrum of 8 (positive mode)
Figure S7. $^1$H NMR of 5-{8-[10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl]-15-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-10,20-dinonylporphyrin 12 (300 MHz, CD$_2$Cl$_2$)
Figure S8. Aromatic part of $^1$H NMR of 12 (300 MHz, CD$_2$Cl$_2$)
Figure S9. MALDI-TOF spectrum of 12 (positive mode)

Figure S10. ESI HRMS spectrum of 12 (positive mode)
Figure S11. $^1$H NMR of magnesium(II) 5-{8-[magnesium(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-[1,3,2] dioxaborolan-2-yl)-10,20-dinonylporphyrin 13 (300 MHz, CD$_2$Cl$_2$)
Figure S12. MALDI-TOF spectrum of 13 (positive mode)

Figure S13. ESI HRMS spectrum of 13 (positive mode)
**Figure S14.** $^1$H NMR of Magnesium(II) 5-{8-[magnesium(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl]-15-[4-{10,20-bis-3,5-di-tert-butyl-phenyl}-porphyrin-5-yl]phenyl]-10,20-dinonyl-porphyrin 1 (300 MHz, THF-d$_8$) *2,6-dimethyl,4-tert-butylphenol
**Figure S15.** Aromatic part of $^1$H NMR of 1 (300 MHz, THF-d$_8$)
Figure S16. MALDI-TOF spectrum of 1 (positive mode)

Figure S17. ESI HRMS spectrum of 1 (positive mode)
4. Optical spectra

**Figure S 20.** Absorption spectrum of 7 in THF

**Figure S 18.** Absorption spectrum of 8 in THF

**Figure S19.** Absorption spectrum of 12 in THF
Figure S 20. Absorption spectrum of 13 in THF

Figure S 21. Absorption spectrum of 1 in THF
5. Computed energy barriers

Figure S23. Change in total energy of 1 upon the change in dihedral angle formed by the Mg(II)porphyrin and C₆H₄ (up) and between the free base and C₆H₄ average planes (bottom). The minima are respectively, 71.5 and 67.5°.
6. Photophysical spectra and decays

Figure S24: Absorption (black), fluorescence (blue) and excitation (red) spectra of 8 (up) and 13 (down) in 2MeTHF at 298K.
Figure S24: Fluorescence decay curve for 8 in 2MeTHF at 298K. $\lambda_{\text{exc}} = 510$ nm, $\lambda_{\text{em}} = 645$ nm. Pre-exp = 0.537 ± 0.005; lifetime = 13.87 ± 0.11 ns; $\chi^2 = 0.850$. 
Figure S25: Log (top) and linear scale (bottom) of the fluorescence decay curve for 13 in 2MeTHF at 298K. \( \lambda_{\text{exc}} = 595 \text{ nm} \), \( \lambda_{\text{em}} = 667 \text{ nm} \). Pre-exp = 0.846 \( \pm 0.007 \); lifetime = 7.58 \( \pm 0.11 \) ns; \( \chi^2 = 1.049 \).
Figure S26. Fluorescence decay curve for 1 in 2MeTHF at 298K. $\lambda_{\text{exc}} = 510$ nm, $\lambda_{\text{em}} = 720$ nm. Fit for the first half (in green): Pre-exp. 1 = 2.45 ± 0.79, lifetime 1 = 0.21 ± 0.06; Pre-exp. 2 = 0.329 ± 0.001, lifetime 2 = 7.11 ± 0.85; $\chi^2 = 0.865$. Fit for the second half (in red): Pre-exp. = 0.335 ± 0.018; lifetime = 11.2 ± 1.20; $\chi^2 = 1.127$. The relative low counts of the decays are due to the sensibility limit of the Strobe detection.
Figure S27. Fluorescence decay curve for 1 in 2MeTHF at 298K. $\lambda_{\text{exc}} = 510$ nm, $\lambda_{\text{em}} = 670$ nm. Pre-exp. = 0.601 ± 0.004, lifetime = 10.99 ± 0.08; $\chi^2 = 0.8043$. The slower components of 0.21 and 7.1 ns associated with the bis(porphyrin unit) are not accurately determined in this decay due to their lower relative intensity.
Figure 28. Rise and decay traces for the transient absorption spectra of 1 in 2MeTHF at 298 K monitored at 480 nm. Laser excitation = 400 nm, pulse width = 0.12 ps, laser power = 0.5 mJ/pulse, abs at 400 nm = 0.1. Note that the shape of the traces remains the same for wavelength > 480 nm. Because the time scale cannot exceed more than 3 ns on this apparatus, the long-lived components cannot be accurately analyzed.