

Excited-state dynamics of strongly coupled porphyrin/core-substituted-naphthalenediimide dyads

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Supporting information

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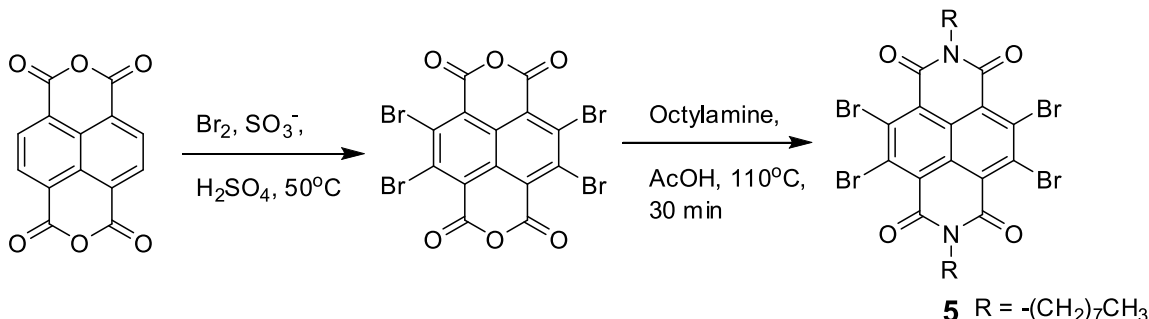
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1. Material and measurements

ortho-Diamino benzene, Naphthalenetetracarboxy dianhydride, octylamine, acetic acid (AcOH), pyrrole, benzaldehyde, trifluoro acetic acid (TFA), Pd/c (10%), bromine (Br₂), Sulfuric acid (H₂SO₄), p-toluene sulfonyl chloride (TsCl), dimethyl formamide (DMF), ethanol (EtOH), nitric acid (HNO₃), chloroform (CHCl₃), chloroform-d (CDCl₃), methanol and dichloromethane (DCM), pyridine, zinc acetate (Zn(OAc)₂·2H₂O) were purchased from Aldrich and used without purification, unless otherwise specified. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40p spectrometer. ¹H NMR, ¹³C-NMR spectra were recorded on a Bruker spectrometer using chloroform-d as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as received.

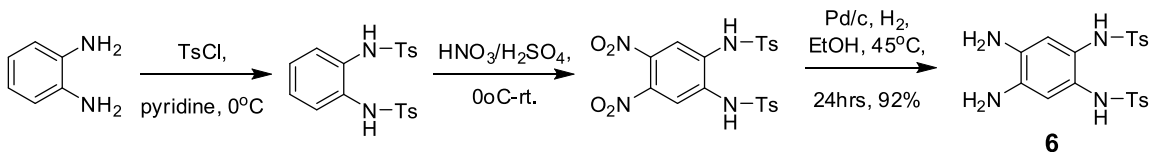
2. Synthesis of target Fb-TPP-NDI 1 and Zn-TPP-NDI 2

2,3,6,7-Tetrabromo-dioctyl-naphthalene diimide (5):¹



Firstly 2,3,6,7-tetrabromo-naphthalene dianhydride was prepared from naphthalene dianhydride by literature method obtained yellow solid with 93% yield.¹ Following literature method compound **5** was synthesized in 30% yields as yellow crystalline solid. M.P. 259 °C. ¹H NMR (CDCl₃, 300 MHz) δ 4.18-4.23 (t, *J* = 7.7 Hz, 4H), 1.71-1.79 (m, 4H), 1.38-1.41 (m, 8H), 1.28-1.35 (m, 12H), 0.87-0.91 (t, *J* = 6.97, 6H). ¹³C NMR (CDCl₃, 125 MHz) δ 159.7, 135.4, 126.5, 125.7, 42.8, 31.8, 29.21, 29.20, 27.9, 27.1, 22.6, 14.1. FT-IR (KBr, Cm⁻¹) ν 2958, 2921, 2853, 1713, 1666, 1502, 1431, 1409, 1374, 1289, 1178, 1154, 1013, 909, 789, 768, 721, 582, 543. HRMS (ESI) *m/z*: calcd for C₃₀H₃₄Br₄N₂O₄ 806.2180, found 806.2176, UV/vis (CH₂Cl₂): λ_{max}/nm (ε/M⁻¹ Cm⁻¹) = 427 (10 900), 403 (12 100). Fluorescence (CH₂Cl₂): No fluorescence output. All spectroscopic data matches with literature.¹

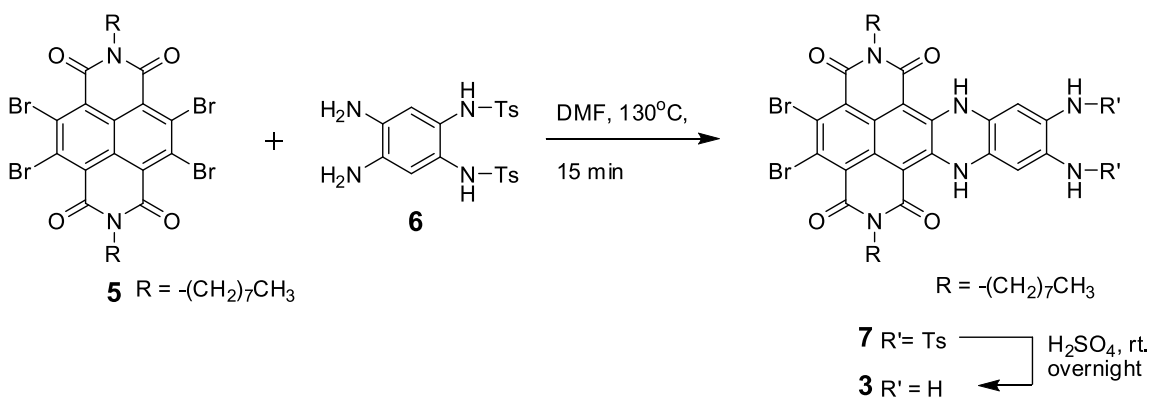
1,2-Diamino-4,5-bis(*p*-toluenesulfonamido)benzene (6). This compounds was synthesized by known literature procedure in four steps.²



4,5-dinitro-4,5-bis(*p*-toluenesulfonamido)benzene^{2a} (1.12 g, 2.20 mmol) and Pd/C (160 mg, 10%) were suspended in ethanol (100 mL). The resulting mixture was carried out at

room temperature for 24 h in a hydrogen atmosphere (5 bar) in a Parr apparatus. After completion of the reaction, the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure. After recrystallization from methanol, product **6** was obtained as a yellowish solid in 92% (900mg). M.P. decomp. 211-214 °C (decomp. Lit. 210°C)⁴; FTIR (KBr) 3445, 3405, 3377, 3291, 3055, 2811, 1662, 1625, 1593, 1521 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 8.53 (s, 2H), 7.54 (d, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 6.19 (s, 2H), 4.56 (s, 4H), 2.37 (s, 6H); ¹³C NMR (DMSO-d₆, 125 MHz) δ 143.9, 137.2, 134.4, 130.3, 127.8, 121.0, 111.7, 21.9; EI-HRMS *m/z* calcd for C₂₀H₂₂N₄O₄S₂ 446.1082, found 446.1084.

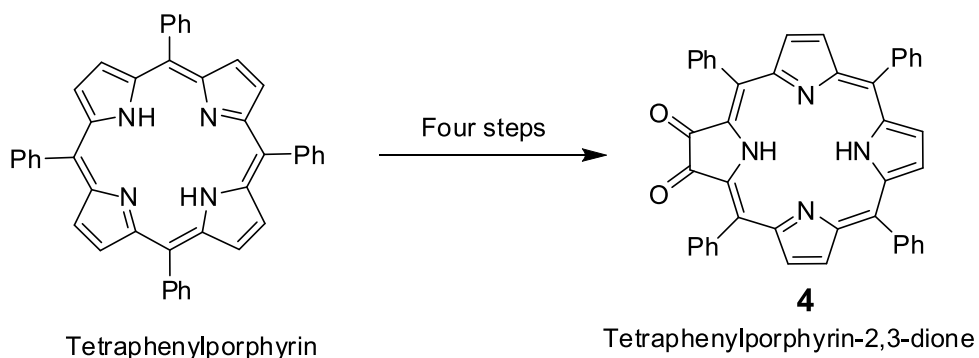
ortho-Diamine functionalized NDIs 3 [11,12-diamino-4,5-dibromo-2,7-dinonyl-[3,8]phenanthrolino[1,10-abc]phenazine-1,3,6,8(2H,7H,9H,14H)-tetraone]



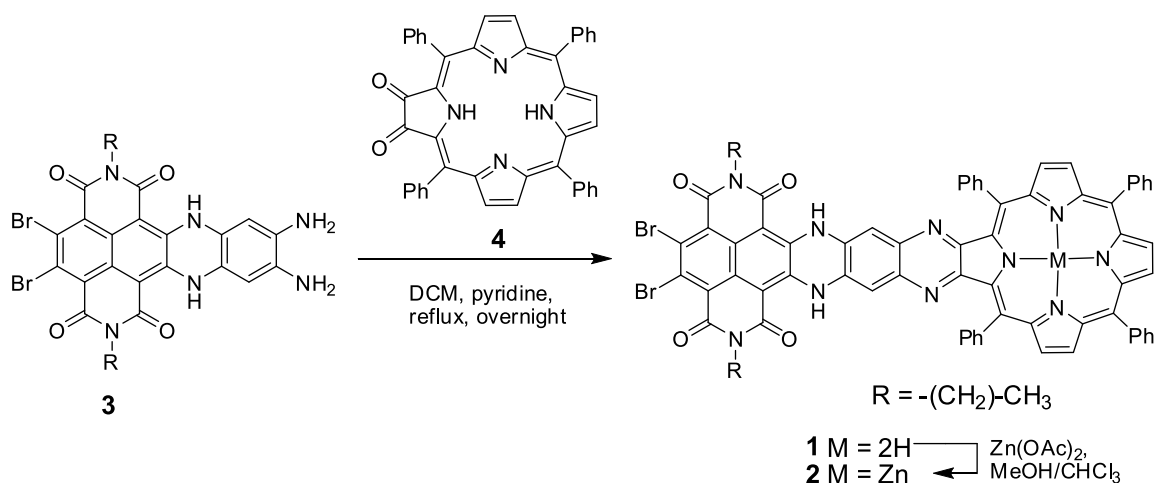
Mixture of 2,3,6,7-tetrabromo-dioctyl-naphthalene diimide **5** (200 mg, 2.39x10⁻⁴ M) and 1,2-diamino-4,5-bis(*p*-toluenesulfonamido)benzene **6** (0.428 mg, 0.00095 mol, 4 equiv) in dry DMF (2 mL) heated at 135°C for 15 min. (colour change was observed yellowish to dark green), completion of the reaction was monitored by TLC. After completion DMF was removed on rotary evaporator, and purified by column chromatography on flash silica column elute with 20:1 DCM/MeOH. Dark blue crystals were obtained of **7** (235mg, 87%). M.P. = 276-279°C. ¹H NMR (CDCl₃, 300 MHz) δ 12.79 (s, 2H), 8.23 (s, 2H), 7.77 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 6.55 (s, 2H), 4.01 (t, *J* = 7.8 Hz, 4H), 2.50 (s, 6H), 1.58 (m, 4H), 1.31-1.21 (m, 20H), 0.91 (t, *J* = 7.03, 6H). ¹³C NMR

(CDCl₃, 75 MHz) δ 164.1, 160.1, 144.4, 141.3, 135.5, 129.8, 127.7, 127.2, 125.8, 114.3, 68.7, 50.3, 42.0, 31.7, 30.9, 29.2, 27.7, 22.6, 21.4, 13.9. HRMS (ESI) m/z : calcd for C₅₂H₅₈Br₂N₆O₈S₂ 1116.2124, found 1116.2127. Followed by deprotection of tosyl: Conc. H₂SO₄ (5 mL) was degassed by bubbling with argon for 20 min, and then compound **7** (100mg, 8.93x10⁻⁵M) was added. The solution was stirred for overnight and the resulted green solution was poured into ice. Then the solid was suspended in satd sodium bicarbonate (50 mL) for 1 h. The solid was collected by filtration. Washing with water, then hexane afforded *ortho*-Diamine functionalized NDIs **3** (60 mg, 83%) as a green solid, used for next step without purification.

Synthesis of 2,3-dioxo-5,10,15,20-tetrakis(phenyl)porphyrin (tetraphenylporphyrin-2,3-dione) **4**: Porphyrin dione **4** was obtained in four steps by literature procedures.³



Synthesis of FbTPP-NDI **1** (free base porphyrin-core substituted NDI).



A mixture of *ortho*-Diamine functionalized NDIs **3** (50mg, 6.3x10⁻⁵M) and tetraphenylporphyrin-2,3-dione (42mg, 6.4x10⁻⁵M) was dissolved in dichloromethane/pyridine (4:1, 10 mL) and mixture was heated to reflux under argon atmosphere in the dark for 2 h. Completion of reaction was monitored by TLC. The mixture was evaporated to dryness and the residue purified by chromatography over silica (chloroform). The first major band gave FbTPP-NDI **1** (62 mg, 89%) as a purple amorphous powder. ¹H NMR (CDCl₃, 300 MHz) δ 12.45 (s, 4H), 8.92 (d, *J* = 8.2 Hz, 2H), 8.86 (d, *J* = 8.0 Hz, 2H), 8.64 (s, 2H), 8.53-8.15 (m, 14H), 7.99 (s, 6H), 6.62 (s, 2H), 3.77 (t, *J* = 7.8 Hz, 4H), 1.69 (m, 4H), 1.40-1.27 (m, 20H), 0.98 (t, *J* = 7.03, 6H), -3.38 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 160.2, 159.8, 148.9, 146.1, 145.1, 144.4, 142.3, 141.3, 140.3, 137.3, 137.2, 135.6, 135.5, 134.3, 132.5, 131.3, 129.4, 128.6, 127.9, 127.6, 127.1, 127.9, 125.3, 122.7, 114.2, 67.9, 50.1, 48.4, 32.0, 31.0, 29.6, 29.2, 27.5, 27.0, 22.4, 21.7, 14.0. FTIR (KBr) 2965, 2904, 2868, 1713, 1666, 1509, 1476, 1425, 1393, 1363, 1334, 1297, 1282, 1248, 1185, 1165, 1120, 1106, 1072, 1002, 943, 908 and 856. Ms (MALDI-TOF, no matrix) *m/z*: calcd for C₈₀H₆₆Br₂N₁₀O₄ 1391.2526 and 1388.3635 (exact mass), found 1391.1282 and 1388.1378 (exact mass) respectively.

Synthesis of ZnTPP-NDI **2.**⁴ To a solution of FbTPP-NDI **1** (25 mg, 2.15x10⁻⁵M) dissolved in CHCl₃ (5 mL) was added Zn(OAc)₂·2H₂O (30 mg, excess) dissolved in MeOH (1 mL), and the solution was stirred for 14hrs at room temperature. The solution was then washed with water and dried over anhydrous sodium sulfate. The compound

was purified over silica gel column using CHCl_3 as eluent obtained purple solid (25 mg, 96%). Ms (MALDI-TOF, no matrix) m/z : calcd for $\text{C}_{80}\text{H}_{64}\text{Br}_2\text{N}_{10}\text{O}_4\text{Zn}_1$ Mo. Wt. = 1454.6468, found 1453.9989, 1455.9900, (bromine isotopic pattern) respectively.

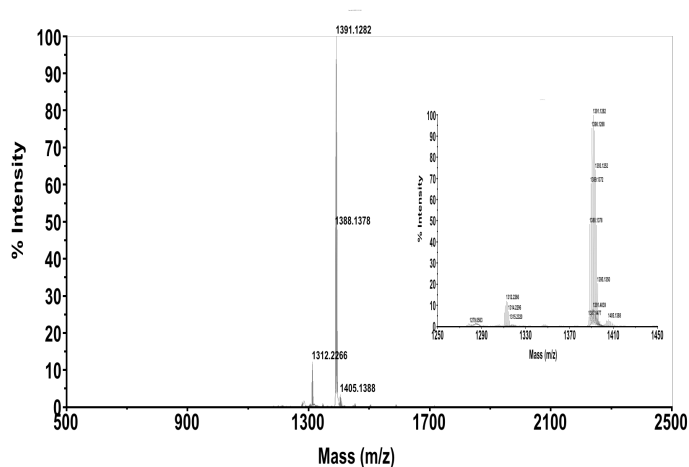


Figure S1: HRMS (ESI) of FbTPP-NDI 2

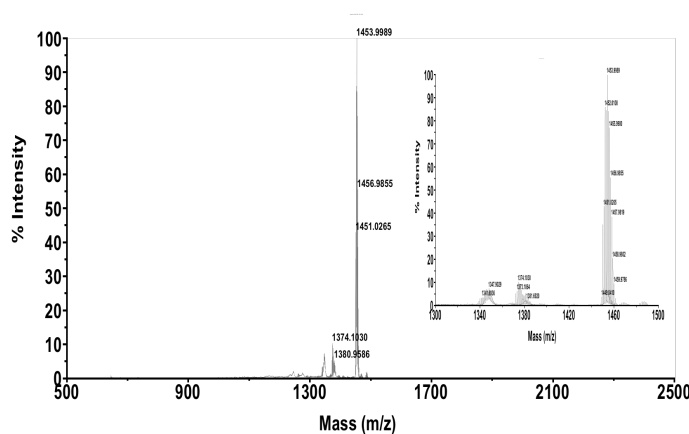


Figure S2: HRMS (ESI) of Zn-TPP-NDI 2

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3. Steady-state spectra

Table S1: Emission (first 3 rows) and absorption maxima in cm^{-1} of the various compounds in toluene.

HBNDI	FbTPP	ZnTPP	FbTPPNDI	ZnTPPNDI
13315			13680	
14600	13930	15430	14125	
15920	15315	16695	15528	~14200
16340	15410	16980	15700	15220
17700	16895	18185	17120	16950
19050	18250	19570	18550	18250
~20400	19460	23640	23150	22880
22940	20660			
24275	23865			

4. Transient absorption spectra

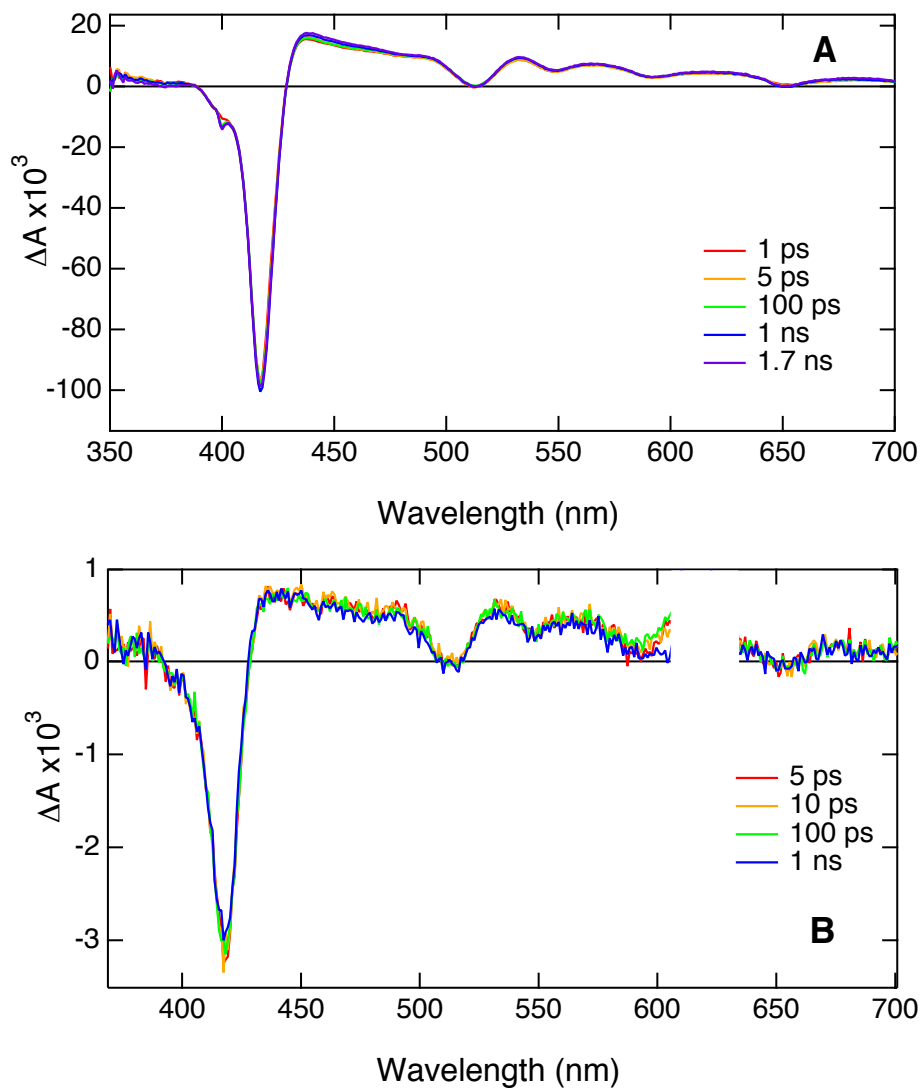


Figure S3: Transient absorption spectra measured at different time delays after excitation of FbTPP in toluene at 400 nm (A) and 615 nm (B)

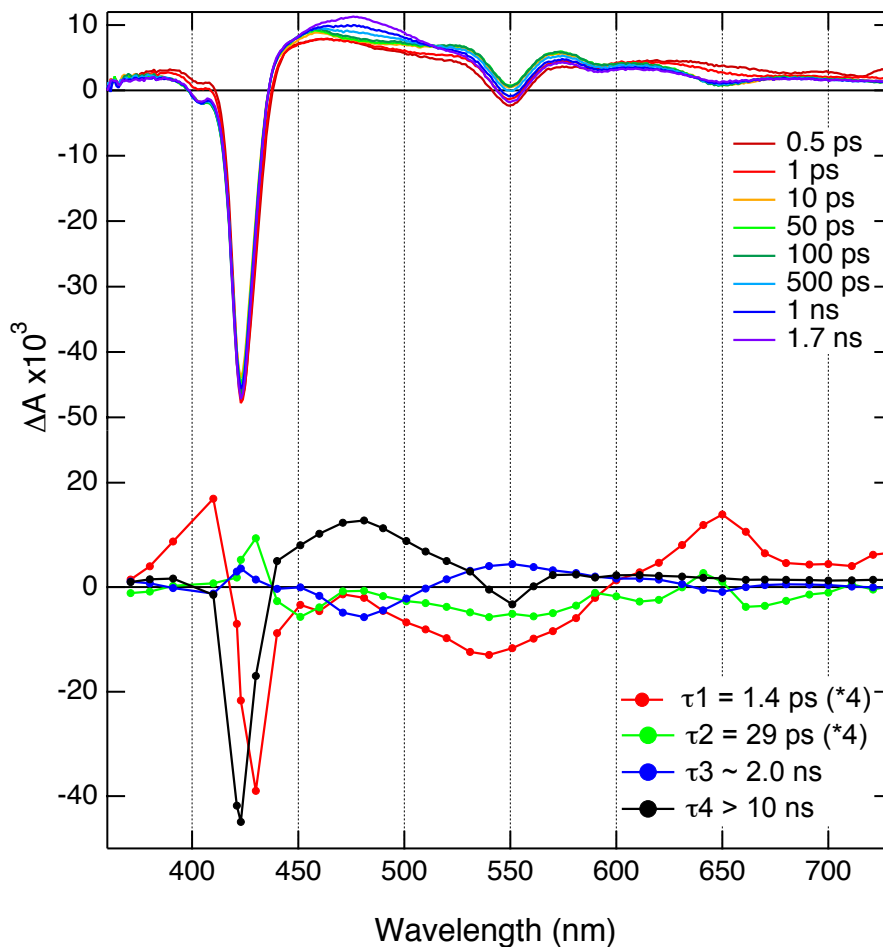


Figure S3: Transient absorption spectra measured at different time delays after excitation of ZnTPP in toluene at 400 nm (top) and decay-associated spectra obtained from multiexponential global analysis (bottom).

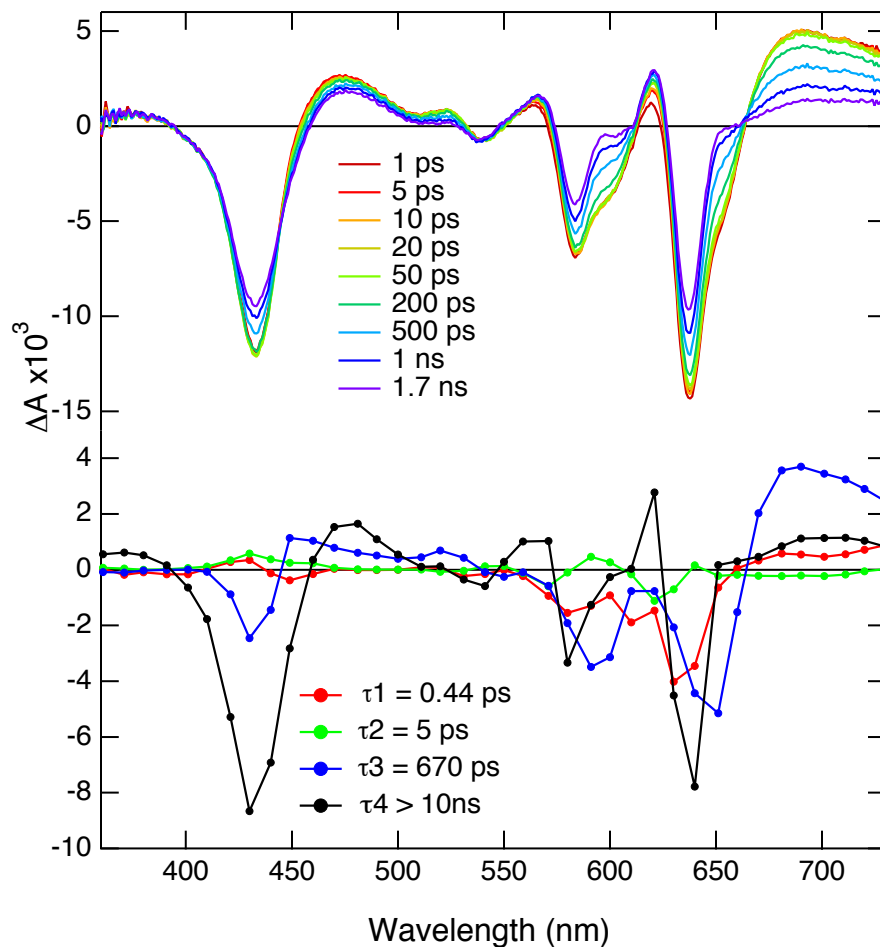


Figure S5: Transient absorption spectra measured at different time delays after excitation of FbTPPNDI in toluene at 615 nm (top) and decay-associated spectra obtained from multiexponential global analysis (bottom).

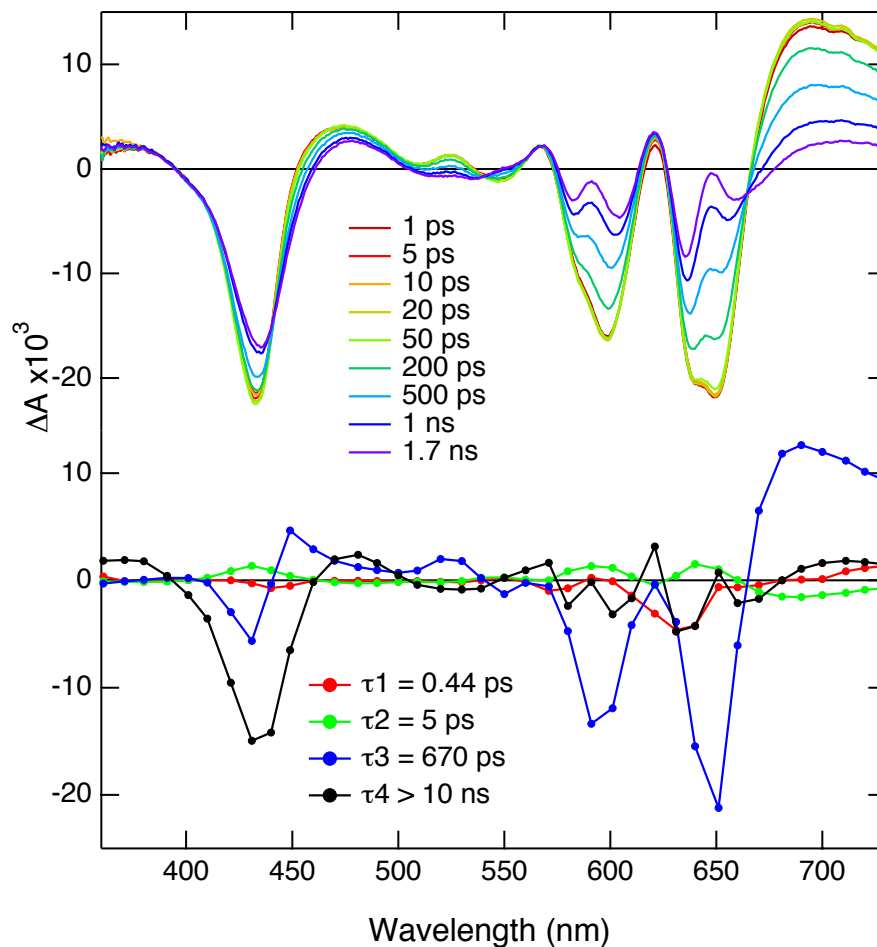


Figure S6: Transient absorption spectra measured at different time delays after excitation of a concentrated solution of FbTPPNDI in toluene at 615 nm (top) and decay-associated spectra obtained from multiexponential global analysis (bottom).

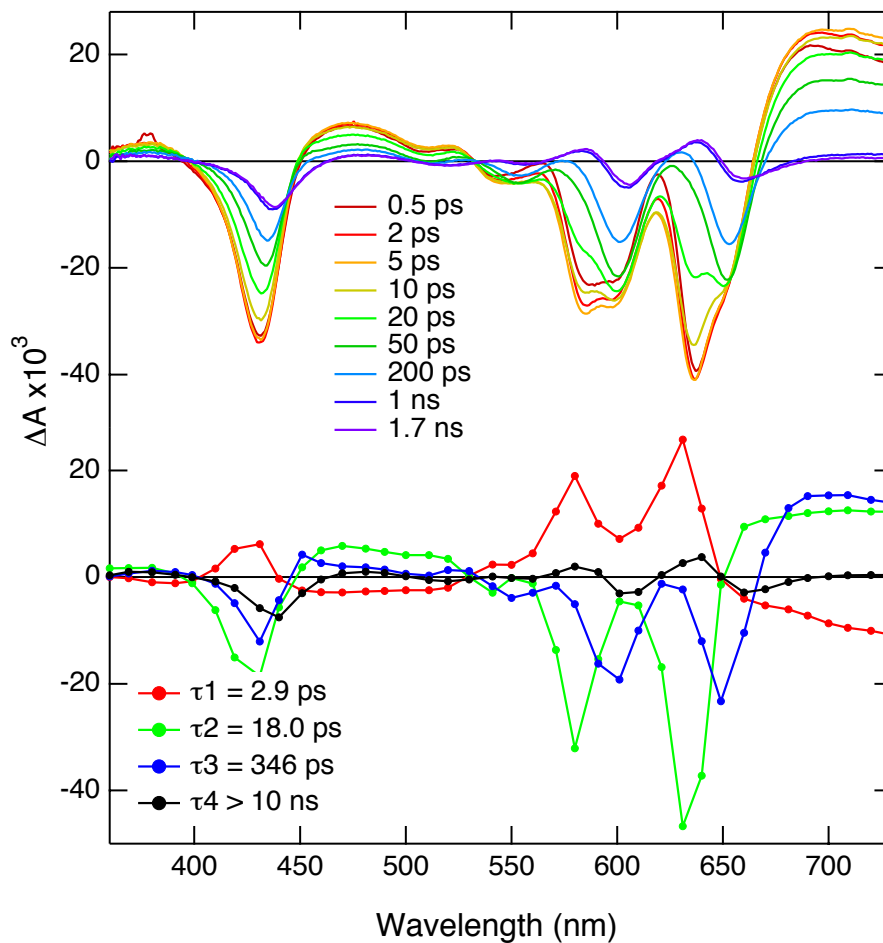


Figure S7: Transient absorption spectra measured at different time delays after excitation of FbTPPNDI in DCM at 615 nm (top) and decay-associated spectra obtained from multiexponential global analysis (bottom).