Supporting information to Berera et al., A simple light harvesting dyad as a model for excess energy dissipation in oxygenic photosynthesis.



Figure 6: Evolution-associated difference spectra (EADS) that follow from a global analysis of the transient absorption data of dyad **3** in acetone.



Figure 7: Target analysis with the model depicted in figure 4 (*Upper*) for (A) dyad 2 and (B) dyad 3 dissolved in acetone. The corresponding fractions and rate constant are reported in Table 1. The SADS corresponding to the long-lived mix of Pc and carotenoid triplet (T) for dyad 2 displays a substantial negative signal below 500 nm. This probably

corresponds to a fraction of carotenoid triplets coexisting with Pc triplets on the timescale of the experiment. This causes some carotenoid ground state bleach below 500 nm.



Wavelength (nm)

Figure 8: Transient absorption spectra at different time delays in the region 850-980 nm for dyad **3** dissolved in DMSO. The signal is flat and decays uniformly with the lifetime of the Qy state of Pc, indicating that no transient carotenoid radical is formed.



Figure 9: EADS of the vibrationally relaxed excited state of model carotenoid **2'** in hexane (red line), THF (blue line) and DMSO (green line), following excitation at 475 nm.

Synthesis of the compounds

The ¹H-NMR spectra were recorded on Varian spectrometers at 300 or 500 MHz. Unless otherwise specified, samples were dissolved in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). All chemicals were purchased from Aldrich, Acros or Lancaster. The ester carotenoids, methyl 8'-apo- β -caroten-8'-oate (9 double bonds), methyl 6'-apo- β -caroten-6'-oate (10 double bonds), and methyl 4'-apo- β -caroten-4'-oate (11 double bonds), were prepared using literature procedures (1, 2) and the corresponding acids were obtained by base catalyzed hydrolysis. Solvents were obtained from EM Science. Tetrahydrofuran was distilled from sodium metal and benzophenone in a nitrogen atmosphere immediately prior to use. Toluene was distilled from CaH₂ and dichloromethane was distilled from potassium carbonate. All solvents were stored over the appropriate molecular sieves prior to use. Thin layer chromatography (TLC) was done with silica gel coated glass plates from Analtech. Column chromatography was carried out using EM Science silica gel 60 with 230-400 mesh.

4-Hexanamidophthalonitrile. A solution of 3-nitrophthalonitrile (5.15 mg, 29.77 mmol) in methanol (125 mL) was flushed with N₂ and a portion of 10% Pd/C (0.515 mg) was added. This mixture was then stirred under H₂ (50 psi) for 1h. The catalyst was removed by filtration through celite and the solvent was distilled under vacuum to obtain the desired amine (3.66 g, 86% yield). A portion of the amine obtained (3.60 g, 25.17 mmol) was dissolved in pyridine (90 mL) and then hexanoyl chloride (8.6 mL, 61.52 mmol) was added. The mixture was stirred under N₂ for 2h. The solvent was distilled under vacuum and the mixture was re-dissolved in CH₂Cl₂, and washed with HCl 0.1 M five times, washed with NaHCO₃ 5% three times to neutral pH. The solution was dried over MgSO₄ and filtered, and the solvent was distilled under vacuum. The crude product was chromatographed on silica gel (CH₂Cl₂/MeOH 5%) and 4.30g (71% yield) of the desired nitrile was obtained. ¹H-NMR (300 MHz, CDCl₃) δ 0.92 (3H, t, -CO(CH₂)₄<u>CH₃</u>), 1.36 (4H, m, -CO(CH₂)₂<u>CH₂</u>CH₂CH₃), 1.74 (2H, q, -COCH₂<u>CH₂(CH₂)₂CH₃), 2.43 (2H, t, -CO<u>CH₂(CH₂)₃CH₃), 7.62 (1H, s, -NHCO-), 7.74 (1H, d, *J* = 9 Hz, Bz 3-H), 7.87 (1H, d, *J* = 9 Hz, 2Hz Bz 5-H), 8.18 (1H, d, *J* = 2 Hz, Bz 6-H).</u></u>

1,2-Dibutoxybenzene. Catechol (technical grade) (13.2 g, 120 mmol) was dissolved in 120 mL of DMF. Potassium carbonate (41.4 g, 300 mmol) and *n*-butylbromide (49.2 g, 360 mmol) were added and the reaction mixture was stirred at 95°C under N₂ for 24 h. Portions of potassium carbonate (30 g, 217 mmol) and *n*-butylbromide (30 g, 219 mmol) were added and the stirring continued for 3 h. Potassium carbonate (30 g, 217 mmol) was added and the reaction was continued overnight. The mixture was allowed to cool down to room temperature and ether (1L) was added. The organic layer was washed with water six times. The organic layer was dried over magnesium sulfate, the solvent was distilled under vacuum and the liquid obtained was fractionally distilled at reduced pressure collecting the fraction between 69-73°C. This fraction consisted of pure 1,2-dibutoxybenzene (19.05 g, 70.8% yield). ¹H-NMR (300 MHz, CDCl₃) $\tilde{\delta} \Box \Box$ (6H, t, -OCH₂CH₂CH₂CH₃), 1.52 (4H, s, -OCH₂CH₂CH₂CH₃), 1.81 (4H, q, -OCH₂CH₂CH₂CH₃), 4.01 (4H, t, -O-<u>CH₂CH₂CH₂CH₃), 6.90 (4H, s, Bz 3,4,5,6-H).</u>

1,2-Dibromo-4,5-dibutoxybenzene. A portion of 1,2-dibutoxybenzene (19.0 g, 86 mmol) was dissolved in CH_2Cl_2 (200 ml) and cooled to 0°C under N₂. Bromine (9.6 mL,

187 mmol) was added slowly; one half at 0°C and the other half at room temperature. The reaction mixture was stirred for 2 h. The solution was flushed with N₂, washed with a 10% NaHSO₃ solution and then with 10% NaHCO₃ solution. The organic layer was dried over Na₂SO₄ and the solvent was distilled under vacuum to yield 31.71 g (95.6%) of the desired dibromobenzene. ¹H-NMR (300 MHz, CDCl₃) $\tilde{\delta} \square \square$ (6H, t, -OCH₂CH₂CH₂CH₂CH₃), 1.48 (4H, s, -OCH₂CH₂CH₂CH₃), 1.78 (4H, q, -OCH₂CH₂CH₂CH₃), 3.95 (4H, t, -O-CH₂CH₂CH₂CH₂CH₃), 7.06 (2H, s, Bz 3,6-H).

4,5-Dibutoxyphthalonitrile. A solution of 1,2-dibromo-4,5-dibutoxybenzene (31.7 g, 83.4 mmol) in DMF (400 mL) was stirred and CuCN (22.8 g, 255 mmol) added. The mixture was heated to reflux under N₂ for 6 h. The mixture was cooled to room temperature and poured into 1.1 L of concentrated NH₄OH and bubbled with air for 20 h. The mixture was filtered and the solid obtained was washed with 10% NH₄OH until the filtrate was clear, then with water to neutral pH and air-dried. The crude product was extracted with hexanes in a soxhlet for 1 week. The solvent was reduced to 200 mL and filtered. The solid was recrystallized from CH₂Cl₂ and CHCl₃ / hexanes and decolorized with activated carbon. The desired dinitrile (10.53 g) was obtained in 46% yield. ¹H-NMR (300 MHz, CDCl₃) δ_{1} (6H, t, -OCH₂CH₂CH₂CH₂), 1.51 (4H, s, -OCH₂CH₂CH₂CH₃), 1.85 (4H, q, -OCH₂CH₂CH₂CH₃), 4.06 (4H, t, -O-<u>CH₂CH₂CH₂CH₂CH₃), 7.12 (2H, s, Bz 3,6-H).</u>

Zinc-9,10,16,17,23,24-hexabutoxy-2-hexanamidophthalocyanine. Portions of 4hexanamidophthalonitrile (1.5 g, 6.1 mmol) and 4,5-dibutoxyphthalonitrile (2.5 g, 9.1 mmol) were dissolved in 80 mL of dimethoxyethane (DME) and stirred under an ammonia flow at 100°C for 2 h. A portion of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.3 mL) was added and the stirring was continued for 15 min. Zinc acetate (1.15 g) was added and the mixture was stirred at 100°C overnight. The green mixture was cooled to room temperature and 60 mL of a water/methanol mixture (1:1) was added. The precipitate that formed was collected, washed with water and dried. The product was purified by column chromatography (silica gel, CHCl₃ / MeOH 1 %). Zinc-9,10,16,17,23,24-hexabutoxy-2-hexanamidophthalocyanine was obtained in 18.5 % yield (790 mg). ¹H-NMR (500 MHz, DMSO-CDCl₃) δ 1.02 (3H, t, -CO(CH₂)₄CH₃), 1.12 -1.20 (18H, m, -OCH₂CH₂CH₂CH₂CH₃), 1.47 - 1.53 (4H, m, -CO(CH₂)₂CH₂CH₂CH₃), 1.70 -1.80 (12H, m, -OCH₂CH₂CH₂CH₃), 1.87(2H, q, -COCH₂CH₂(CH₂)₂CH₃), 2.00 - 2.10 (12H, m, -OCH2CH2CH2CH3), 2.63 (2H, t, -COCH2(CH2)3CH3), 4.47 - 4.55 (12H, m, -O- $CH_2CH_2CH_2CH_3$), 8.40 (1H, d, J = 8 Hz, Pc 3-H), 8.45 - 8.60 (6H, m, Pc 8,11,15,18,22,25-H), 9.10 (1H, d, J = 8 Hz, Pc 4-H), 9.60 (1H, d, Pc 1-H), 10.6 (1H, s, -NHCO-); MS m/z 1122.4 (M + 1)⁺; UV/vis (95 % CHCl₃ / 5 % MeOH) 355, 612, and 679 nm.

Zinc-2-amino-9,10,16,17,23,24-hexabutoxyphthalocyanine. А portion of the hexanamidophthalocyanine obtained in the above reaction (290 mg, 0.258 mmol) was dissolved in 40 mL of THF and 40 mL of a saturated methanolic solution of KOH. The solution was heated to 75°C and stirred overnight under N₂ after the addition of another 10 mL of THF. The reaction mixture was diluted with chloroform and washed with water (three times). The organic layer was dried over Na₂SO₄ and filtered, and the solvent distilled at reduced pressure. The desired zinc 2-amino-9,10,16,17,23,24hexabutoxyphthalocyanine (214 mg) was obtained in 81 % yield.

Dyad 1. The 8'-apo-β-caroten-8'-oic acid (49 mg, 0.11mmole) was dissolved in 6 mL of toluene and 2 mL of pyridine. One drop of thionyl chloride was added and the mixture stirred under N₂ for 15 min. The solvent was distilled under vacuum and the residue kept under vacuum for an extra 15 min. The residue was re-dissolved in 2.5 mL of pyridine and 6 mL of dry chloroform. The solution of the aminophthalocyanine prepared above (100 mg, 0.1mole) dissolved in 6 mL chloroform was added to the solution of the acid chloride and the mixture stirred overnight under N2. The reaction mixture was diluted with chloroform, washed with water and dried under vacuum. The product was purified by flash chromatography (silica, chloroform-methanol 0.2%). A second column (silica, $CHCl_3$) was necessary to obtained 73 mg (52% yield) of pure carotenophthalocyanine 1. ¹H-NMR (500 MHz, DMSO/CDCl₃) δ1.03 (6H, m, Car 16- CH₃, Car 17-CH₃), 1.16-1.21 (18H, m, -OCH₂CH₂CH₂CH₃), 1.46 (2H, s, Car-2), 1.59 (2H, s, Car-3), 1.71 (3H, s, Car18), 1.75-1.83 (12H, m, -OCH2CH2CH2CH3), 1.96 (3H, s, Car-19), 2.0 (5H, m, Car-20, Car-4), 2.08 (15H, m, -OCH₂CH₂CH₂CH₃, Car-20'), 2.32 (3H, s, Car 19'), 4.50-4.57 (12H, m, -OCH₂CH₂CH₂CH₃), 6.16-6.81 (11H, m, Car-7, 8, 10, 11, 12, 14, 15, 11', 12', 14', 15'), 7.44 (1H, s, J = 10, Car-10'), 8.45-8.6 (7H, m, Pc-3, 8, 11, 15, 18, 22, 25), 9.1 (1H, d, Pc-4), 9.63 (1H, s, Pc-1), 10.4 (1H, s, -NH-CO-); MS m/z: 1437.3 (M)⁺; UV/vis (95% CH₂Cl₂ / 5% MeOH) 352, 454, 616, and 683 nm.

Dyad 2 was prepared by the same procedure described above for **dyad 1**. ¹H-NMR (500 MHz, DMSO/CDCl₃) δ 1.01 - 1.04 (6H, m, Car 16-CH₃, Car 17-CH₃), 1.16 - 1.21 (18H, m, -OCH₂CH₂CH₂CH₂CH₃), 1.46 (2H, m, Car 2-CH₂), 1.59 (2H, m, Car 3-CH₂), 1.71 (3H, s, Car 18-CH₃), 1.75 - 1.83 (12H, m, -OCH₂CH₂CH₂CH₃), 1.96 (3H, s, Car 19-CH₃), 2.00 (5H, m, Car 20-CH₃, Car-4), 2.08 (15H, m, -OCH₂CH₂CH₂CH₂CH₃), 6.16 - 6.81 (13H, m, Car =CH-), 7.44 (1H, d, *J* = 10 Hz, Car 10'-H), 8.45 - 8.60 (7H, m, Pc 3,8,11,15,18,22,25-H), 9.10 (1H, d, *J* = 8 Hz, Pc 4-H), 9.63 (1H, s, Pc 1-H), 10.40 (1H, s, -NHCO-); MS *m/z* 1466.4 (M + 2)⁺; UV/vis (97 % CHCl₃ / 3 % MeOH) 356, 476, 616, and 684 nm. UV/vis (THF) 354, 468, 612, and 679 nm.

Dyad 3 was prepared by the same procedure described above for **dyad 1**. ¹H-NMR (500 MHz, DMSO/CDCl₃) δ 0.96 - 0.98 (6H, m, Car 16-CH₃, Car 17-CH₃), 1.12 - 1.21 (18H, m, -OCH₂CH₂CH₂CH₂<u>CH₃</u>), 1.41 (2H, m, Car 2-CH₂), 1.56 (2H, m, Car 3-CH₂), 1.65 (3H, s, Car 18-CH₃), 1.75 (12H, s, -OCH₂CH₂CH₂CH₃), 1.91 (3H, s, Car 19-CH₃), 1.92 (3H, s, Car 20-CH₃), 1.95 - 2.00 (5H, m, Car-4, Car 20'-CH₃), 2.08 (15H, m, -OCH₂CH₂CH₂CH₂CH₃, Car 19'-CH₃), 4.53 - 4.57 (12H, m, -O-<u>CH₂CH₂CH₂CH₂CH₃), 6.05 - 7.32 (16H, m, Car =CH-), 8.29 (1H bs Pc 3-H), 8.65 - 8.73 (6H, m, Pc 8,11,15,18,22,25-H), 9.19 (1H, bs, Pc 4-H), 9.75 (1H, s, Pc 1-H), 10.37 (1H, s, -NHCO-); MS *m/z* 1491.3 (M)⁺; UV/vis (97 % CHCl₃ / 3 % MeOH) 356, 476, 616, and 684 nm. UV/vis (THF) 354, 468, 612, and 679 nm.</u>

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