

Supporting Information:

Spectroscopic and Dynamic Properties of Electronically Excited Pendant Porphyrin Polymers with Backbones of Differing Flexibility

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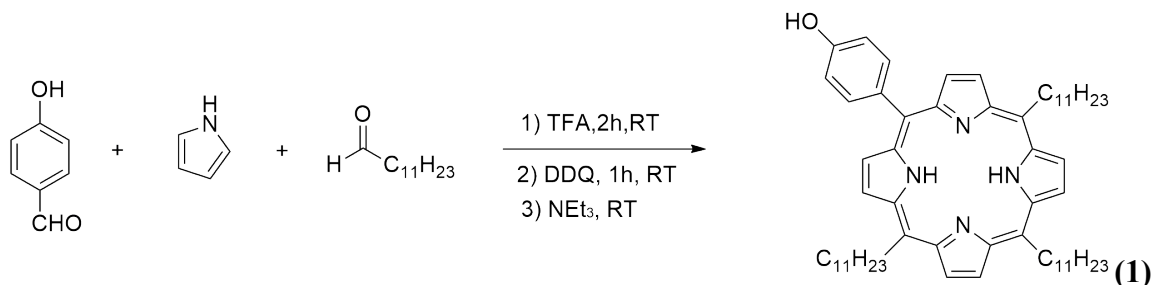
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1. Syntheses.

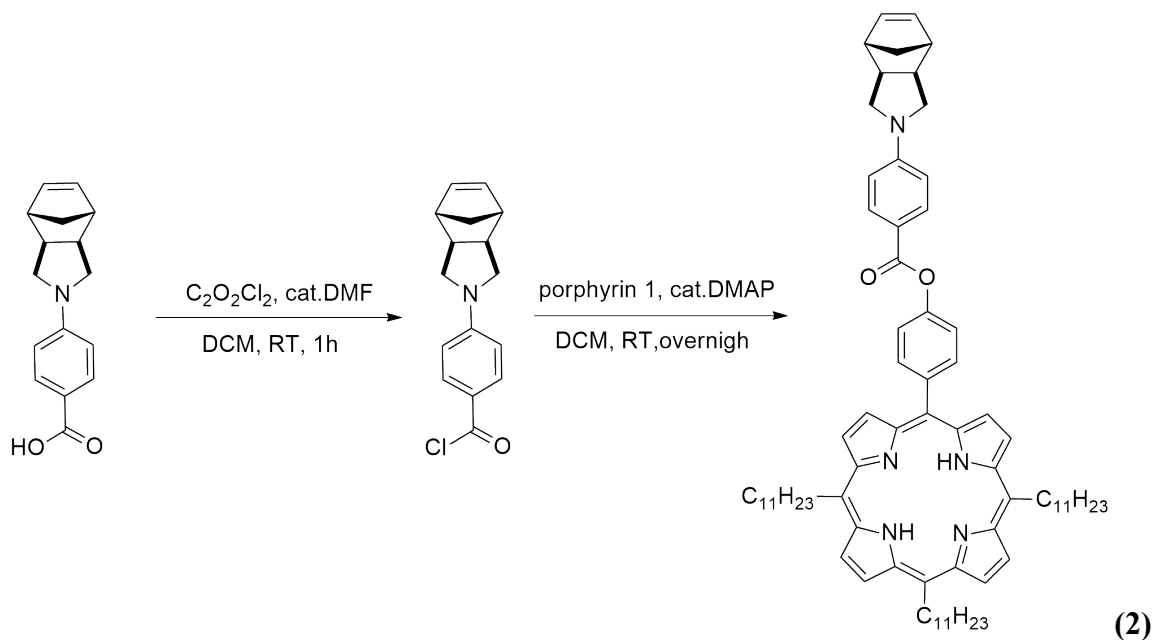
A. Substituted porphyrin: 21*H*,23*H*-5-(4-Hydroxyphenyl)-10,15,20-tris(undecyl)porphyrin (**1**)



Trifluoroacetic acid (TFA) (0.8 mL, 10⁻²M) was added very slowly to a mixture of 4-hydroxybenzaldehyde (0.628 g, 5 mmol), dodecanal (3.006 g, 15 mmol) and pyrrole (1.4 mL, 20 mmol) in dichloromethane (DCM) (800 mL) under nitrogen, and the mixture was stirred for 2 h in the dark. The resulting mixture was then treated with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (15 mmol, 3.405 g). After stirring for 1 h at RT, NEt₃ (2.5 mL) was added to neutralize the TFA. The solvent was removed by rotary evaporator and the resulting residue was purified by repeated column chromatography on silica gel (eluent: DCM : EtOAc = 20:1) to give **1** as a bright purple solid (333 mg, 8 %).

¹H NMR (600 MHz, CDCl₃): δ=9.51 (dd, *J*=15.1, 3.7 Hz, 4H, β-H), 9.36 (d, *J*=4.1 Hz, 2H, β-H), 8.81 (d, *J*=3.5 Hz, 2H, β-H), 8.00 (d, *J*=7.9 Hz, 2H, Ar-H), 7.15 (d, *J*=8.1 Hz, 2H, Ar-H), 4.92-4.99 (m, 6H, CH₂), 2.50-2.55 (m, 6H, CH₂), 1.77-1.82 (m, 6H, CH₂), 1.48-1.54 (m, 6H, CH₂), 1.19-1.40 (m, 36H, CH₂), 0.85-0.90 (m, 9H, CH₃), -2.67 (s, 2H, NH) ¹³C NMR (100 MHz, CDCl₃): δ=14.10, 22.68, 29.33, 29.35, 29.63, 29.67, 29.70, 29.73, 30.60, 30.67, 31.90, 35.44, 38.72, 38.92, 113.48, 119.06, 135.13, 135.47 ppm. HRMS ESI (positive mode) C₅₉H₈₅N₄O: Calcd. 856.6718; Found: 856.6718 [M+ H⁺].

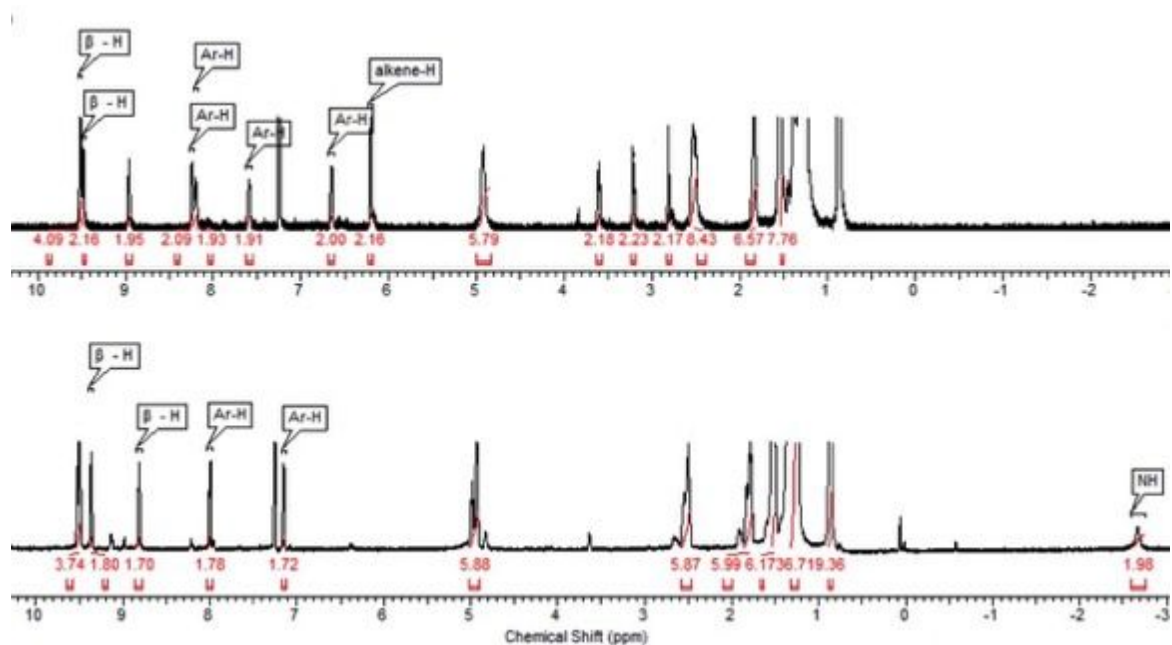
B. Norbornene appended porphyrin (**2**).



To a solution of the carboxylic acid (179 mg, 0.70 mmol) in dry dichloromethane (16 mL) at 0°C was added oxalyl chloride (0.2 mL, 2.08 mmol) and dimethylformamide (DMF) (one drop). The reaction mixture was gradually warmed to RT and stirred for 1 h under dry nitrogen atmosphere. The solvent was removed under reduced pressure to give the crude acid chloride, which was used for the next reaction without further purification.

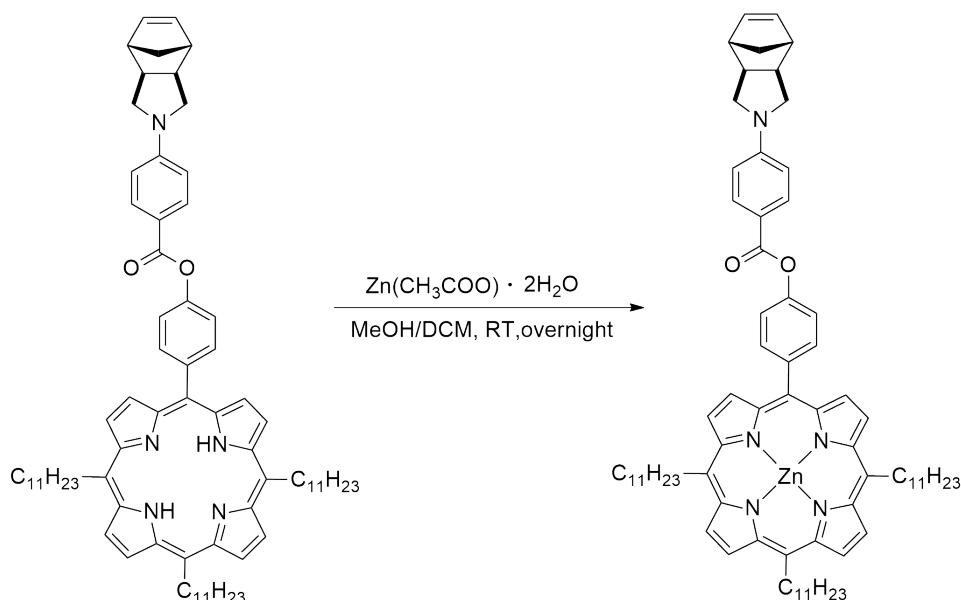
Next, freshly prepared acid chloride in dry CH_2Cl_2 (15 mL) was added to a mixture of **1** (300 mg, 0.347 mmol), triethylamine (NEt_3) (0.7 mL), and 4-dimethylaminopyridine (DMAP) (trace amount) in CH_2Cl_2 (15 mL) at 0°C. The mixture was gradually warmed to RT and stirred overnight. Then the saturated NaHCO_3 was added and the solution was washed with water and brine, and then dried (MgSO_4). The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel (eluent petroleum/ CH_2Cl_2 / NEt_3 2:1:0.01) to give **2** (0.25g, 66%).

^1H NMR (600 MHz, CDCl_3): δ =9.51 (dd, J =15.2, 3.7 Hz, 4H, β -H), 9.38 (d, J =4.1 Hz, 2H, β -H), 8.86 (d, J =4.6 Hz, 2H, β -H), 8.23 (d, J =8.7 Hz, 2H, Ar-H), 8.18 (d, J =7.7 Hz, 2H, Ar-H), 7.58 (d, J =8.1 Hz, 2H, Ar-H), 6.66 (d, J =8.2 Hz, 2H, Ar-H), 6.22 (s, 2H, alkene-H), 4.93-5.01 (m, 6H, CH_2), 3.60-3.71 (m, 4H, H on norbornene), 3.22 (d, J =9.9 Hz, 2H, H on norbornene), 2.81 (s, 2H, H on norbornene), 2.50-2.57 (m, 6H, CH_2), 1.78-1.83 (m, 6H, CH_2), 1.51-1.56 (m, 8H, 6H, CH_2 ; 2H on norbornene), 1.25-1.39 (m, 36H, CH_2), 0.85-0.93 (m, 9H, CH_3), -2.66 (s, 2H, NH). ^{13}C NMR (100 MHz, CDCl_3): δ =14.11, 22.68, 23.81, 29.34, 29.72, 30.61, 31.90, 35.46, 38.67, 38.94, 40.82, 42.29, 44.38, 47.78, 52.71, 57.68, 89.05, 111.50, 119.18, 120.08, 128.15, 132.15, 135.12, 137.61 ppm. HRMS ESI (positive mode) $\text{C}_{75}\text{H}_{100}\text{N}_5\text{O}_2$: Calcd. 1102.7872; Found: 1102.7883 $[\text{M}+\text{H}^+]$.



NMR. Porphyrin **1** (bottom) and appended Zn-Porphyrin **3** (top).

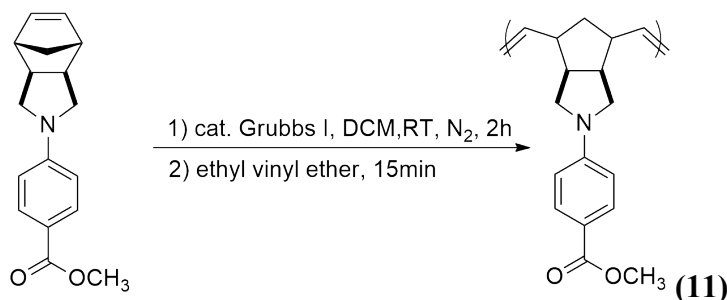
C. Zinc porphyrin – appended norbornene (**3**)



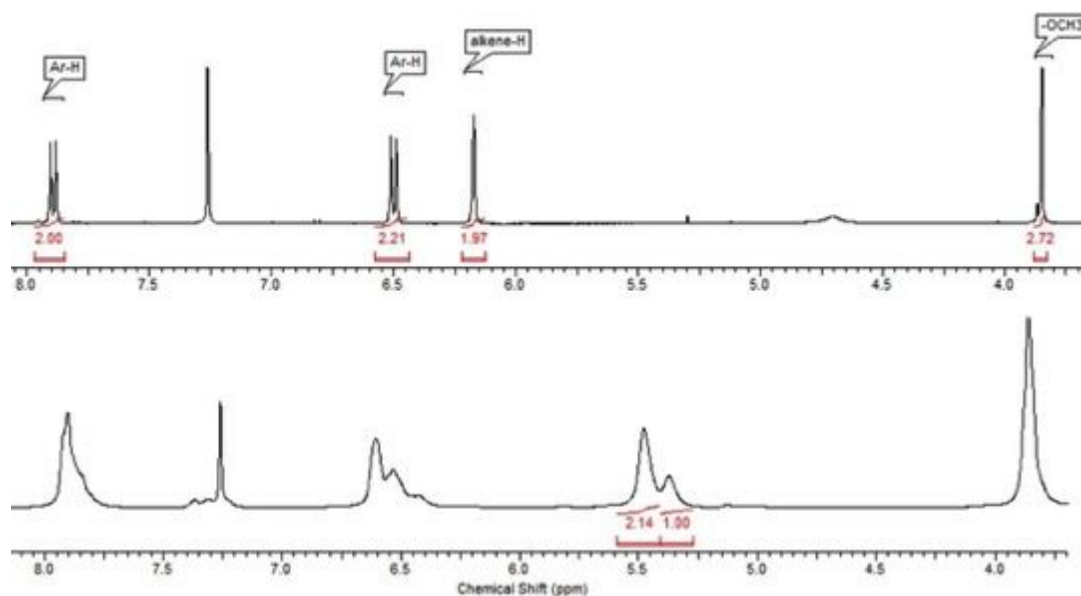
Zinc acetate dihydrate (306.1 mg, 1.3945 mmol) was added to the solution of appended porphyrin **2** (246.6 mg, 0.2237 mmol) in a combination of methanol (50 mL) and CH_2Cl_2 (125 mL), and the resulting mixture was stirred at RT in the dark overnight. The solution was poured into water (70 mL) and extracted with CH_2Cl_2 (50 mL, 3 times). The organic layer was washed with $NaHCO_3$, water and brine, and dried ($MgSO_4$). The solvent was removed by rotavaporator, and the residue was purified by column chromatography on silica gel (eluent petroleum/ CH_2Cl_2 / NEt_3 2:1:0.01) to afford monomer **3** (175.2 mg, 68%). 1H NMR (600 MHz, $CDCl_3$): δ = 9.51 (dd, J =15.2, 3.7 Hz, 4H, β -H), 9.48 (d, J =1.5 Hz, 2H, β -H), 8.96 (d, J =2.3 Hz, 2H, β -H), 8.24 (d, J =7.6 Hz, 2H, Ar-H), 8.19 (d, J =6.9 Hz, 2H, Ar-H), 7.60 (d, J =4.0 Hz, 2H, Ar-H), 6.66 (d, J =7.3 Hz, 2H, Ar-H), 6.21 (s, 2H, alkene-H on norbornene), 4.85-4.90 (m, 6H, CH_2), 3.59-3.62 (m, 2H, H on norbornene), 3.21 (d, J =10.4 Hz, 2H, H on norbornene), 2.81 (s, 2H, H on norbornene), 2.49-2.54 (m, 8H, 6H, CH_2 ; 2H on norbornene), 1.82-1.85 (m, 6H, CH_2), 1.54 (m, 8H, 6H, CH_2 ; 2H, H on norbornene), 1.27-1.38 (m, 36H, CH_2), 0.85-0.87 (m, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 22.69, 29.36, 29.66, 29.75, 30.76, 31.91, 35.83,

38.97, 42.29, 44.38, 47.78, 52.71, 111.50, 119.96, 128.75, 128.87, 131.97, 132.14, 135.03, 137.61, 144.83, 149.08, 149.51, 149.68, 149.85 ppm. HRMS ESI (positive mode) $C_{75}H_{98}N_5O_2Zn$: Calcd. 1164.7007; Found: 1164.7009 $[M+H]^+$.

D. Synthesis of model polynorbornene **11** via ROMP

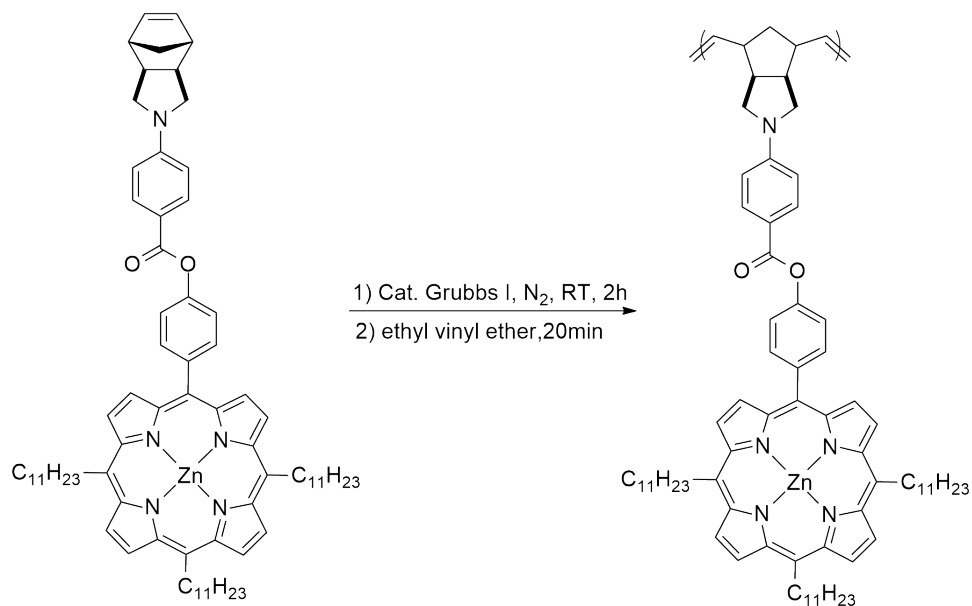


Methyl ester monomer (190 mg, 0.7 mmol) in anhydrous CH_2Cl_2 (5 mL) was treated with first generation Grubbs catalyst (28.8 mg, 0.035 mmol) in CH_2Cl_2 (5 mL) under N_2 . The mixture was stirred at RT for 2 h. Then the reaction was quenched with ethyl vinyl ether (1 mL) for 15 min, and poured into methanol (40 mL). The resulting solid was collected by centrifugation. This procedure was repeated twice and the solid was collected to afford **11** (98 mg, 52%) as a greyish solid. 1H NMR (400 MHz, $CDCl_3$): δ =7.90 (br, 2H, Ar-H), 6.53-6.50 (br, 2H, Ar-H), 5.48 (trans), 5.37 (cis), 3.86 (br, 3H, OCH_3), 3.36 (br, 2H, exo-H), 2.55 (br, 2H, CH_2N), 2.38 (br, 2H, CH_2N), 2.04 (br, 2H, CH), 1.41 (br, 2H, CH_2), 1.26 (br, 2H, CH_2).



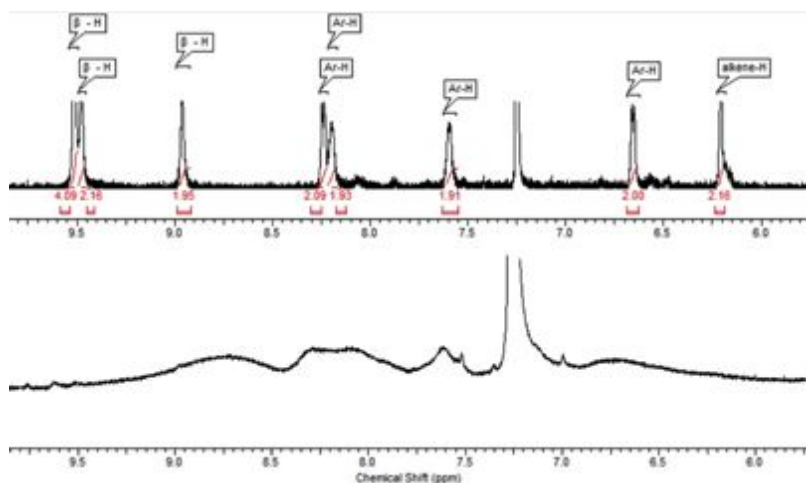
NMR. ¹H NMR spectrum of the model methylester monomer (top), and the resulting polymer **11** (bottom). Integration in the region 5.6-5.2 ppm allows the E/Z ratio to be determined as ca 2.14:1.

E. Porphyrin-appended polynorbornene (**4**)

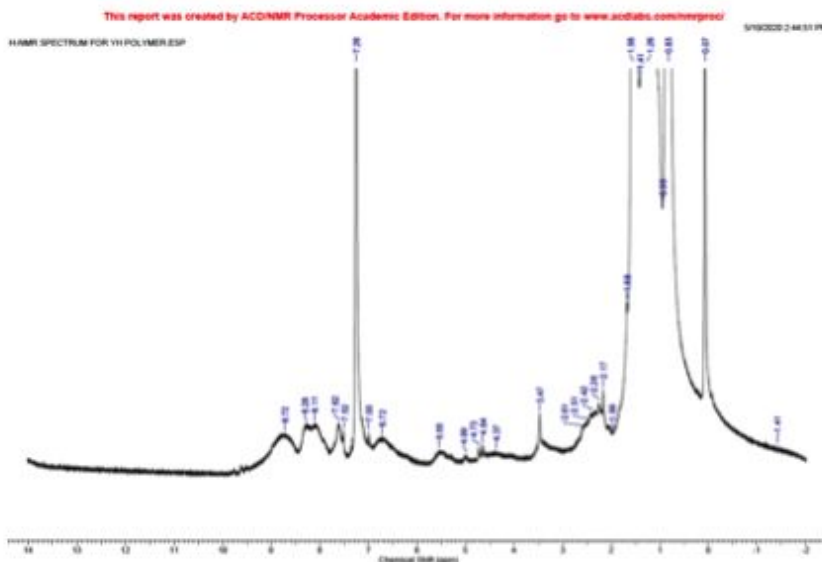


Monomer **3** (50 mg, 0.043 mmol) was dissolved in anhydrous CH_2Cl_2 (0.7 mL) under N_2 . The first generation of Grubbs catalyst (2.4 mg, 0.003 mmol, 0.07 equivalent) was added, and the mixture was

stirred at RT for 2 h. Then the reaction was quenched with ethyl vinyl ether (0.4 mL), and poured into methanol (5 mL). The resulting solid was collected by centrifugation. The precipitate was redissolved in CH₂Cl₂ (0.5 mL) and reprecipitated by adding MeOH (50 mL). The solid was collected by centrifugation to give **4** (22 mg, 44%) as a dark purple solid. ¹H NMR (400 MHz, CDCl₃): δ= 8.5-9.3 (br, 2H), 7.8-8.4 (br, 2H), 7.5-7.8 (br, 2H), 6.1-6.9 (br, 2H), 5.0-5.7 (br, 2H), 4.1-4.8 (br, 2H), 3.0-3.7 (br, 2H), 2.0-3.0 (br, 4H), 1.4-2.0 (br, 8H), 0.9-1.4 (br, 15H), 0.6-0.9 (br, 9H, CH₃).



NMR. ¹H nmr spectrum of monomer **3** (top) and partial spectrum of resulting polymer **4** (bottom).



NMR. Full ¹H nmr spectrum spectrum of resulting polymer **4** (bottom).

2. Figures.

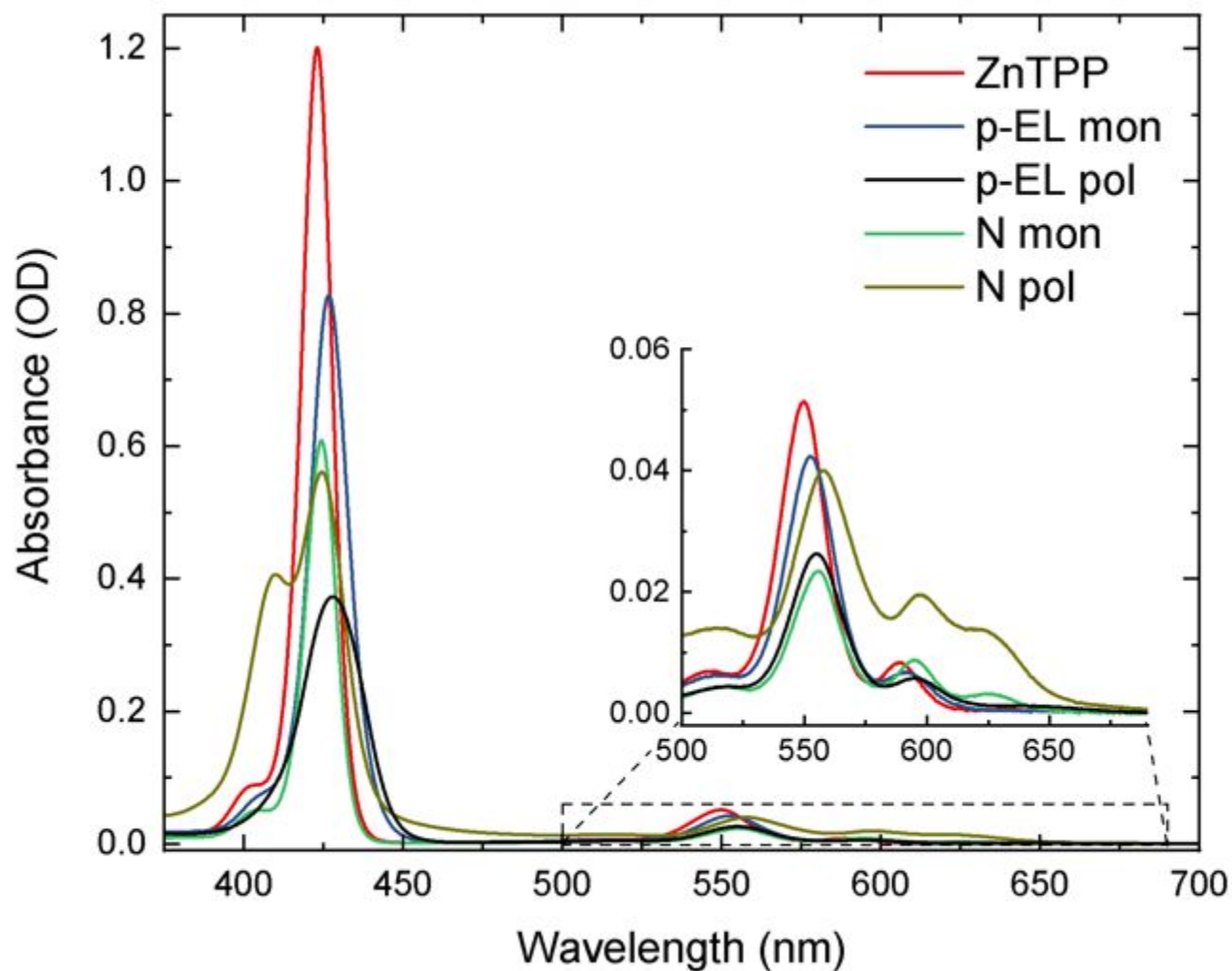


Figure S1: Comparison of the absorption spectra of the norbornene monomer (N mon) and polymer (N pol) and the *p*-ether-linked porphyrin monomer (*p*-EL mon) and its flexible porphyrin pendant polymer (*p*-EL pol) in toluene at room temperature. The concentration of all samples is 2 μM , or 0.0006% (w/v) in the case of N mon, where the *p*-EL polymer spectrum has been divided by 26, to account for the 26 pendant porphyrins along the polymer.

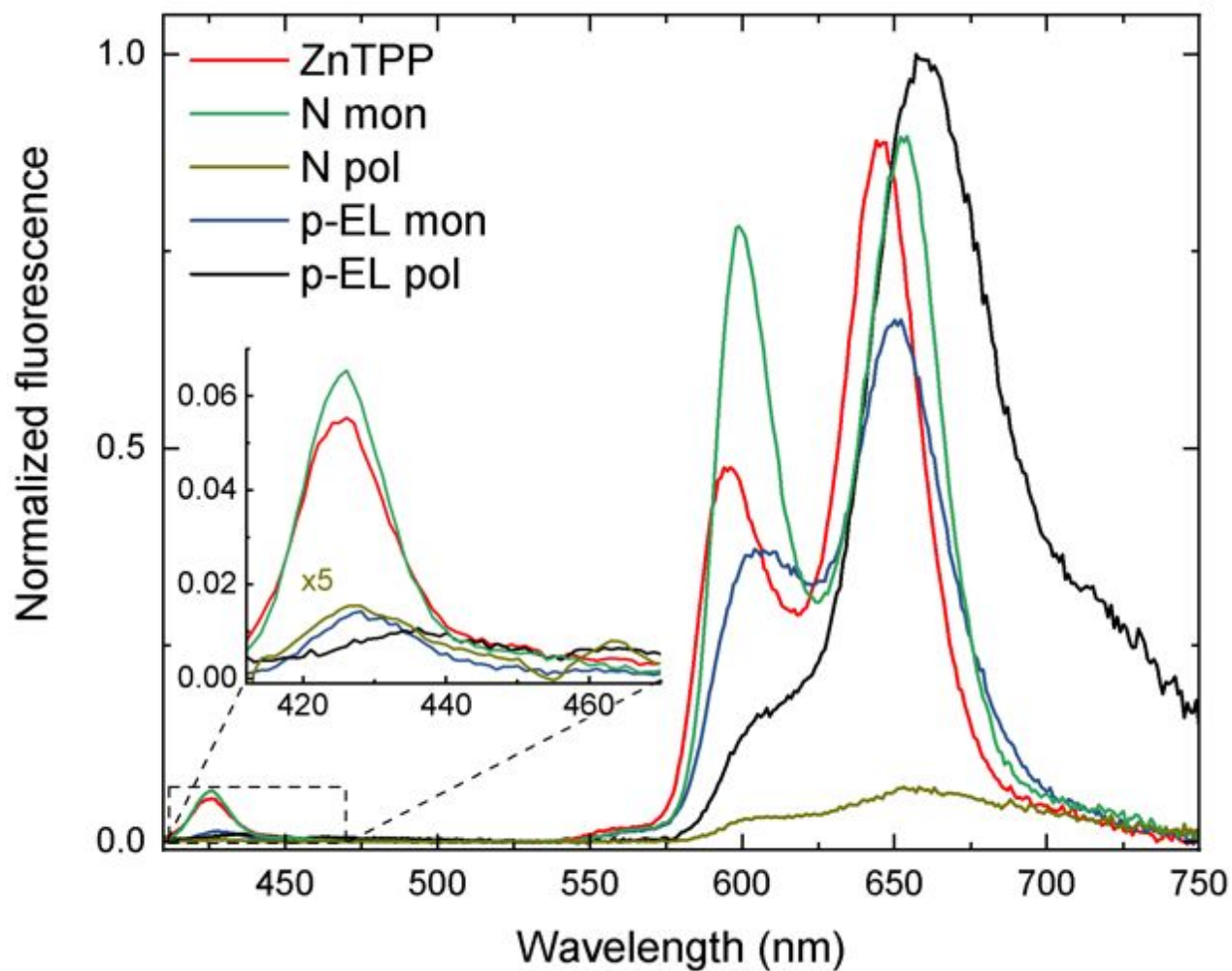


Figure S2: Comparison of the fluorescence emission spectra of the norbornene monomer (N mon), its pendant porphyrin polymer (N pol), and ZnTPP as a reference with those of the flexible monomer (*p*-EL mon) and polymer (*p*-EL pol) excited at 405 nm in toluene. The count rates have been corrected to the same absorbance at 405 nm.

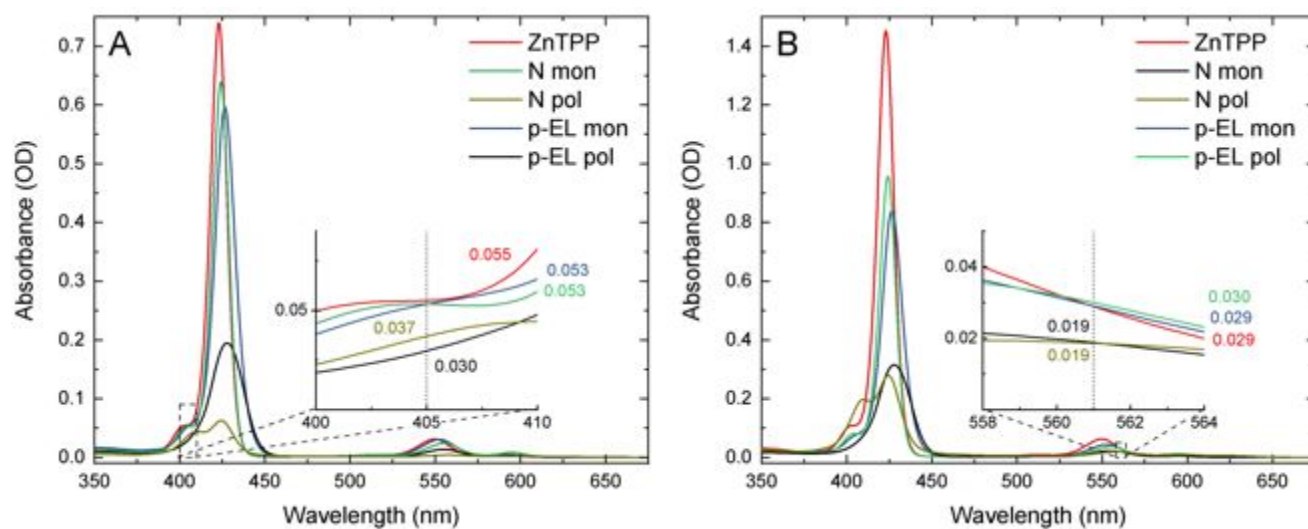


Figure S3: Absorbance corrections for fluorescence quantum yield measurements in a 1 cm pathlength cuvette at 405 nm (A) and 561 nm (B).

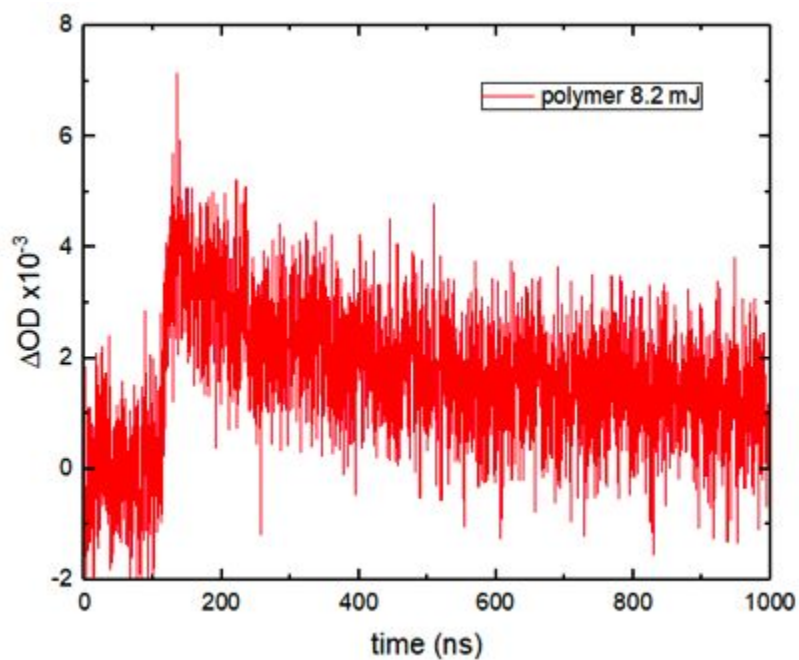
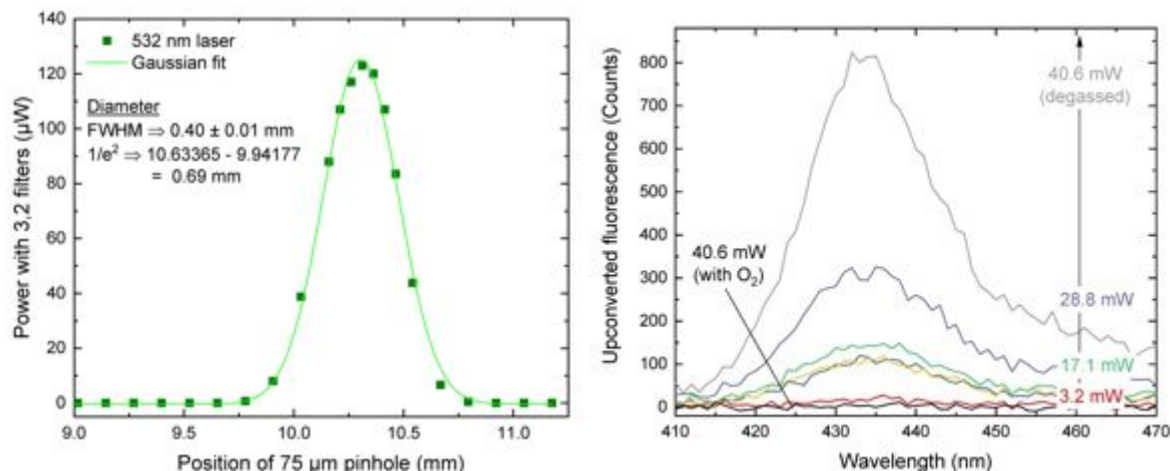


Figure S4: Decay of the transient absorption of the norbornene polymer (N pol) triplet state in degassed toluene. The time delay between pump and probe is 100 ns.

3. Upconversion via sequential two-photon absorption and intrachain TTA; the model

Consider the spatial power distribution of the 532 and 561 nm cw lasers used for excitation in the upconversion experiments. With no filters in place the peak power of the 561 nm laser is 40.6 mW.



Maximum incident power = 40.6 mW at 561 nm in a cylindrical beam of $2r = 0.40$ mm diameter; $P = 40.6 \times 10^{-3} \text{ J s}^{-1}$. The photon energy is $E = hc/\lambda = 3.55 \times 10^{-19} \text{ J/photon}$.

Incident photon rate $I_{h\nu,0} = P/E = 1.15 \times 10^{17} \text{ photons/s}$; fraction absorbed in 1 cm = F

Absorbed photon density, $I_{h\nu,abs} = (I_{h\nu,0})(F)/V$, where $V = \pi r^2(1 \text{ cm}) = 1.26 \times 10^{-3} \text{ cm}^3$
 If $A_{561} = 0.25$, $F = 0.44$ in a 1 cm path and $I_{h\nu,abs} = 4.00 \times 10^{19} \text{ photons s}^{-1} \text{ cm}^{-3}$

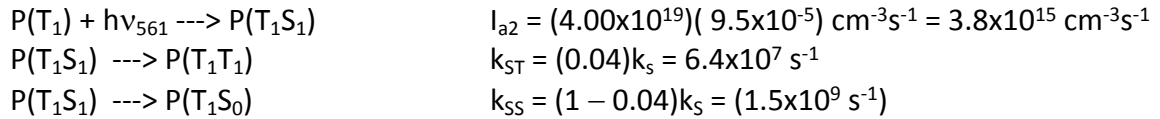
Chromophore density is # of Zn porphyrins/ $\text{cm}^3 = D_{\text{porph}}$. Assume that the molar absorptivity/pendant at 561 nm is about the same as for the monomer; $\epsilon_{561} = 1.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. At $A_{561} = 0.25$, $c = A_{561}/(\epsilon l) = 2.00 \times 10^{-5} \text{ moles/litre}$. Assume also that pendants in the polymer absorb independently (one triplet exciton in a molecule makes no difference to the absorptivity of the remaining pendants). $D_{\text{porph}} = 1.20 \times 10^{16} \text{ chromophores/cm}^3$

The lifetime of the triplet in the polymer is $\tau_T \approx 0.7$ microsecond, so the rate constant for its overall decay is $k_T = 1.4 \times 10^6 \text{ s}^{-1}$. The quantum yield of polymer triplets when excited initially to S_1 is ϕ_{T1} , which is estimated to be ≈ 0.04 from the triplet TA results. Apply steady state kinetics to the singly-excited polymer triplet, $P(T_1)$:

$$[P(T_1)]_{ss} = 4.00 \times 10^{19} \phi_{T1} \text{ cm}^{-3} \text{ s}^{-1} / 1.4 \times 10^6 \text{ s}^{-1} = 1.14 \times 10^{12} \text{ cm}^{-3}$$

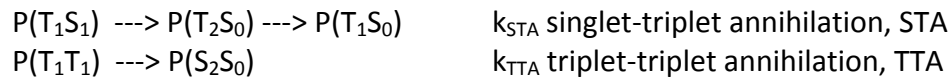
Compare this with $D_{\text{porph}} = 1.20 \times 10^{16}$ absorbing chromophores/ cm^3 . The fraction of chromophores that are triplets in the steady state mix is thus 9.5×10^{-5} . Now ask if this is large enough to reasonably expect sequential absorption of a second photon – this time by other chromophores in the polymer triplet – and then produce the observed S_2 upconversion fluorescence count rate *via* an intrachain

triplet-triplet annihilation (TTA) scheme. Assume that the singlet state produced by absorption of the second photon has a lifetime in the polymer, ignoring exciton migration leading to annihilation, that is no longer than the observed lifetime of the polymer S_1 state when singly excited – *i.e.* no longer than 0.64 ns – so the decay constant for the singlet exciton in the doubly excited polymer is $k_s = 1.6 \times 10^9 \text{ s}^{-1}$ in the absence of annihilation. Let the quantum yield of triplet from the singlet exciton produced by the second absorbed photon be the same as that obtained from the S_1 produced by the first absorbed photon, if it does not undergo singlet-triplet annihilation (STA), *i.e.* $(\phi_{T1})_{\text{noSTA}} = 0.04$.



Then the steady state concentration of $P(T_1S_1)$ if there were no exciton migration leading to annihilation would be $[P(T_1S_1)]_{\text{ss no ann}} = I_{a2}/(k_{ST} + k_{SS}) = (3.8 \times 10^{15})/(1.6 \times 10^9) \text{ cm}^{-3} = 2.4 \times 10^6 \text{ cm}^{-3}$.

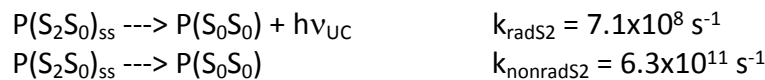
Now consider exciton migration and annihilation.



Assume that the relative rates of these two processes are determined primarily by the relative rates of singlet and triplet exciton migration in the polymer. These relative rates can be estimated by considering the effect of polymerization on the S_1 and T_1 lifetimes of the porphyrin-appended monomer. Polymerization speeds up the S_1 decay rate by a factor of ca. 3.4 (from 2.12 ns to 0.64 ns) and the T_1 decay rate by a factor of ca. 320 (from 223 μs to ca. 0.7 μs). The calculated rate of FRET for the set of cofacial porphyrins in the E region is $6.2 \times 10^9 \text{ s}^{-1}$ (see text and Supporting Information). If the rate of cofacial FRET in the Z region is much faster than in the E region, then many exciton “hops” can occur during the observed 0.64 ns lifetime of the S_1 exciton prior to decay or annihilation. Although the rate of triplet exciton migration will be substantially slower (an electron exchange mechanism is required), the rate of TTA is expected to be orders of magnitude faster than the rate of triplet exciton migration once the two triplet excitons encounter one another. As a working hypothesis, assume that the rates of STA and TTA are determined by the observed lifetimes of the S_1 and T_1 excitons in the polymer, *i.e.* $k_{TTA}/k_{STA} = 1.4 \times 10^6/1.6 \times 10^9 = 9.1 \times 10^{-4}$, which is also the fraction of the $[P(T_1S_1)]_{\text{ss no ann}}$ that yields the upconverted S_2 product. Thus

$$[P(S_2S_0)]_{\text{ss}} = (2.4 \times 10^6 \text{ cm}^{-3})(9.1 \times 10^{-4}) = 2.2 \times 10^3 \text{ cm}^{-3}$$

Now consider the decay of the product $P(S_2S_0)$.



Here we assume that the lifetime of the upconverted S_2 state and the quantum yield of its fluorescence is similar to that of the monomer because the upconverted emission spectrum is almost

identical to that of the directly Soret-excited monomer. The quantum yield of S_2 emission from the polymer excited in the Soret bands in the E region (i.e. showing no excimer emission) is $\phi_{S2hv} = 1.14 \times 10^{-3}$ (Table 1), i.e. $\phi_{S2hv} = k_{radS2}/(k_{radS2} + k_{nonradS2}) = 1.14 \times 10^{-3}$. The expected S_2 emission rate from the excited sample volume, V , is then $I_{S2hv} = (k_{radS2})[P(S_2S_0)]_{ss} V \phi_{S2hv} = (7.1 \times 10^8 s^{-1})(2.2 \times 10^3 cm^3)(1.26 \times 10^{-3} cm^3)(1.14 \times 10^{-3}) = 2.2 \times 10^6 s^{-1}$. (Note, however, that if the S_2 emission quantum yield were to be that of the Z region (i.e. $\phi_{S2hv} = 7 \times 10^{-5}$, Table 1) then the emission rate from the excited volume would be $1.4 \times 10^5 s^{-1}$.)

Only a small fraction of the total emission in the excitation volume is detected by the spectrometer as the observed upconversion count rate. Assume that the upconverted fluorescence is emitted radially in a spatially uniform fashion. Let the fraction of the emitted photons detected by the PMT in the spectrometer be C . If we have a 3 mm x 10 mm spectrometer entrance slit at 50 mm from the $1.26 \times 10^{-3} cm^3$ source, then the fraction of the emitted photons entering the spectrometer will be approximately $30 mm^2 / (4\pi (50^2) mm^2) = 9.5 \times 10^{-4}$. The fraction of those photons reaching the PMT detector through the exit slit via the double diffraction grating will be X . The PMT detection efficiency is typically 0.1 in the blue. So C is approximately $10^{-4}X$ and the expected count rate will be $(2.2 \times 10^6)(0.1)(9.5 \times 10^{-4})X s^{-1} \approx 200X s^{-1}$. X is <1 but not by more than an order of magnitude since the exit slit width used in the photon upconversion experiments is 10 mm (giving an exit spectral bandwidth of 29 nm) and therefore accommodating almost the entire S_2 upconversion emission spectrum. The upconversion count rate resulting from sequential two photon absorption and intrachain TTA calculated in this model is thus of the order of magnitude observed at maximum incident power, 800 cps, provided the assumptions are valid. Photon upconversion via sequential two-photon absorption, exciton migration and intrachain triplet-triplet annihilation is a viable mechanism.

Note in this model that because $T_1 + S_1 \rightarrow T_2 + S_0$ STA consumes most of the annihilating singlet excitons produced by absorption of the second photon, and because every STA event produces one T_1 via rapid $T_2 - T_1$ internal conversion following annihilation, we expect that the net effect of the intrachain biexcitonic annihilation processes is the loss of only one triplet state. Consequently, the S_2 upconverted fluorescence is expected to exhibit a measured power dependence between linear and quadratic. The observed power dependence (slope in Figure 7B) is 1.44 ± 0.09 .

4. Calculation of energy transfer rate between porphyrins in the norbornene polymer

The rate of energy transfer (k_{ET}) between nearest porphyrin chromophores in the norbornene polymer assuming a Förster resonance energy transfer mechanism can be determined using:^{S1}

$$k_{ET} = \frac{1}{\tau_D} \left[\frac{R_0}{R} \right]^6$$

Where R is the porphyrin-porphyrin separation, τ_D is the porphyrin monomer donor singlet state lifetime ($\tau_D = 2.15$ ns from Table 2), and R_0 is the critical transfer distance given by:

$$R_0 = 0.2108 \left[\kappa^2 \Phi_0 n^{-4} J \right]^{\frac{1}{6}}$$

Here Φ_0 is the fluorescence quantum yield of the donor in the absence of acceptor ($\Phi_0 = 0.0297$, Table 1), n the solvent refractive index (for toluene $n = 1.496$), J the spectral overlap integral of the normalized emission spectrum of the donor (D) porphyrin and the porphyrin acceptor (A) absorption spectrum:

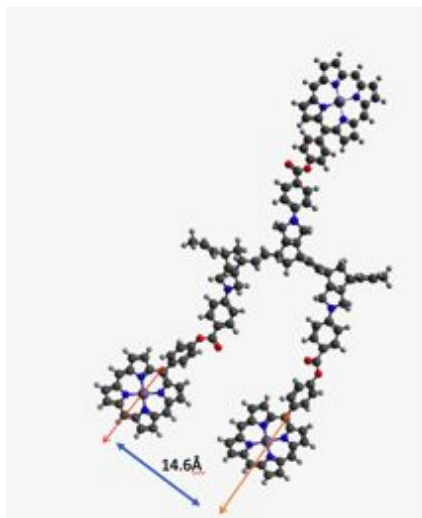
$$J = \int_0^{\infty} \varepsilon_A(\lambda) \lambda^4 F_D(\lambda) d\lambda$$

and gives a value of $J = 2.49 \times 10^{14} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$. κ^2 is the orientation factor and depends on the relative orientation of the interacting chromophore transition dipoles. For parallel donor emission and acceptor absorption transition dipoles in the optimized geometry of the closest porphyrin chromophores of the E isomer (see Figure below) $\kappa^2 = 1$.⁵²

From the above information, R_0 is calculated to be 22.5 Ångstrom for porphyrin to porphyrin energy transfer in the E isomer. The porphyrin to nearest porphyrin separation in the E isomer can be estimated from the optimized molecular structure shown in the Figure below to give $R = 14.6$ Ångstrom. For this separation k_{ET} is calculated to be $6.2 \times 10^9 \text{ s}^{-1}$. The energy transfer efficiency (E) is given by:

$$E = \frac{1}{1 + \left[\frac{R}{R_0} \right]^6}$$

$E = 93\%$ for the transfer efficiency between closest porphyrins in the E isomer.



UFF optimized structure for the E isomer triad showing centre-to-centre distance for closest side chain porphyrins.^{S3}

Supporting Information References

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S2. Stake, A., Kobuke, Y. Artificial photosynthetic systems:assemblies of slipped cofacial porphyrins and phthalocyanines showing strong electronic coupling. *Org. Biomol. Chem.* **2007**, *5*, 1679-1691.

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