Author/s:
Stevens, AL;Awuku, S;Ghiggino, KP;Hao, Y;Novakovic, S;Steer, RP;White, JM

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

Date:
2020-12-24

Citation:
Stevens, A. L., Awuku, S., Ghiggino, K. P., Hao, Y., Novakovic, S., Steer, R. P. & White, J. M. (2020). Spectroscopic and Dynamic Properties of Electronically Excited Pendant Porphyrin Polymers with Backbones of Differing Flexibility. The Journal of Physical Chemistry A, 124 (51), pp.10748-10757. https://doi.org/10.1021/acs.jpca.0c09501.

Persistent Link:
https://hdl.handle.net/11343/345171

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

Amy L. Stevens,[b] Stephen Awuku,[b] Kenneth P. Ghiggino,[a]* Ying Hao,[a]
Sacha Novakovic,[a] Ronald P. Steer[b]*, Jonathan M. White[a]

a School of Chemistry and ARC Centre of Excellence in Exciton Science
University of Melbourne
Parkville, VIC 3010, Australia

b Department of Chemistry
University of Saskatchewan
Saskatoon, SK
Canada S7N5C9

*Authors to whom correspondence should be addressed.
email: ron.steer@usask.ca, ghiggino@unimelb.edu.au

Abstract:

A zinc porphyrin-pendant norbornene polymer with a rigid backbone characterized by a 2:1 E:Z isomeric structure ratio has been synthesized and its spectroscopic and photophysical properties examined. Zinc tetraphenylporphyrin, the porphyrin-substituted norbornene monomer and a previously reported zinc porphyrin-pendant polymer with a flexible polymethylene backbone have been used as comparators. Unlike its flexible counterpart, the rigid norbornene polymer exhibits clear exciton splitting of its Soret band, much more rapid relaxation rates of its excited singlet states, and a very small yield of an unusually short-lived triplet state. Unlike the flexible pendant polymer, which exhibits excimeric S_2 fluorescence as a result of chromophore rotation, anti-Kasha emission from the norbornene polymer originates primarily from the unperturbed porphyrin E region. The low triplet yield in the polymer is attributed to greatly increased rates of competing internal conversion within the singlet manifold. Nevertheless, upconverted delayed fluorescence that is quenched by oxygen is observed upon intense steady-state Q-band excitation of degassed the polymer solutions, signalling direct triplet involvement. Consistent with the polymer's rigid structure, this biexcitonic process is assigned to ultrafast singlet exciton migration and triplet-triplet annihilation following absorption of a second photon by the small steady-state concentration of polymer triplets.

Introduction:

Meso-substituted metalloporphyrins containing d^0 or d^{10} metal ions can provide a wide range of readily measurable excited state lifetimes with which to probe exciton dynamics when two or more of these chromophores are incorporated into larger structures. For example monomeric zinc tetraphenylporphyrin (ZnTPP), often used as a model compound, absorbs throughout the visible spectrum, exhibits picosecond S_2 lifetimes when excited in its Soret band, nanosecond S_1 lifetimes when excited in its Q bands and by intersystem crossing forms large yields of T_1 triplets with unquenched lifetimes in the hundreds of microseconds range.[1-3] All three of these excited species can be observed by transient absorption methods[4] and the S_2 and S_1 states also provide readily measurable fluorescence with temporal profiles[1] that can be measured using standard pulsed laser technology. Such transient absorption and fluorescence lifetime measurements can be taken over a wide range of temperatures in solution, in thin films or in matrices.

Metalloporphyrins can also be incorporated into a wide variety of larger structures, including dyads,[5] tapes,[6-8] polymers,[9-12] MOFs[13,14] and larger aggregates.[15] Particular attention has been paid to zinc porphyrin arrays that mimic the photosynthetic "special pair".[16] Materials such as these that exhibit deviations of their S_2, S_1 and T_1 relaxation parameters from the well-established values of the monomer can thus provide quantitative insight into exciton migration, energy transfer and electronic quenching in systems containing multiple chromophores. Of importance, porphyrin structures ranging from linear and pendant polymers and copolymers to macrocyclic porphyrin species of moderate size are now known.[5-12] In any such species it may be possible to measure triplet-triplet annihilation rates by following the temporal profile of delayed fluorescence from the S_2 product state[17] ($2\ T_1 \rightarrow S_2 + S_0$ if homo-chromophoric), whereas electronic energy transfer or electron

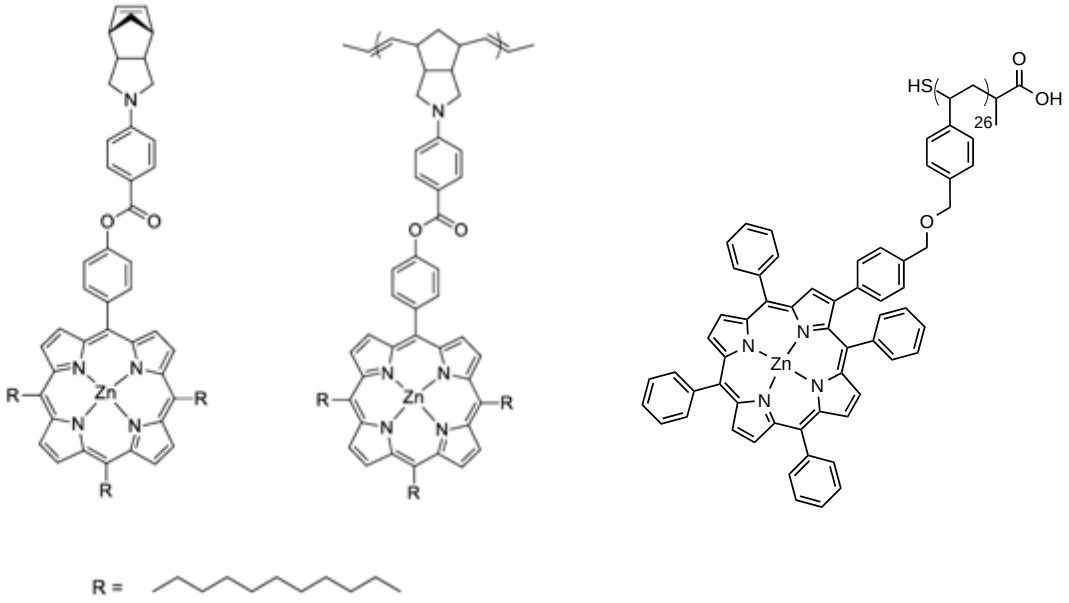
transfer rates may be measured by following fluorescence quenching in covalently[5] or non-covalently[3] bound donor-acceptor systems.

We have recently become interested in following exciton migration rates by observing emission quenching and the generation of upconverted fluorescence in multi-chromophoric polymers,[19-21] with the aim of investigating not only interchain events but also events brought about by intrachain biexcitonic processes. We have found evidence of rapid intrachain triplet biexcitonic annihilation in a diphenylanthracene pendant polymer excited by sensitization methods[21] and have tried to find evidence of similar processes in a pendant zinc porphyrin polymer by observing upconverted delayed S_2 fluorescence following excitation in the porphyrin Q bands.[20] However, in the latter case upconversion proved to be inefficient because the polymer employed in these experiments had a saturated carbon backbone that permitted internal rotation of the chromophores resulting in kinetically competitive excimeric quenching of the excited species.

The recent work of Lin, *et al.*[9] who have synthesized and characterized a number of pendant porphyrin polymers with rigid backbones and a range of E:Z isomeric pendant conformations has sustained our interest in these materials. They and Fujitsuka, *et al.*[11,12] have followed the singlet-triplet and singlet-singlet annihilation processes in these polymers using femtosecond transient absorption and nanosecond fluorescence methods. Here we report the use of triplet transient absorption, S_2 fluorescence upconversion and ultrafast fluorescence decay methods on novel rigid pendant porphyrin polymers to further extend our understanding of these interesting and potentially important systems. We also compare the detailed photophysical behaviour of these rigid polymers with that of their flexible counterparts to identify differences in their radiative and radiationless relaxation pathways, and to assess their potential importance if used in optoelectronic devices.

Experimental Section:

The structures of the zinc porphyrin-substituted N-arylpyrrolidine-fused norbornene monomer and its Grubbs-catalyzed ROMP polymer synthesized for this study are shown in Scheme 1. The



Scheme 1: Structures of the zinc porphyrin-substituted norbornene monomer (N-mon) and its polymer (N-pol) synthesized for the present study (left) and, for comparison, the previously reported[20] pendant zinc porphyrin polymer with a non-rigid backbone (*p*-EL pol, right). R is $C_{11}H_{23}$.

structure of a representative pendant porphyrin polymer with a saturated hydrocarbon backbone, previously reported,[20] is also provided for comparison purposes. Details of the syntheses are provided in the Supporting Information. The *p*-methylester-substituted norbornene monomer without the porphyrin pendant was polymerized to determine the optimum conditions for the final synthesis. The nmr spectrum of this polymer (Supporting Information) was used to determine its E:Z ratio of 2.14:1. Because the features of the nmr spectrum of the pendant porphyrin polymer were too broad to determine its E:Z ratio directly, this ratio of 2.14:1 was used as a reasonable estimate of the pendant porphyrin polymer backbone isomeric structure as well. This approach is supported by

the results reported previously[9] where the E:Z ratio of a porphyrin-substituted norbornene polymer (after ethanolysis) was found to be almost identical to that of an authentic ethyl ester-substituted polymer prepared by the same method.

All solution samples were made using spectroscopic grade toluene (Sigma-Aldrich) and all measurements were made at room temperature. The absorption spectra were measured using a Cary-6000i dual-beam spectrophotometer. The steady-state fluorescence emission spectra were taken using a standard PTI QuantaMaster double-monochromator fluorometer and/or a custom-modified SPEX fluorometer with a set of cw lasers at 405, 532 and 561 nm as the excitation source. For the fluorescence quantum yields, dilute solutions and thin 10 mm x 2 mm rectangular cuvettes were employed, thus circumventing artifacts from reabsorption and fluorescence collection efficiency effects.

The S_1 fluorescence lifetimes were measured by TCSPC based on a Spectra-Physics Mira Ti:Sapphire laser and pulse picker. The 800 nm output was frequency doubled to yield 400 nm excitation pulses at 4 MHz. The instrument response function of 100 ps (FWHM) was measured at the excitation wavelength using solvent scatter. Following background subtraction, fluorescence lifetimes were obtained by iterative reconvolution using one or two exponential decay functions.

Picosecond time-resolved emission measurements were conducted using fluorescence upconversion spectroscopy as described in detail previously,[1] using detection wavelengths that were set at or near the maxima of the S_2 and S_1 fluorescence emission. The samples were continuously stirred by a magnetically-controlled stir bar and the peak count rate was limited to ≤ 5% of the repetition rate of the laser in order to eliminate photon-counting artifacts in the detection electronics.

Transient triplet absorption spectra and decay data were measured using an Edinburgh Instruments LP920 nanosecond flash photolysis system using the second harmonic output of a Qantel Brilliant B Nd:YAG laser for excitation (10 ns pulse width, λ_{exc} = 532 nm, 8.2 mJ pulse energy). Transient spectra were captured using a gated Andor DH720 ICCD camera and decay curves recorded with a Hamamatsu R2856 photomultiplier/Tektronix TDS 3012 digital oscilloscope combination. Samples in toluene with absorbance of 0.020 at 532 nm in 1 cm path length cells were thoroughly degassed by four freeze-pump-thaw cycles.

Fluorescence upconversion experiments were conducted using the SPEX spectrofluorometer fitted with a 561 nm cw laser (CNI) with a peak output power of *ca.* 40 mW as the excitation source and a set of neutral density filters to attenuate the laser's power at the sample. Samples in toluene were thoroughly degassed by repetitive freeze-pump-thaw cycles on a high vacuum line. The cross-sectional dimensions of the excitation beam were obtained by translating a 75 μm diameter pinhole across the collimated laser output.

Results and Discussion:

The absorption spectra of the porphyrin-substituted norbornene monomer, its polymer and ZnTPP as a reference, all in toluene at room temperature, are shown in Figure 1. A comparison of these spectra with the absorption spectra of the previously reported pendant porphyrin polymer with a flexible polymethylene backbone is provided in Figure S1 in the Supporting Information. The norbornene monomer exhibits a slight red shift of the Q band absorption relative to ZnTPP whereas its Soret band absorption remains unshifted. The $S_2 - S_1$ electronic energy spacing of the norbornene

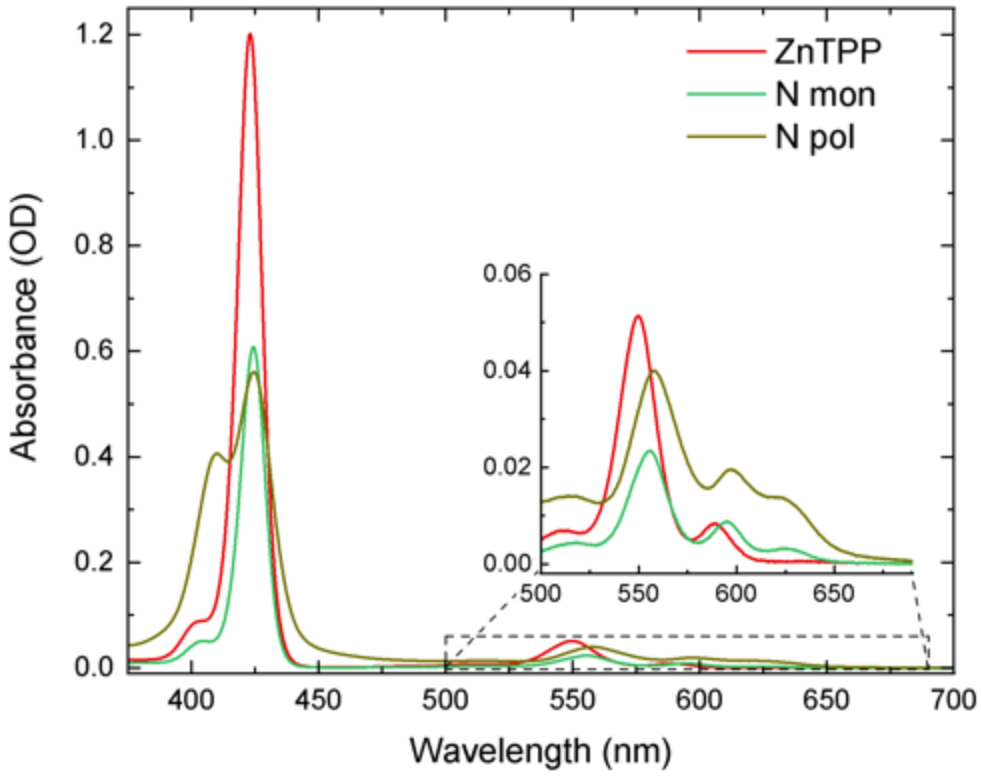


Figure 1: Absorption spectra of the porphyrin-substituted norbornene monomer (N mon, 2 µM) and its polymer (N pol, 0.0006% (w/v)) in toluene, with ZnTPP in toluene (2 µM) as a reference. The inset shows the Q band ($S_1 - S_0$) transition in greater detail. All measurements were taken in a 1 cm pathlength cuvette at room temperature.

monomer is thus slightly larger in this particular trialkyl-substituted zinc porphyrin than in ZnTPP. Small differences in their relative radiationless decay rates are thus expected (*vide infra*).

The absorption bands of the porphyrin-substituted norbornene polymer exhibit some broadening relative to those of the monomer, and, in agreement with the work of Lin, *et al.*[9] and others,[10-12] the Soret band shows definite evidence of hypsochromic exciton splitting, assignable to *in situ* static cofacial interactions between a subset of the porphyrin pendants. The polymer absorption (and fluorescence) spectra are independent of solute concentration, ruling out interchain interactions as a source of these features. In keeping with the measured E:Z ratio of 2.14:1 for the

porphyrin-free pendant norbornene polymer (assumed to hold approximately also for its porphyrin-containing counterpart, *vide supra*), the blue-shifted Soret exciton band is of significantly lower intensity than its unshifted counterpart. (Although this is in qualitative disagreement with the work of reference 9, we note that the relative magnitudes of the exciton-split Soret features may be attributed, at least in part to the different solvents used in recording of the spectra.) A substantial fraction of the porphyrin pendants in this norbornene polymer are thus relatively unperturbed, and are reasonably assignable to those located in its terminal and E isomeric regions. The latter observations are important because the pendant porphyrin polymer examined in our previous studies (*cf.* Scheme 1 and Figure S1) exhibited no such excitonic splitting of its Soret bands, an absence attributable to a structure that allowed pendant rotation about the polymer backbone. Such structural variations in the polymer backbone are expected to result in significant differences in their photophysical behaviour (*vide infra*).

The fluorescence spectra of the porphyrin-substituted norbornene monomer, its polymer and ZnTPP as a reference,[1] each excited at 405 nm and 561 nm in toluene at room temperature, are shown in Figure 2. Figure S2 in the Supporting Information provides a comparison of these fluorescence spectra with those previously reported[20] for the pendant porphyrin polymer (*p*-EL pol) with a flexible backbone. A further comparison of these two polymers (N pol and *p*-EL pol) is provided in Figure 3 where the differences in their fluorescence spectra obtained when exciting at 410 nm (at the wavelength of the hypsochromic-shifted Soret band of the norbornene polymer) and at 425 nm (near the maximum of the unshifted Soret band of the norbornene polymer) are recorded. Although the latter spectra have been normalized to the peak of the S_1 emission, the intensities are

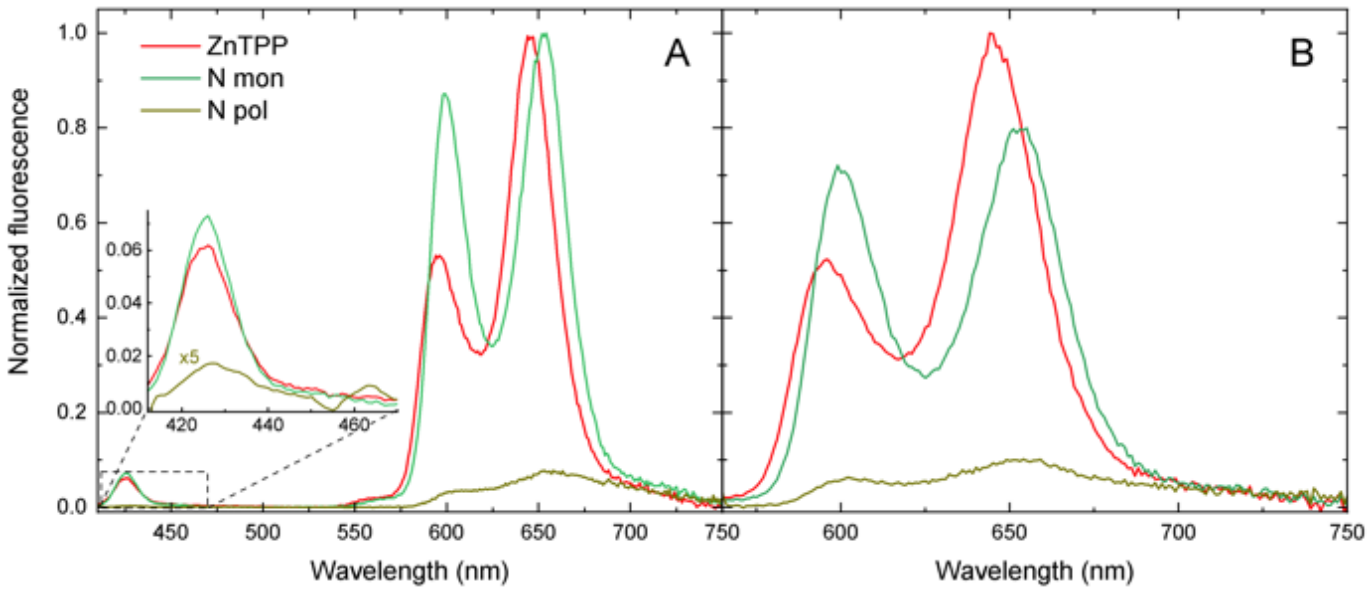


Figure 2: Fluorescence emission spectra of the norbornene monomer (N mon), its pendant porphyrin polymer (N pol) and ZnTPP as a reference excited at 405 nm (left) and at 561 nm (right) in toluene. The count rates have been corrected slightly to what they would exhibit for identical absorbances at the excitation wavelengths.

Table 1: Quantum yields of fluorescence, ϕ_f, as a function of excitation wavelength.[#]

Sample	$\phi_f(S_2 - S_0)$, λ_{ex} = 405 nm	$\phi_f(S_1 - S_0)$, λ_{ex} = 405 nm	$\phi_f(S_1 - S_0)$,[c] λ_{ex} = 410 nm	$\phi_f(S_1 - S_0)$,[c] λ_{ex} = 425 nm	$\phi_f(S_1 - S_0)$, λ_{ex} = 561 nm
ZnTPP[a]	1.14×10^{-3}	2.93×10^{-2}	2.93×10^{-2}	2.93×10^{-2}	2.93×10^{-2}
Norbornene monomer	1.14×10^{-3}	2.96×10^{-2}	2.96×10^{-2}	2.96×10^{-2}	2.97×10^{-2}
Norbornene polymer	0.07×10^{-3}	0.13×10^{-2}	0.10×10^{-2}	0.22×10^{-2}	0.36×10^{-2}
p-EL polymer[b]	0.50×10^{-3}	1.1×10^{-2}	0.80×10^{-2}	0.83×10^{-2}	2.1×10^{-2}

Corrected for small absorbance differences at the excitation wavelengths, *cf.* Figure S3, Supporting Information. Error estimated to be ± 10%.

a. Reference standard (ref. 1). b. Flexible porphyrin polymer (ref. 20) for comparison (original data except for 410, 425). c. Estimated from the original, unnormalized emission spectra.

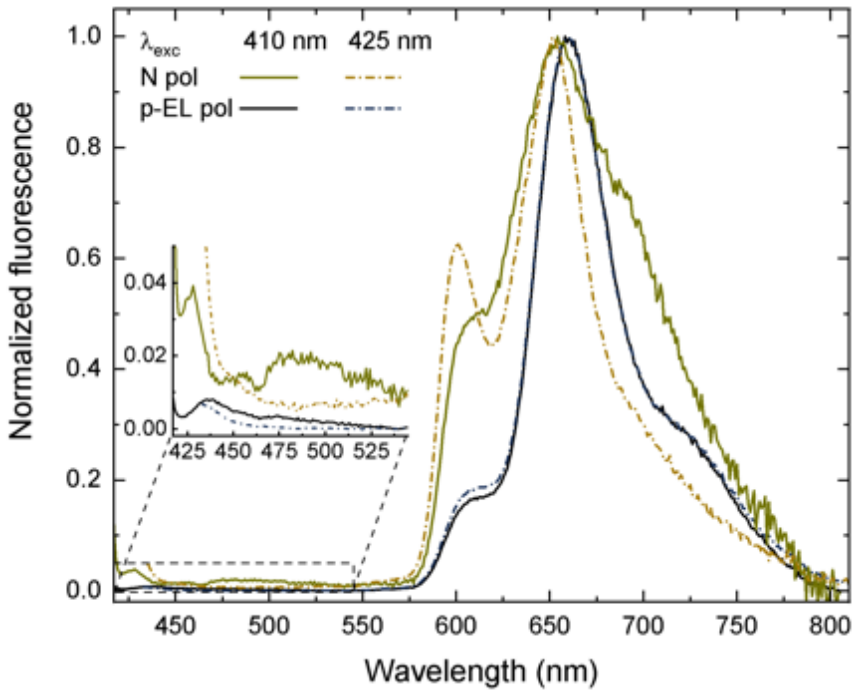


Figure 3: Comparison of the normalized fluorescence spectra of the norbornene polymer (N pol, 0.0006% (w/v)) excited in its two exciton-split absorption bands at 410 nm (solid lines) and at 425 nm (dashed lines) and the flexible polymer (*p*-EL pol, 0.2 μM) excited at the same wavelengths, each in toluene at room temperature. Background scatter has been subtracted.

very different, as documented by the quantum yield data in Table 1. Assignments of the strong bands in these S_1 and S_2 emission spectra are straightforward, but comparing the weaker features obtained from excitations of the two polymers at 410 nm and 425 nm are particularly revealing.

First, excitation of the norbornene polymer at 425 nm in its unshifted Soret absorption band produces clearly identifiable S_1 emission very similar to that of ZnTPP and the porphyrin-substituted norbornene monomer. Assignment of this emission to fluorescence from relatively unperturbed porphyrin chromophores in the polymer E region is clear. “Anti-Kasha” anomalous fluorescence from the S_2 state cannot be seen due to scatter when exciting at 425 nm, but is clearly seen when exciting at 405 nm at the maximum of the Soret vibronic absorption feature (*cf*. ZnTPP and N mon) which is overlapped by the exciton-split band at 410 nm in the norbornene polymer. Second, the fluorescence

spectra of the flexible porphyrin polymer previously reported[20] exhibit no significant differences when excited at 410 nm and 425 nm. However, there are substantial differences in the weak bands of both the S_1 and S_2 fluorescence spectra of the porphyrin pendant norbornene polymer when it is excited in the hypsochromically-shifted band at 410 nm compared with 425 nm.

Note that the norbornene polymer fluorescence in the red to near infrared is exceptionally weak when excited at 410 nm compared with 425 nm. This is consistent with excited chromophore self-quenching in the Z regions of the polymer. In addition, excitation at 410 nm produces two very weak features that are not present in the other spectra; one is a broad feature with a maximum near 475 nm that lies to the red of where the unperturbed "anti-Kasha" S_2 emission band is located and the other is a noisy broad shoulder on the S_1 emission located near 700 nm and trailing into the infrared. We tentatively assign these features to excimer emission in the norbornene polymer. We suggest that the emission feature with a maximum near 475 nm results from excitation of the polymer at 410 nm where interactions between pairs of porphyrin chromophores in the Z regions could produce "anti-Kasha" anomalous fluorescence from very short-lived $S_2\cdots S_0$ excimers with a variety of possible structures. Ultrafast electronic relaxation of these $S_2\cdots S_0$ pairs would then produce vibrationally hot $S_1\cdots S_0$ species that in a few ps would thermalize (but not by separation in the Z isomer sets) to a second excimeric species emitting in the red/near infrared region. A hint of this weak excimeric infrared emission is also seen in the fluorescence spectrum of the norbornene polymer excited at 561 nm in its Q absorption bands, Figure 2. Further evidence of excimer involvement is also provided by the temporal behaviour of the various excited species (*vide infra*).

The picosecond time-resolved S_2 and S_1 fluorescence profiles of the porphyrin-substituted norbornene monomer, its polymer and the ZnTPP reference, excited in their Soret absorptions at 400

nm, are shown in Figure 4. Their S_1 fluorescence decay profiles on a nanosecond time scale are shown in Figure 5. Fitting data are assembled in Table 2. The monomer has an S_2 lifetime of 1.57 ps, slightly longer than that of ZnTPP in keeping with its slightly larger $S_2 - S_1$ electronic energy spacing and the energy gap law of radiationless transition theory.[1,22] The S_1 fluorescence rise time matches the S_2 decay time, consistent with $S_2 - S_1$ internal conversion as its dominant S_2 decay process.

When excited on the high energy side of its exciton-split Soret band at 400 nm, the norbornene polymer exhibits a bi-exponential S_2 fluorescence decay consisting of a 0.4 ps major component and a 1.6 ps minor component, both leading to a small amount of a longer-lived residual emission at the 442 ± 5 nm observation wavelength. The rapid S_2 decay component of the polymer is matched by a short-lived (0.22 ps) exponential increase in its S_1 emission intensity, an indication that one major S_2 decay process of the polymer is S_2 to S_1 relaxation, just as seen in the monomer and the

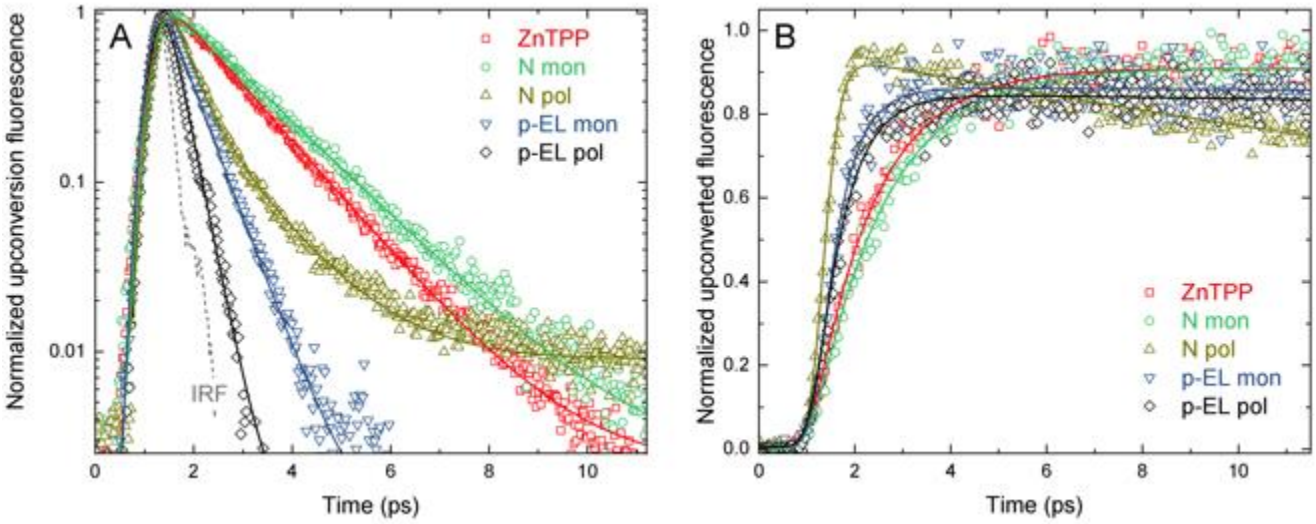


Figure 4: Picosecond time-resolved fluorescence profiles of the norbornene monomer (N mon, green), polymer (N pol, yellow) and ZnTPP reference (red) obtained by fluorescence upconversion when excited at 400 nm in toluene. Comparable data for the flexible *p*-EL polymer (black) and its monomer (blue) are shown for comparison. Left: S_2 fluorescence decay measured at 442 nm. Right: S_1 fluorescence rise and decay measured at 657 nm. Fitting data are in Table 2.

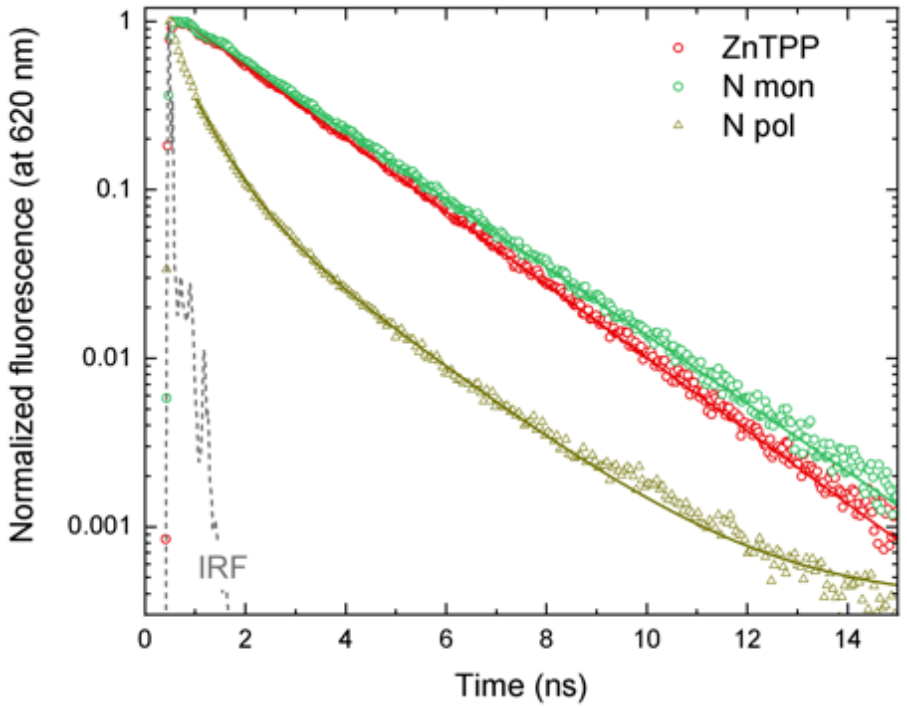


Figure 5: Nanosecond time-resolved S_1 fluorescence decay profiles of the polymer (N pol), monomer (N mon) and ZnTPP standard excited in toluene at 400 nm and measured by TCSPC at 620 nm.

Table 2: Parameters describing the temporal behaviour of the norbornene monomer and polymer with ZnTPP[a] and the previously reported flexible polymer[b] as references.

Sample	τ (S_2) decay, ps λ_{det} = 442 nm	τ (S_1) rise, ps λ_{det} = 657 nm	τ (S_1) decay, ns λ_{det} = 620 nm
ZnTPP[a]	1.32	1.29	2.00
Norbornene monomer	1.57	1.50	2.15
Norbornene polymer[c]	0.45 (0.89); 1.6 (0.11)	0.22	0.64 (0.85); 2.3 (0.15)[d]
p-EL polymer[c]	0.60	0.30	0.57(0.71); 1.5 (0.29)

a. Reference standard (ref. 1). b. Flexible porphyrin polymer (ref. 20) for comparison.
c. Polymer decays are fit with biexponential functions, τ_1 (a_1); τ_2 (a_2). d. A unique 6.3 ps decay (*cf*. Figure 4) of fluorescence at 657 nm is not included in this table.

ZnTPP standard, but at a rate that is several times faster than those of the monomers. Static cofacial interactions between adjacent porphyrin pendants in the Z isomer regions are responsible for the hypsochromic exciton band that is responsible for the majority of the polymer's absorption at the 400 nm excitation wavelength. We therefore conclude that these static interactions in the Z regions promote an enhanced rate of $S_2 – S_1$ internal conversion in the norbornene polymer and are the source of the fast major component of its fluorescence. The minor S_2 emission component of the polymer has a lifetime equal to that of the monomer, indicative of anti-Kasha fluorescence from that fraction of pendants that are free from significant interchromophore interaction when excited at 400 nm. This is consistent with absorption within the weak vibronic feature of the Soret spectrum of the unperturbed zinc porphyrin chromophore underlying the hypsochromically split band at 410 nm (*cf*. Fig. 1).

The nanosecond S_1 fluorescence decay profiles of the norbornene monomer and polymer are unremarkable and are similar to those previously seen in the flexible pendant porphyrin polymers.[20] Despite its *meso*-trialkyl porphyrin substitution, the monomer has an S_1 lifetime of 2.15 ns, similar to that of the ZnTPP standard. The polymer exhibits bi-exponential fluorescence decay with a major component of 0.64 ns and a minor component whose lifetime is similar to that of the monomer. Similar to the S_2 fluorescence decay profiles, the minor longer-lived component of the polymer S_1 fluorescence arises from the radiative decay of unperturbed pendants and the major component from pendants in the Z region that are interacting with others in their ground states and thus inducing non-radiative relaxation at an increased rate. The very small net yield of triplet states produced from excitation in both the Q and Soret absorption bands of the norbornene polymer

indicates that rapid relaxation of the excited singlets to the ground state dominates the decay and effectively eliminates much of the intersystem crossing to the triplet manifold that characterizes the monomer's S_1 decay (*vide infra*).

Among our measurements, the small amount of longer-lived (on a ps time scale) residual emission observed at 442 nm and the minor 6.3 ps relaxation component of the S_1 emission observed at 657 nm are unique to the norbornene pendant porphyrin polymer. The steady-state fluorescence of the polymer in the 420 to 460 nm region following excitation in the excitonically split Soret band at 405 nm (*cf.* Figure 2), although weak, is discernably broader than that of the monomer. Observing at 442 nm (with a 10 nm bandwidth) appears to capture components of both the unperturbed S_2 emission with a maximum near 425 nm and a red-shifted band of emission that is similar in location and shape to that previously observed in the flexible pendant porphyrin polymer with the saturated hydrocarbon backbone.[20] We tentatively assign this latter weak component to porphyrin $S_2 \cdot\cdot S_0$ excimer emission, which is expected to be red-shifted relative to the unperturbed S_2 fluorescence and has been seen previously in the delayed S_2 emission of ZnTPP resulting from triplet-triplet annihilation in degassed fluid solution.[23] In the latter report the intensity of the delayed upconverted S_2 fluorescence resulting from the intermolecular $2\ T_1 \rightarrow S_2 + S_0$ process is seen to be reduced by self-quenching of the S_2 state by its companion S_0 product molecule. In this TTA process, the product pair cannot separate to a significant extent during the short ps lifetime of the excited species and the emission is red-shifted and significantly diminished in its intensity. We suggest that a similar process is occurring in a small fraction of the metalloporphyrin interactions in the Soret-excited norbornene polymer, and that the lifetime of the resulting excimeric species in the polymer is revealed in the form of the initial 6.3 ps decay component of the polymer's S_1 temporal fluorescence profile.

Assignment of this decay component to vibrational relaxation of the vibrationally excited S_1 state formed initially after $S_2 - S_1$ internal conversion can be ruled out because a similar relaxation process is not seen in the Soret-excited monomer. We can now also be more definitive regarding assignments of the photophysical processes occurring in the previously reported flexible porphyrin polymer,[20] which exhibits only a red-shifted emission with a maximum at 450 nm when it undergoes $2\ T_1 \rightarrow S_2 + S_0$ triplet-triplet annihilation. We now assign this with some confidence to upconverted emission from an excimeric $S_2 \cdot\cdot S_0$ product pair.

The triplet state dynamics of the porphyrin-appended norbornene polymer were measured by transient absorption techniques with 100 nanosecond temporal resolution; the results are shown in Figure 6. These data are unremarkable, except that the quantum yield of triplets is a factor of about four smaller in the porphyrin-appended norbornene monomer than in the ZnTPP reference and the yield of triplet in the polymer is so small as to be unmeasurable by this method. The triplet lifetime of the porphyrin-pendant norbornene monomer in dilute degassed toluene solution is 223 μs. The polymer triplet is barely observable at any concentration and excitation power but its lifetime is of the order of 1 microsecond duration, as shown in the inset of Figure 6 right.

A summary of the important photophysical processes of the one-photon excited pendant porphyrin norbornene polymer is given in Figure 7. The differences between the relative rates of the excited state radiative and radiationless decay routes of the E and Z isomers are represented graphically.

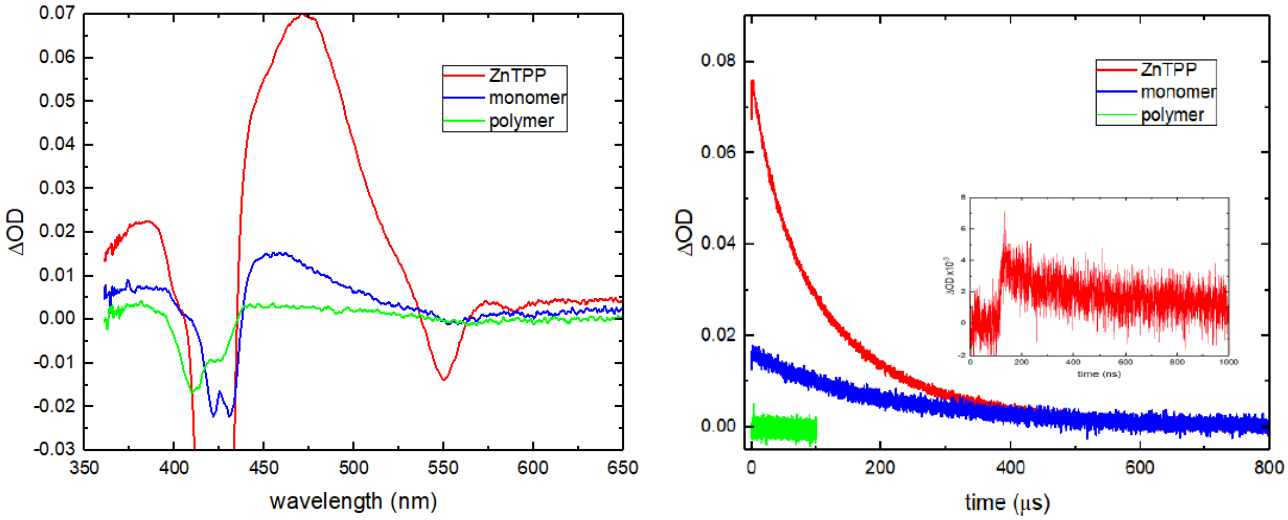


Figure 6: Left. Triplet transient absorption spectra of the norbornene monomer, its polymer and the ZnTPP reference excited at 532 nm in degassed toluene at a time delay of 200 ns. Right. Temporal triplet transient decay profiles measured at the transient maxima; 471 nm for ZnTPP and 455 nm for the monomer and polymer. The insert shows the first microsecond of the polymer triplet decay.

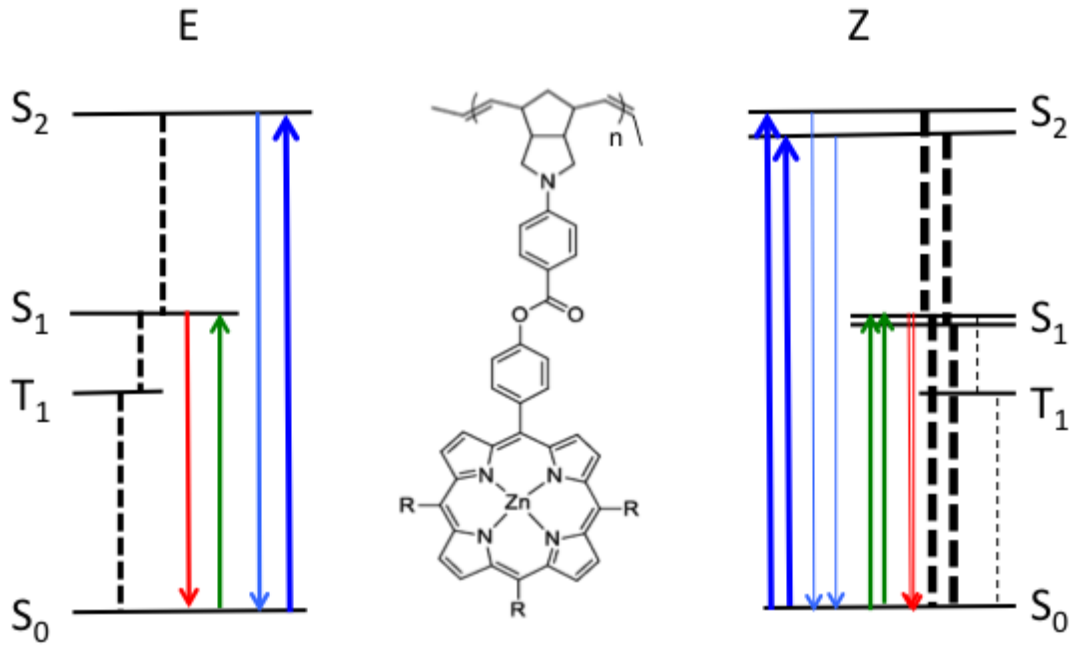


Figure 7: A Jablonski diagram representing the electronic energy levels and relaxation processes in the E and Z isomers of the norbornene polymer. Radiative processes are solid lines; radiationless processes are dashed. The line widths represent their relative importance.

The spectrum of the upconverted emission from the norbornene polymer, excited in the Q bands at 561 nm in degassed toluene, and its intensity as a function of incident power are shown in Figure 8. Three aspects of these data are of particular note. First, the spectrum of the upconverted emission of the norbornene polymer is of readily measurable intensity and is clearly that of the unperturbed porphyrin S_2 state (*cf*. Figures 8 and 2 in which the polymer Soret emissions are of similar shape and wavelength). This is to be contrasted with the upconverted emission of the flexible pendant porphyrin polymer previously examined[20] in which rotation of the pendants around the polymer backbone is possible. In the latter case the upconverted S_2 emission spectrum is red-shifted by about 20 nm and its intensity exhibits a near-linear absorbed power dependence. We conclude that the upconverted S_2 emission in the present rigid pendant porphyrin polymer originates with a subset of porphyrin pendants located in a relatively unperturbed E isomer environment. In contrast, the polymer with the flexible backbone exhibits excimeric upconverted emission following

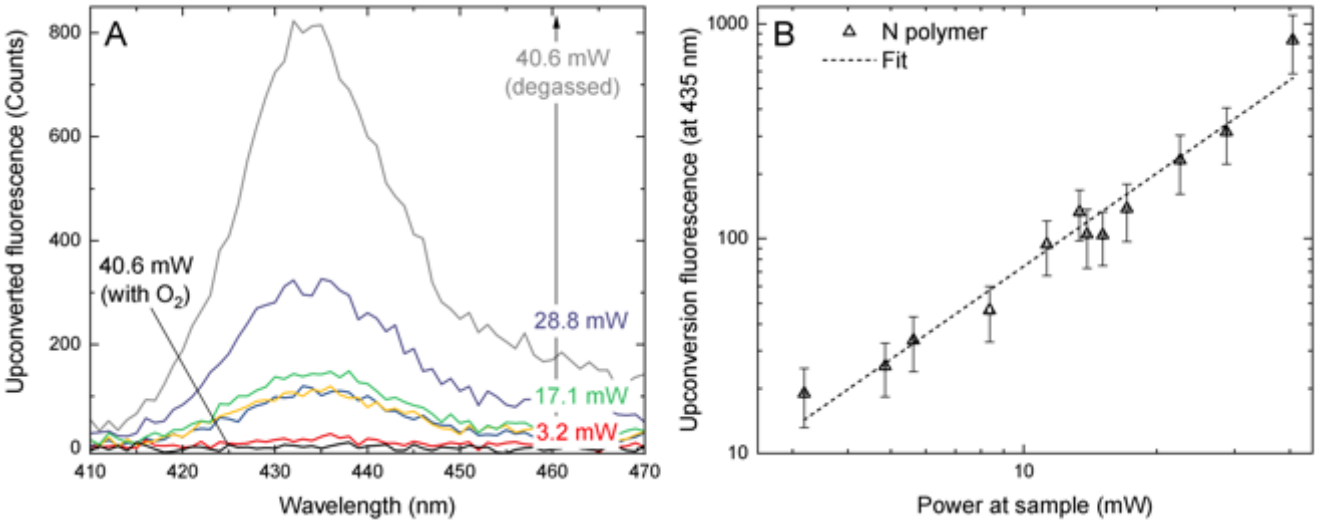


Figure 8: Left. Spectrum of upconverted emission as a function of incident power obtained by excitation of the norbornene polymer at 561 nm in degassed toluene at room temperature; absorbance = 0.25 for 0.003% (w/v). Note that the correction for self-absorption has not been made with these spectra, so the true maximum will be closer to 430 nm. Right. Power dependence of the upconverted emission; the slope is 1.44 $\pm$ 0.09. Vertical scales are in counts per second.

annihilation of the pair of excitons. Clearly the dynamic behaviours of the two polymers are different when their S_2 states are produced by biexcitonic upconversion compared with direct intramolecular one-photon excitation.

Second, the slope of the power dependence curve for the porphyrin-appended norbornene polymer, Figure 8, is 1.44 ± 0.09, closer to the expected value of 2 when biexcitonic annihilation is occurring at low powers (*cf*. 1.2 ± 0.2 for the previous polymer[20] which has a flexible backbone permitting dissociation of its S_1 excimer). The unusual near-linear intensity *vs.* power dependence of the S_2 emission produced by biexcitonic annihilation in the flexible polymer can now be ascribed to self-quenching of the excited product species via this excimer. The excimeric S_2 self-quenching process produces a pendant porphyrin excimer in its S_1 state that, by virtue of its longer lifetime, can escape the excimeric structure by rotation to form a non-interacting S_1 state that then proceeds to regenerate a triplet state of the porphyrin. Thus, for a large fraction of the annihilation events in the flexible pendant polymer, only one triplet state is consumed in the overall process, and this results in a near linear yield *vs.* absorbed power curve for the upconversion process even at low excitation powers. Escape from the S_1 excimeric conformation by rotation of the porphyrin pendant is not available in the norbornene polymer. This forced static interaction results in direct relaxation to the ground state, no recycled triplets are produced via an excimeric route, and so its upconverted S_2 fluorescence yield *vs.* power curve approaches the expected quadratic dependence more closely in the low power region.

Third, it could easily be assumed that the biexcitonic annihilation events that result in S_2 unperturbed or excimeric emission in these polymers involve only triplet-triplet interactions. We do

know that triplets are involved because the upconverted emission is completely quenched when the samples are aerated. Oxygen quenching of singlet excited metalloporphyrin species can be diffusion limited but cannot be kinetically competitive if rapidly decaying excited species such as those parameterized in Table 2 are involved. However, although upconverted emission is readily observed in these systems, the very small yield of triplet states revealed in the triplet transient absorption experiments for the norbornene polymer appears to bring into question the possible assignment of the upconversion process to interchain TTA. Furthermore, the rigidity of the norbornene polymer does potentially lend itself to rapid exciton migration, so the possibility of intrachain annihilation processes must be considered.

To this end the viability of upconversion via a sequential two-photon absorption process has been assessed using steady state kinetics and the data of Tables 1 and 2. The model used incorporates the following features. First the steady state concentration of polymer triplets developed at the maximum cw laser Q band excitation rate is calculated. Although the triplet lifetime is unusually short, its concentration is sufficient under the intense cw laser excitation of the upconversion experiments to absorb a second photon and establish a significant concentration of biexcitonic singlet-triplet species. Calculations using experimental structural data for the polymer then show that singlet excitons absorbed independently in sequence by the low concentration of polymer triplets can undergo rapid and extensive migration by a long-range FRET mechanism within the rigid polymer structure (*vide infra*). If a migrating singlet exciton in the doubly-excited species encounters the porphyrin pendant triplet from the first photon absorption that is trapped largely in an E region of the structure, then STA should occur efficiently. The only electron spin-allowed electronically excited product of STA is an upper excited triplet (e.g. T_2), which should relax rapidly to

T_1. Assuming that the lifetime and photophysical processes, including decay by intersystem crossing to T_1, of the singlet exciton in the doubly excited polymer molecule can reasonably be represented by those observed in the mono-excited species, the rate of S_2 upconverted emission by TTA can then be calculated. Further estimates of the photon collection and detection efficiencies of the spectrofluorometer then show that the observed maximum upconverted S_2 emission count rate is reasonable. The details are provided in the Supporting Information. The spectra and kinetics of S_2 fluorescence produced by intermolecular TTA of zinc porphyrin triplets in solution have been described previously in great detail.[17,20,23]

The conclusions from this analysis are as follows. The model is viable provided: (i) intrachain singlet exciton migration competes with the lifetime of the unperturbed S_1 singlet species, and (ii) the ratio of the rate constants for the migration/annihilation by the two routes, k_{STA}/k_{TTA} is reasonably approximated by the inverse ratio of the respective lifetimes of the singlet and triplet excitons in the mono-excited polymer. If these conditions are met, the model predicts the correct order-of-magnitude of the observed upconverted fluorescence count rates.

Ultrafast singlet exciton migration in multi-porphyrin arrays has been clearly demonstrated previously in a variety of structures, with migration distances of many tens of nm in times as fast as tens of fs reported in rigid multiporphyrin and similar chromophore arrays.[6-8,11-16,24] In the zinc porphyrin-pendant norbornene polymer a wide variety of interchromophore distances and orientations are expected, but the observation of clear excitonic splitting of the Soret band, the estimate of E:Z = 2.14:1 for the rigid backbone isomeric structures and the increased relaxation rates of all of the monoexcitonic excited polymer species clearly suggest that the singlet exciton migration rate in the biexcitonic polymer will be at least as rapid as its monoexcitonic S_1 decay rate.

The singlet exciton migration rate in the polymer can be estimated assuming energy transfer steps occur by a Förster resonance energy transfer mechanism[25] where the rate (k_{ET}) is given by:

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

R is the interchromophore separation in the polymer and τ_D is the donor singlet lifetime. R_0, the critical transfer distance, can be obtained from the photophysical and spectroscopic properties of the energy donor and acceptor and is given by:

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

Here Φ_0 is the fluorescence quantum yield of the donor in the absence of acceptor, n the solvent refractive index, J the spectral overlap integral (in units of $M^{-1}cm^{-1}nm^4$) while κ^2 is the orientation factor, the value of which depends on the relative orientation of the interacting chromophore transition dipoles. R_o was determined from the porphyrin monomer spectroscopic and photophysical properties with κ^2 calculated from the optimized geometry of nearest porphyrins in the E isomer segments of the polymer (see Supplementary Information for full calculation details). An R_0 value of 22.5 Ångstrom was determined for porphyrin to porphyrin energy transfer in the E isomer. The separation (R) between porphyrins in the polymer was estimated from the optimized geometry of a segment of the polymer chain (see Supplementary Information). While there is some degree of rotational freedom available for the pendant side chains, a value for R of 14.6 Ångstrom was determined for an optimized arrangement of nearest neighbor chromophores to provide a value for k_{ET} of 6.2 x 10^9 sec^{-1} corresponding to an energy transfer efficiency of 93%. For the case of the Z isomer, interchromophore separations will be substantially smaller and thus k_{ET} will be larger. These

calculations confirm that intrachain singlet exciton migration between porphyrins is a highly efficient process in the norbornene polymer.

Conclusions:

The spectroscopic and photophysical properties of the zinc porphyrin-pendant norbornene polymer with a rigid backbone synthesized for this study have been compared with those of similar non-rigid pendant-porphyrin polymers to provide information relevant to understanding the dynamics of photon-initiated processes in many multi-chromophoric systems, including photosynthesis.[16] Unlike its flexible polymer counterpart, the rigid norbornene polymer exhibits clear exciton splitting of its Soret band, much more rapid relaxation rates of its one-photon excited states, and a very small yield of unusually short-lived triplet states. Unlike the flexible pendant polymer, which exhibits excimeric S_2 fluorescence as a result of chromophore rotation during the excited state lifetime, anti-Kasha emission from the norbornene polymer originates primarily from the unperturbed porphyrin chromophores in the E region. The rigid polymer's faster excited state decay rates and considerably lower triplet yield are attributed to greatly increased rates of internal conversion within the singlet manifold due to chromophore interactions that are semi-static, and stronger in the Z isomeric regions. Despite the low yield and short lifetime of the triplet state, oxygen-quenched upconverted fluorescence following cw excitation in the polymer Q bands is observed. Consistent with its rigid structure, this biexcitonic process is assigned to ultrafast singlet exciton migration and triplet-triplet annihilation (competing with singlet-triplet annihilation) following absorption of a second photon by the small steady-state concentration of polymer triplets.

A substantial variety of metalloporphyrin-containing multimers and polymers have now been synthesized and their photophysical properties assessed.[5-16] In this study we have identified polymer backbone flexibility as a key structural element in determining the suitability of pendant-porphyrin polymers for use in optoelectronic and other devices. While the more structurally rigid norbornene polymers appear to provide excellent intrachain singlet exciton mobility, the unforeseen very low yield of porphyrin triplet states essentially rules out their use as dual monoexcitonic/biexcitonic photon harvesters.[26]

Associated Content:

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b09321.

Detailed synthesis and characterization procedures for the polymer. Spectra showing direct comparisons of the rigid norbornene and the flexible polymethylene pendant-porphyrin polymers. Spectra documenting the absorbances needed for quantum yield measurements. The model and calculations concerning the assignment of upconverted S_2 fluorescence to a sequential two-photon absorption and intrachain triplet-triplet annihilation process. The calculation of the energy transfer rate between adjacent pendant porphyrins in the polymer.

Author Information:

Corresponding Authors

*K. P. Ghiggino. E-mail: ghiggino@unimelb.edu.au.
*R. P. Steer. E-mail: ron.steer@usask.ca.

ORCID
Jonathan M. White: 0000-0002-0707-6257

Kenneth P. Ghiggino: 0000-0001-6621-4448
Ronald P. Steer: 0000-0003-2333-8218
Amy L. Stevens: 0000-0002-0998-1795

Notes:

The authors declare no competing financial interest.

Acknowledgements:

The authors thank the Natural Sciences and Engineering Research Council of Canada and the Australian Research Council Centre of Excellence in Exciton Science (CE170100026) for their continuing financial support. The Saskatchewan Structural Science Centre provided equipment and technical assistance. Thanks to George Belev. Professor Matthew Paige is thanked for his consultations and support. This work was made possible by support from the Australian Renewable Energy Agency which funds the project grants within the Australian Centre for Advanced Photovoltaics (ACAP). Responsibility for the views, information, or advice expressed herein is not accepted by the Australian Government.

References:

1. Tripathy, U.; Kowalska, D.; Liu, X.; Velate, S.; Steer, R. P. Photophysics of Soret-excited tetrapyrroles in solution. I. Metalloporphyrins: MgTPP, ZnTPP, CdTPP. *J. Phys. Chem. A* **2008**, *112*, 5824-5833.

2. Papkovsky, D. B.; O'Riordan, T. C. Emerging applications of phosphorescent metalloporphyrins. *J. Fluoresc.* **2005**, *15*, 569-584.

3. Stevens, A. L.; Joshi, N. K.; Paige, M. F.; Steer, R. P. Photophysics of zinc porphyrin aggregates in dilute water-ethanol solutions. *J. Phys. Chem. B* **2017**, *121*, 11180-11188.

4. Rodriguez, J.; Kirmaier, C.; Holten, D. Optical properties of metalloporphyrin excited states. *J. Amer. Chem. Soc.* **1989**, *111*, 6500-6506.

5. Yeow, E. K. L.; Ziolek, M.; Karolczak, J.; Shevyakov, S. V.; Asato, A. E.; Maciejewski, A.; Steer, R. P. Sequential S2- S2 and back S1 – S1 (cyclic) energy transfer in a novel azulene-zinc porphyrin dyad. *J. Phys. Chem. A*, **2004**, *108*, 10980-10988.

6. Cho, H. S.; Jeong, D. H.; Cho, S.; Kim, D.; Matsuzaki, Y.; Tanaka, K.; Tsuda, A.; Osuka, A. Photophysical properties of porphyrin tapes. *J. Am. Chem. Soc.* **2002**, *124*, 14642-14654.

7. Cho, H. S.; Song, N. W.; Kim, Y. H.; Jeoung, S. C.; Hahn, S.; Kim, D.; Kim, S. K.; Yoshida, N.; Osuka, A. Ultrafast energy relaxation dynamics of directly linked porphyrin arrays. *J. Phys. Chem. A* **2000**, *104*, 3287−3298.

8. Kim, D.; Osuka, A. Photophysical properties of directly linked linear porphyrin arrays. *J. Phys. Chem. A* **2003**, *107*, 8791−8816.

9. Lin, N.-T.; Satyanarayana, K.; Chen, C.-H.; Tsai, Y.-F.; Yu, S. S.; Chan, S. I.; Luh, T.-Y. Controlling the orientation of pendants in two-dimensional comb-like polymers by varying stiffness of polymeric backbones. *Macromolecules* **2014**, 47**,** 6166-6172.

10. Terazono, Y.; Kodis, G.; Chachisvilis, M.; Cherry, B. R.; Fournier, M.; Moore, A.; Moore, T. A.; Gust, D. Multiporphyrin Arrays with π-π Interchromophore Interactions. *J. Am. Chem. Soc.* **2015**, *137*, 245−258.

11. Fujitsuka, M.; Satyanarayana, K.; Luh, T.-Y.; Majima, T. Singlet-singlet and singlet-triplet annihilations in structure-regulated porphyrin polymers. *J. Photochem. Photobiol. A* **2016**, *331*, 56-59.

12. Fujitska, M.; Okada, A.; Tojo, S.; Takei, F.; Onitsuka, K.; Takahashi, S.; Majima, T. Rapid exciton migration and fluorescent energy transfer in helical polyisocyanides with regularly arranged porphyrin pendants. *J. Phys. Chem. B* **2004**, *108*, 11935-11941.

13. Gao, W.-Y.; Chrzanowski, M.; Ma, S. Metal-metalloporphyrin frameworks: a resurging class of functional materials. *Chem. Soc. Rev.* **2014**, *43*, 5841-5866.

14. Zhang, Q.; Zhang, C.; Cao, L.; Wang, Z.; An, B.; Lin, Z.; Huang, R.; Zhang, Z.; Wang, C.; Lin W. Förster energy transport in metal−organic frameworks Is beyond step-by-step hopping. *J. Am. Chem. Soc.* **2016**, *138*, 5308−5315.

15. Drain, C. M.; Varotto, A.; Radivojevic, I. Self-organized porphyrinic materials. *Chem. Rev.* **2009**, *109*, 1630-1658.

16. Moretti, L.; Kudisch, B.; Terazono, Y.; Moore, A. L.; Moore, T. A.; Gust, D.; Cerullo, G.; Scholes, G. D.; Maiuri, M. Ultrafast dynamics of nonrigid zinc-porphyrin arrays mimicking the photosynthetic "Special Pair". *J. Phys. Chem. Lett.* **2020**, *11*, 3443−3450.

17. Rautela, R.; Joshi, N. K.; Novakovic, S.; Wong, W. W. H.; White, J. M.; Ghiggino, K. P.; Paige, M. F.; Steer, R. P. Determinants of the efficiency of photon upconversion by triplet-triplet annihilation in the solid state: zinc porphyrin derivatives in PVA. *Phys. Chem. Chem. Phys.* **2017**, *19*, 23471-23482.

18. Sugunan, S.; Robotham, B.; Sloan, R. P.; Szmytkowski, J.; Ghiggino, K. P.; Paige, M. F.; Steer, R. P. Photophysics of untethered ZnTPP-fullerene complexes in solution. *J. Phys. Chem. A*, **2011**, *115*, 12217-12227.

19. Boutin, P. C.; Ghiggino, K. P.; Kelly, T. L.; Steer, R. P. Photon upconversion by triplet-triplet annihilation in $Ru(bpy)_3$- and DPA-functionalized polymers. *J. Phys. Chem. Lett.* **2013**, *4*, 4113-4118.

20. Stevens, A. L.; Novakovic, S.; White, J. M.; Wong, W. W. H.; Smith, T. A.; Ghiggino, K. P.; Paige, M. F.; Steer, R. P. Exciton dynamics of photoexcited pendant porphyrin polymers in solution and in thin films. *J. Phys. Chem. A* **2018**, *122*, 9605-9614.

21. Tilley, A. J.; Robotham, B. E.; Steer, R. P.; Ghiggino, K. P. Sensitized non-coherent photon upconversion by intramolecular triplet-triplet annihilation in a diphenylanthracene pendant polymer. *Chem. Phys. Lett.* **2015**, *618*, 198-202.

22. Englman, R.; Jortner, J. Energy gap law for radiationless transitions in large molecules. *J. Mol. Phys.* **1970**, *18*, 145-164.

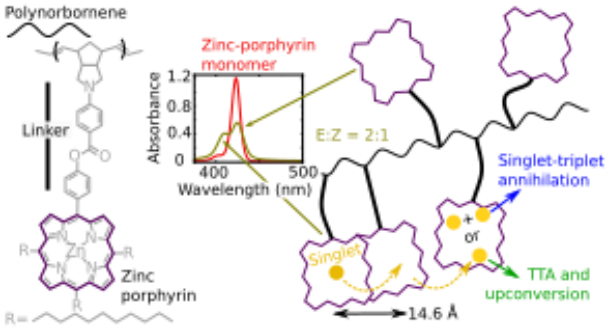
23. Ksenofontova, N. M.; Stel'makh, G. F.; Tsvirko, M. P. Dimeric nature of annihilation fluorescence from upper electronic states of metal porphyrins. *Dokl. Akad. Nauk SSSR* **1986**, *289*, 405-409.

24. Zhu, T.; Wan, Y.; Huang, L. Direct imaging of Frenkel exciton transport by ultrafast microscopy *Acc. Chem. Res.* **2017**, *50*, 1725−1733.

25. Förster, T. Zwischenmolekulare energiewanderung und fluoreszenze. *Ann. Phys*. **1948**, *2*, 55-57.

26. Steer, R. P. Prospects for efficient solar energy upconversion using metalloporphyrins as dual absorber-upconverters. *Dalton Trans.* **2018**, *47*, 8517-8525.

TOC Graphic


Polynorbornene
Linker
Zinc
porphyrin
Zinc-porphyrin
monomer
Absorbance
1.2
0.8
0.4
0
400
500
Wavelength (nm)
E:Z = 2:1
Singlet
14.6 Å
+
or
Singlet-triplet
annihilation
TTA and
upconversion