## Supporting Information

## Quantum Amplified Isomerization in Polymers based on Triplet Chain Reactions

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Instrumentation. NMR measurements were performed at 300 MHz for ${ }^{1} \mathrm{H}$ and 75 MHz for ${ }^{13} \mathrm{C}$. HPLC analysis was carried out using reverse phase methods with linear solvent gradients from $90 \%$ Solvent A/10\% Solvent B to $100 \%$ Solvent B over 10 min. Method 1: Hypersil BDS-C18 column ( $5 \mu \mathrm{~m} \times 3 \mathrm{~mm} \times 50 \mathrm{~mm}$ ); Solvent A was 0.1 M aq. ammonium acetate, Solvent B was 1:1 acetonitrile:isopropanol; flow rate was $2.0 \mathrm{~mL} / \mathrm{min}$. Method 2: YMC ODS-AQ 120A column ( $5 \mu \mathrm{~m} \times 3 \mathrm{~mm} \times 100 \mathrm{~mm}$ ); Solvent A was 0.1 M aq. ammonium acetate, Solvent B was acetonitrile; flow rate was $1.0 \mathrm{~mL} / \mathrm{min}$. GC/MS analysis was carried out using a Restek RTX-5MS column ( $30 \mathrm{~m} \times 0.25 \mathrm{~mm} \times 0.25 \mu \mathrm{~m}$ ) using a temperatures ramp starting at 50 ${ }^{\circ} \mathrm{C}$ (hold 2 min ) and increasing at $15^{\circ} \mathrm{C} / \mathrm{min}$ to $320^{\circ} \mathrm{C}$ (hold 3 min ). Differential Scanning Calorimetry (DSC) was performed under nitrogen at a heating rate of $10^{\circ} \mathrm{C} / \mathrm{min}$. The $T_{\mathrm{g}}$ was determined as the midpoint of the transition on the second heating scan (i.e., after heating above $T_{\mathrm{g}}$ during the first scan and quenching). Size-exclusion chromatography (SEC) with viscometry detection was carried out in uninhibited THF using three Polymer Laboratories Plgel mixed-C columns. Absolute molecular weights were calculated from the viscosity data and a universal calibration curve constructed from narrow-molecular weight distribution polystyrene standards between $580(\log \mathrm{M}=2.76)$ and 2,300,000 $(\log \mathrm{M}=6.36)$. Distributions and molecular weight averages were corrected for axial dispersion assuming a Gaussian band-broadening function.

Materials. Crude porcine liver esterase ( 24 units $/ \mathrm{mg}$ ) was obtained from Aldrich. Buffer was made from potassium phosphate $(0.1 \mathrm{M})$ and adjusted to pH 7.8 with $10 \% \mathrm{HCl}$. Most co-sensitizers were obtained through commerical sources or were gifts from Kodak Research Laboratories. DB2 and DB3 were synthesized as previously reported. ${ }^{\text {S1,S2 }}$

S1. Dopper, J. H.; Greijdanus, B.; Oudman, D.; Wynberg, H. Tetrahedron Lett. 1975, 4297.
S2. Koster, J. B.; Timmermans, G. J.; van Bekkum, H. Synthesis 1971, 139.










