Visible-Light-Mediated Diels-Alder Reactions Under Single-Chain Polymer Confinement: Investigating the Role of the Crosslinking Moiety on Catalyst Activity

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Supporting Information

I. Materials and Methods. All chemicals were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, or TCI America, and used as received unless otherwise indicated. NMR spectroscopic characterization was conducted on a Bruker Avance 500 or 400 MHz spectrometer using CDCl₃ unless otherwise indicated. Chemical shifts are reported in ppm, and referenced to residual CHCl₃. Internal standards were used for conversion and yields of small-molecule transformations. Catalyst incorporation ratios within the polymers were calculated with a combination of ¹H- and ¹⁹F-NMR spectroscopy using 1,3,5-trimethoxybenzene (TMB) and 1,4-dioodotetrafluorobenzene (DITFB) respectively, as internal standards (See Sect. III for details).

Polymer molecular weights and dispersities were measured using a TOSOH EcoSEC HLC-8320 GPC, coupled UV and RI detectors, controlled by an EcoSEC-WS program, and calibrated with poly(methyl methacrylate) standards. The column and guard column utilized were pre-packed from TOSOH in THF (TSK_{gel} GMH_{HR}-H; mixed bed column, 7.8 mm I.D. x 30 cm) and the column temperature was maintained at 24 °C. All samples were measured with a mobile phase consisting of THF (Sigma-Aldrich, HPLC grade, inhibitor free). The injection volume was 8 μ L and the flow rate was 1 mL min⁻¹. UV-visible absorption spectra were obtained on a PerkinElmer Lambda 365 UV-visible spectrophotometer using a semi-micro quartz cuvette (Fisherbrand). Polymer solutions for UV-Vis analysis were prepared in acetonitrile (Sigma-Aldrich, HPLC grade). Polymer emission data was obtained on a Shimazu RF-6000 Spectro Fluorophotometer. Acetonitrile was purchased from Fisher Scientific (ACS grade) and *trans*-anethole was purchased

from Sigma Aldrich (ACS grade) and used as received. Samples were measured at 0.1 mM with the excitation wavelength set at 450 nm.

¹H DOSY experiments were performed on a Bruker Avance NEO 400 MHz spectrometer equipped with a BBFO iprobe. Self -diffusion coefficients were measured using the pulsed field gradient stimulated echo (PGSTE) sequence with bipolar gradients. Gradient amplitude was incremented linearly from 0.96 G to 47.19 G in 16 steps. Echo attenuation due to molecular self diffusion is

given by the Stejskal- Tanner Equation $I_{(g)} = I_{(0)}e^{-\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)D}$ where $I_{(0)}$ is the echo intensity in the absence of any gradient, γ is the magnetogyric ratio (4257.6 Hz/G for ¹H), g is the gradient amplitude, δ is the duration of the gradient pulse, Δ is the time interval between the diffusion encoding and decoding gradients and D is the diffusion coefficient. PGSTE measurements were carried out at 298 K with a gradient pulse duration (δ) of 3.5 ms, diffusion encoding time, Δ of 100 ms and a relaxation delay of 4 seconds. Each data point was recorded with 16 scans. Diffusion data was processed using the T1/T2 analysis mode in Topspin using the peak at 3.615 ppm.

Photoredox experiments were conducted using Kessil LED photoredox lights (440 nm; PR160L) using either 20 mL scintillation vials or 1 dram vials pending reaction scale. All reactions were irradiated using two Kessil PR 160L LEDs with 440 nm irradiation (100% light intensity) at a vial-to-lamp distance of 6.5 cm have a total irradiance of 64.7 mW/cm² and a cooling fan positioned either adjacent to the reactions (household desk fan) or above the reactions (Kessil rig).



Experimental setup for photoredox reactions (left) prior to any samples being added and lights turned on and (right) during reaction.



The emission spectra for the Kessil PR-series LEDs is above. While we screened the reaction using 427 nm, 440 nm, and 456 nm (see Table S6), the 440 nm LED was used as it provided for faster product formation. Although we recognize that photochemical action plots show that optimal wavelength choices for photoinitiated reactions often do not correlate with the absorption properties of the photosensitizer,² and investigating this for our SCNPs might enable heightened yields, the choice to move forward with 440 nm LEDs was motivated by the decreased probability of TPT photobleaching by limiting the population of excited state TPT molecules.

Specifications	
Power consumption	427 nm & 440 nm (max 45 W), 456 nm (max
	50 W)
Input voltage	100 – 240 VAC
Operating temperature	0-40 °C
Beam angle	56 °
Wavelength options	427 nm, 440 nm, 456 nm
Angle intensity of PR160 series	352 mW/cm ² (measured from 1 cm distance)
Dimensions	11.4 cm x 6.3 cm (height x diameter)

Table S1: Kessil lamp operating specifications

More information and specifics can be found at: <u>http://www.kessil.com/science/resources.php</u>.



Figure S1: Normalized UV-vis spectral overlay of TPT monomer (blue) & SCNP (orange).

The UV-vis spectra of the TPT monomer and SCNP (Figure S1) indicate shared absorption bands and the retention of electronic features upon polymer incorporation. These characteristics informed decisions for excitation wavelengths to examine for catalysis.

II. Small Molecule Synthesis. The synthesis of the styrylnaphthalene, styrylphenanthrene, and TPT monomers was accomplished following our prior reports.¹

Synthesis of Styryl Pyrene Monomer¹



Scheme S1: Synthesis of styryl pyrene monomer (3).

Compound 1 (824.7 mg; 2.5742 mmol) was dissolved in a vial with DCM (2.574 mL) to yield a yellow paste. Triethylamine (0.395 mL; 2.8316 mmol; 1.1 eq.) was added dropwise to the vial, resulting in an orange suspension that was cooled to 0 °C. Compound 2 (395 μ L; 2.8316 mmol; 1.1 eq.) was then added dropwise to the reaction mixture, ejecting a turbid white gas and yielding a yellow solution. The reaction mixture was held at room temperature while monitoring using TLC (7:3 hexanes:ethyl acetate) until completion. Upon completion, the reaction mixture was diluted with EtOAc (50 mL) and extracted with H₂O (50 mL), KOH (1M; 50 mL), and brine (50 mL). The organic layer was dried over anhydrous Na₂SO₄ before concentrating under vacuum to yield **3** as a yellow powder (966 g; 2.49 mmol; 97%).

¹**H-NMR** (400 MHz, CDCl₃) δ 8.49 (d, 1H, J = 9.30 Hz), 8.31 (d, 1H, J = 8.10 Hz), 8.19 (m, 5H), 8.07 (s, 2H), 8.03 (t, 1H, J = 7.71 Hz), 7.72 (d, 2H, J = 8.53 Hz), 7.35 (d, 1H, J = 16.05 Hz), 7.24 (d, 2H, J = 8.57 Hz), 6.43 (s, 1H), 5.82 (s, 1H), 2.14 (s, 3H).

¹³**C-NMR** (100 MHz, CDCl₃) δ 207.0, 165.9, 150.5, 135.9, 135.5, 131.8, 131.5, 131.0, 130.9, 130.8, 128.4, 126.0, 125.9, 123.3, 125.2, 125.1, 123.7, 123.0, 122.0, 53.5, 30.9, 18.5.



Figure S2: ¹H-NMR spectrum of 3 (CDCl₃, 400 MHz).



Figure S3: ¹³C-NMR spectrum of 3 (CDCl₃, 100 MHz).

Synthesis of Styryl Methyl Monomer ^{1,3}



Scheme S2: Synthesis of SMeth-OH precursor (5)

Ethyl triphenylphosphonium bromide (5.57 g; 15 mmol; 1.5 eq.) was dissolved in THF (20 mL). Then, potassium *tert*-butoxide (2.81 g; 25 mmol; 2.5 eq.) was slowly added. The reaction mixture was held for 10 minutes at room temperature and a solution of 4 (1.075 mL; 10 mmol; 1 eq.) in THF (10 mL) was added dropwise. The resulting suspension was held at room temperature for four hours and monitored for completion using TLC (7:3 hexanes:ethyl acetate). Upon completion, the reaction mixture was quenched with NH₄Cl (saturated, 50 mL) and concentrated under vacuum to remove THF. The remaining solution was extracted with CH_2Cl_2 (500 mL) and the organic layer was washed with brine (20 mL) before drying over anhydrous MgSO₄. The solution was then concentrated and purified with column chromatography (15:1 – 4:1 hexanes:ethyl acetate). Both *trans* and *cis* products were obtained in the ratio 4:1 (*trans:cis*); the labeled peaks in the ¹H NMR spectrum correspond to the major (*trans*) product signals.

¹**H-NMR** (400 MHz, CDCl₃) δ 7.21 (m, 2H), 6.81 (m, 2H), 6.37 (dd, 1H, *J* = 11.69, 1.84 Hz), 6.09 (m, 1H), 5.70 (m, 1H), 1.87 (m, 3H).

¹³**C-NMR** (100 MHz, CDCl₃) δ 14.6, 115.0, 123.6, 125.2, 127.1, 129.2, 130.2, 130.5, 153.9.



Figure S4: ¹H-NMR spectrum of 5 (CDCl₃, 400 MHz).



Figure S5: ¹³C-NMR spectrum of 5 (CDCl₃, 100 MHz).



Scheme S3: Synthesis of SMeth-co-MMA.

Compound **5** (936 mg; 6.98 mmol; 1 eq.) was dissolved in a vial with CH_2Cl_2 (4 mL) to yield a cloudy solution. Triethylamine (1.07 mL; 7.68 mmol; 1.1 eq.) was added dropwise to the vial, resulting in a clear solution that was cooled to 0 °C. Compound **2** was then added dropwise to the reaction mixture, ejecting a turbid white gas. The reaction mixture was held at room temperature while monitoring via TLC (0.5:9.5 hexanes:ethyl acetate) until completion. Upon completion, the reaction mixture was diluted with EtOAc (50 mL) and washed with H₂O (50 mL), KOH (1M; 30 mL), and brine (50 mL). The organic layer was dried over anhydrous Na₂SO₄ before concentrating under vacuum to yield a colorless liquid (700 mg; 3.46 mmol; 50%). Both isomers of **6** are retained; the peaks of major product (*trans*) are highlighted in the spectra.

¹**H-NMR** (400 MHz, CDCl₃) δ 7.34 (d, 2H, J = 8.55 Hz), 7.08 (d, 2H, J = 8.55 Hz), 6.43 (d, 1H, J = 11.95 Hz), 6.35 (s, 1H), 5.81 (m, 2H), 2.08 (s, 3H), 1.89 (dd, 3H, J = 7.21, 1.71Hz).

¹³**C-NMR** (100 MHz, CDCl₃) δ 165.9, 149.3, 135.9, 135.3, 129.8, 129.0, 127.2, 127.0, 126.7, 121.6, 121.2, 18.4, 14.6.



Figure S6: ¹H-NMR spectrum of 6 (CDCl₃, 400 MHz).



Figure S7: ¹³C-NMR spectrum of 6 (CDCl₃, 100 MHz).

III. Synthesis of Polymers & Folding into Single-Chain Polymer Nanoparticles (SCNPs)



Scheme S4: Synthetic route for copolymers (R = styryl methyl, styryl naphthalene, styryl phenanthrene, or styryl pyrene).

Copolymers: TPT monomer (1.6410 g; 3.563 mmol), styryl monomer (0.903 mmol), CTA (118 mg; 0.292 mmol), AIBN (9.6 mg; 0.0584 mmol) and MMA (8.165 mL; 87.38 mmol) were dissolved in DMF (12.74 mL) in the dark. The reaction mixture was sparged with N_2 for 20 minutes and the reaction vessel was wrapped in tin foil. The solution was stirred at 80 °C for 24 hours under N_2 . The reaction was then cooled to room temperature and precipitated into MeOH (500 mL). The polymer was filtered off and washed with MeOH (2 x 160 mL). The polymer was dried under vacuum for 45 hours and crushed to yield a powder.

SCNPs: Copolymers were individually dissolved in MeCN in a foil wrapped vial to yield a solution with a concentration of 2 mg/mL. The polymer was allowed to completely dissolve and then the foil was removed. The vial was placed about in front of a white CFL light (light-to-vial distance ~ 6 cm) with a cooling fan above it. The vial was irradiated without stirring for at least 1 hour and then immediately wrapped in foil. Aliquots were pulled for analysis using UV-Vis spectroscopy and/or gel-permeation chromatography to analyze compaction/changes in molecular weight. The solution was then concentrated to a solid before being reconstituted to the appropriate reaction concentration.

Percent incorporations were calculated with a combination of ¹H- and ¹⁹F-NMR spectroscopy using 1,3,5-trimethoxybenzene (TMB) and 1,4-dioodotetrafluorobenzene (DITFB), respectively, as internal standards. The mass of MMA was calculated using the methyl peak ($\delta = 3.52$ ppm) and comparing it to the methoxy peak in TMB ($\delta = 3.69$ ppm) in the ¹H-NMR spectrum. The mass of TPT was calculated using the tetrafluoroborate peak in the ¹⁹F-NMR spectrum ($\delta = -151.37$ ppm) and compared to the Ar—F signals of the internal standard ($\delta = -118.10$ ppm). Masses were calculated using equation (1), mass percentages from equation (2), and percent incorporations using equations (3 - 5). Samples were prepared in triplicate and the average incorporation values were used for polymer catalyst loading.

$$Mass_{x} = \frac{Integral_{x}}{Integral_{calibrant}} * \frac{Protons_{Calirbant}}{Protons_{x}} * \frac{M.M._{Cal}}{M.M._{1}} \frac{Molar mass_{x}}{Molar mass_{Calibrant}} * Mass_{Calibrant}$$
(Eq. 1)
$$Mass \%_{1} = \frac{Mass_{1}}{Mass_{Poly}} * 100\%$$
(Eq. 2)
$$Assuming 100g: \frac{100g * Mass\%_{1}}{M.M._{1}} = Moles_{1}$$
(Eq. 3)

$$Total \ moles = \sum_{i=1}^{n} Moles_i$$
(Eq. 4)

% incorportation =
$$\frac{Moles_1}{Total moles} * 100\%$$
 (Eq. 5)



Figure S8: ¹H-NMR spectrum of TPT-co-SNap_{NL}-co-MMA with TMB (CDCl₃, 400 MHz).



Figure S9: ¹⁹F-NMR spectrum of TPT-co-SNap_{NL}-co-MMA with DITFB (CDCl₃, 376 MHz).



Figure S10: ¹H-NMR spectrum of TPT-co-SP_{NL}-co-MMA with TMB (CDCl₃, 400 MHz).



Figure S11: ¹⁹F-NMR spectrum of TPT-co-SP_{NL}-co-MMA with DITFB (CDCl₃, 376 MHz).



Figure S12: ¹H-NMR spectrum of TPT-co-SPhen_{NL}-co-MMA with TMB (CDCl₃, 400 MHz)



Figure S13: ¹⁹F-NMR spectrum of TPT-co-SPhen_{NL}-co-MMA with DITFB (CDCl₃, 376 MHz)



Figure S14: ¹H-NMR spectrum of TPT-co-SMeth_{NL}-co-MMA with TMB (CDCl₃, 400 MHz).



Figure S15: ¹⁹F-NMR spectrum of TPT-co-SMeth_{NL}-co-MMA with DITFB (CDCl₃, 376 MHz).

Crosslinking studies of TPT-co-StyAr-co-MMA polymers

The StyAr pendant groups were crosslinked by irradiation of the polymers dissolved in acetonitrile (2 mg/mL) with a white compact fluorescent lamp (CFL) for one hour. Each crosslinking was monitored using UV/Vis spectroscopy in which the StyAr absorbances decrease in intensity over time. While UV/Vis spectroscopy indicates successful crosslinking of the StyAr groups, gelpermeation chromatography was used to confirm successful controlled folding of the polymer into a confined SCNP structure devoid of intermolecular crosslinks.



Figure S16: UV-vis spectral overlay of TPT-co-SNap_{NL}-co-MMA polymer before (blue) and after (orange) crosslinking (MeCN).



Figure S17: GPC traces for TPT-co-SPhen_{NL}-co-MMA and TPT-SPhen_{NL}-SCNP (THF).



Figure S18: GPC traces for TPT-co-SP_{NL}-co-MMA and TPT-SP_{NL}-SCNP (THF).



Figure S19: GPC traces for TPT-co-SMeth_{NL}-co-MMA and TPT-SMeth_{NL}-SCNP (THF).



Figure S20: GPC traces for TPT-co-SNap_{NL}-co-MMA and TPT-SNap_{NL}-SCNP (THF).

Changes in compaction from linear polymers to SCNPs are commonly measured through the use of DOSY experiments.^{4, 5, 6} DOSY was run on the optimal polymer, TPT-co-SNap_{NL}-co-MMA, before and after crosslinking (Table S3 and S4).

Table S3. DOSY data for TPT-co-SNap-co-MMA before crosslinking.

Results Comp. 1 = 1.016e+00I[0] Diff Con. = 2.480e-10 m2/sGamma = 4.258e + 03 Hz/GLittle Delta = 3.500m = Big Delta 99.900m RSS = 9.933e-04 SD = 8.137e-03 Gradient Point Expt Calc Difference 9.630e-01 1.000e+001.436e-02 1 1.014e+002 4.045e+00 9.781e-01 9.813e-01 3.165e-03 3 7.126e+00 9.212e-01 9.114e-01 -9.761e-03 1.021e+018.230e-01 8.127e-01 -1.032e-02 4 5 1.329e+01 7.030e-01 6.957e-01 -7.310e-03 6 1.637e+01 5.744e-01 5.717e-01 -2.715e-03 7 1.945e+01 4.469e-01 4.511e-01 4.207e-03 8 2.253e+01 3.339e-01 3.417e-01 7.821e-03 7.913e-03 9 2.562e+01 2.406e-01 2.485e-01 10 2.870e+01 1.719e-01 1.735e-01 1.621e-03 3.178e+01 1.143e-01 1.163e-01 2.017e-03 11 12 3.486e+01 7.776e-02 7.483e-02 -2.929e-03 13 3.794e+01 4.623e-02 -5.257e-03 5.149e-02 4.410e+01 2.965e-02 1.561e-02 -1.404e-02 14 15 4.719e+01 2.007e-02 8.535e-03 -1.154e-02 Table S4. DOSY NMR spectral data for TPT-SNap_{NL}-SCNP.

Results Comp. 1 I[0] = 1.004e+00Diff Con. = 2.753e-10 m2/sGamma = 4.258e + 03 Hz/G3.500m Little Delta = Big Delta = 99.900m RSS = 2.458e-03SD = 1.431e-02Point Gradient Calc Difference Expt 1 9.630e-01 1.000e+001.002e+00 1.666e-03 2 4.045e+009.730e-01 9.655e-01 -7.486e-03 3 7.126e+00 8.955e-01 8.895e-01 -6.034e-03 4 1.021e+01 7.865e-01 7.832e-01 -3.322e-03 5 1.329e+01 6.591e-01 9.894e-03 6.492e-01 6 1.637e+01 1.033e-02 5.197e-01 5.301e-01 7 1.945e+01 4.008e-01 4.075e-01 6.691e-03 8 2.253e+01 2.919e-01 2.994e-01 7.457e-03 9 2.870e+01 1.493e-01 1.411e-01 -8.187e-03 10 3.486e+01 7.804e-02 5.547e-02 -2.257e-02 3.250e-02 -2.292e-02 11 3.794e+01 5.542e-02 12 4.410e+01 4.048e-02 9.742e-03 -3.074e-02

Our results show a higher diffusion coefficient for the SCNP compared to the linear polymer, confirming the observed change in size observed through GPC.

IV: Calculations for TPT-co-SNap_{NL}-co-MMA Polymer

Sample calculation of TPT percent incoporation in a SCNP photocatalyst

¹⁹F-NMR spectroscopy was used to elucidate the TPT content in each polymer. Resonances corresponding to the TPT counteranion and DITFB, along with their relative integrations, were used to calculate the mass % and moles of TPT in our synthesized polymers. The ¹⁹F-NMR spectrum below is provided as a representative of TPT-co-SNap_{NL}-co-MMA, wherein the mass of polymer and DITFB are 11.9 mg and 13.1 mg, respectively.



Assuming 100g of polymer:

 $\frac{100 \ g * 4.86\%}{460.25g * mol^{-1}} \equiv 10.6 \ mmol \ (eq. \ 10)$

Moles of MMA are calculated through the same process using TMB as an internal standard, while the moles of SNap incorporated are calculated from the difference in mass between the polymer sample and calculated TPT and MMA masses.

The % incorporation of TPT is determined by dividing the calculated moles of TPT (10.6 mmol) by the total moles of monomers in the polymer (808 mmol).

% Incorporation_{TPT} = $\frac{10.6 \text{ mmol}}{808 \text{ mmol}} * 100\% = 1.31\%$ (eq. 11)

Sample Calculation of 3.3 mol % of SCNP photocatalyst

The moles of TPT needed for the reaction are calculated based on the desired loading of photocatalyst (3.3 mol %) using 0.1 mmol of *trans*-anethole:

 $0.1 mmol anethole * \frac{3.3 mmol TPT}{100 mmol anethole} = 0.0033 mmol TPT (eq. 12)$

The moles are then multipled by the molar mass of the TPT monomer (460.25 g mol⁻¹) to determine the mass of TPT necessary prior to use in photoredox experiments.

$$0.0033 \ mmol \ TPT * \frac{460.25 \ mg \ TPT}{1 \ mmol \ TPT} \approx 1.5 \ mg \ TPT \ (eq. \ 13)$$

The calculated mass of TPT monomer needed (1.5 mg) is then divided by the average weight % of TPT (5.8 %; see Table S3). This determines the mass of polymer needed to achieve 3.3 mol % loading of photocatalyst with respect to the dienophile.

$$1.5 mg TPT * \frac{100 mg SCNP}{5.8 mg TPT} = 30.9 mg SCNP (eq. 14)$$

For the formulation of polymers used to collect the data in Figure 1 (and related supplemental figures), the calculated molar ratio of TPT:acene are presented in Table 1.

V: Photoredox Catalysis using TPT-SNap_{NL}-SCNP

The [4+2]-cycloaddition of *trans*-anethole and isoprene was optimized using TPT-SNap_{NL}-SCNP. Different solvents, catalyst loadings, and isoprene loading was investigated, along with different light sources as illustrated below. All the experiments were carried out in at least triplicates to validate the reported outcomes with yields being calculated through ¹H NMR spectroscopy in the presence of an internal standard.

General procedure: A dienophile (0.1 mmol) and diene (10 eq.) were added to a freshly prepared photocatalyst solution (0.1 M MeCN; 3.3 mol % catalyst). The reaction mixture was then irradiated for five hours with 440 nm Kessil LED lamps (100% intensity setting). Air streams were then used to concentrate the reaction mixture into a residue. Deuterated chloroform and an internal standard (trioxane) were then added prior to analyzing the reaction mixture using ¹H-NMR spectroscopy.

	3.3 mol % TPT-SNap _{NL} -S Me MeCN (0.1 M), air		P MeO	
MeO 0.1 r	0.1 mmol x equiv.	Me Me 440 nm Kessil lamp 100% light intensity, 5 h x equiv.	Me''' Me	
entry	variation	% anethole remaining	Yield, [4+2] cyclooadduct	
1	None (10 eq. diene)	4%	99%	
2	15 eq. diene	2%	94%	
3	7.5 eq. diene	4%	92%	
4	5 eq. diene	52%	39%	
5	2.5 eq. diene	52%	44%	
6	1.1 eq. diene	17%	42%	

Table S5: Effect of isoprene loading on catalytic activity

Table S6: Optimization for the TPT-SNap_{NL}-SCNP mediated Diels-Alder reaction of isoprene and *trans*-anethole

	Me +	3.3 mol % TPT-SNap _{NL} -SCNP MeCN (0.1 M), air	MeO
Me	0.1 mmol 10 equiv.	440 nm Kessil lamp 100% light intensity, 5 h	Me
entry	variation	% anethole remaining	Yield, [4+2] cyclooadduct
1	None	0%	99%
2	DCM	48%	45%
3	Toluene	74%	22%
4	Dioxane	80%	15%
5	THF	94%	1%
6	DMF	95%	Trace
7	1.3 mol% catalyst	24%	75%
8	5.3 mol% catalyst	5%	87%
9	N ₂ purge	96%	3%
10	427 nm	53%	45%
11	456 nm	16%	83%
12	CFL bulb	53%	45%
13	75% intensity	1%	98%
14	50% intensity	2%	97%
15	25% intensity	72%	28%
16	No TPT-SNap _{NL} SCNP	91%	0%
17	No light	95%	0%

Additional Experiments:

General procedure: A dienophile (0.1 mmol), diene (10 eq.), and the additive (See Table S8; eq. with respect to dienophile) were added to a freshly prepared SCNP solution (0.1 M MeCN; 3.3 mol % catalyst). The reaction mixture was then irradiated for five hours with 440 nm Kessil LED lamps (100% intensity setting). Air streams were then used to concentrate the reaction mixture into a residue. Deuterated chloroform and an internal standard (trioxane) were then added prior to analyzing the reaction mixture using ¹H-NMR spectroscopy.

Table S7: TPT-SNap_{NL}-SCNP mediated Diels-Alder reaction of isoprene and *trans*-anethole in the presence of additives. Experiments in this table follow the same general procedure described above with the described additives.



entry	variation from standard conditions	% anethole remaining	Yield, [4+2] cycloadduct
1	None	trace	99%
2	+ 1.0 eq NaN ₃	86%	5%
3	+1.0 eq CuCl ₂	70%	trace
4	+1.0 eq TEMPO	85%	trace
5	+ 0.5 eq pyrene	0%	86%
6	+ 1.0 eq pyrene	15%	68%
7	TPT-SP _{NL} -SCNP instead; + 0.5 eq naphthalen	ie 0%	62%
8	TPT-SPhen _{NL} -SCNP instead; + 0.5 eq naphthal	ene 0%	88%

Table S8: Turnover number (TON) calculated for different catalysts investigated (both small molecule and SCNP).

Catalyst	TON (Substrate/catalyst)
TPT-SNap _{NL} -SCNP	30
TPT-SPhen _{NL} -SCNP	21
TPT-SP _{NL} -SCNP	8
TPT-co-MMA	1
TPT	1

<u>Reaction conditions</u>: 440 nm (100% light intensity), 5 h, 1.2 mL MeCN, 0.1 mmol *trans*anethole, 10 eq. isoprene, 3.3 mol % catalyst (with respect to TPT content).

VI. Quenching Studies

The fraction of TPT excited state (TPT*) quenched by the electron relay (f_{ER}) is given by:

$$f_{ER} = \frac{k_{q,ER}[TPT^*][ER]}{k_{q,ER}[TPT^*][ER] + k_{q,anethole}[TPT^*][anethole] + k_r[TPT^*]}$$
(Eq. 15)

where $k_{q,ER}$ is the quenching rate constant for TPT* with the electron relay, [ER] is the concentration of the electron relay, $k_{q,anethole}$ is the quenching rate constant for TPT* with anethole, [anethole] is the concentration of anethole, and k_r is the rate constant for the excited state relaxation of the TPT* and is the inverse of the excited state lifetime (t₀).

F_{ER} can be rewritten to remove [TPT*] giving:

$$f_{ER} = \frac{k_{q,ER}[ER]}{k_{q,ER}[ER] + k_{q,anethole}[anethole] + k_r}$$
(Eq. 16)

The Stern-Volmer relationship for quenching of TPT* by the electron relay is given by:

$$\frac{I_0}{I_{ER}} = 1 + K_{SV,1}[ER]$$
(Eq. 17)

Where I_0 is the emission intensity in the abscene of a quencher, I_{ER} is the emission intensity in the prescence of the electron relay, and $K_{SV,1} = k_{q,ER}/k_r$.

The Stern-Volmer relationship for quenching of TPT* by anethole is given by:

$$\frac{I_0}{I_{anethole}} = 1 + K_{SV,2}[anethole]$$
(Eq. 18)

Where I_0 is the emission intensity in the abscene of a quencher, $I_{anethole}$ is the emission intensity in the prescence of anethole, and $K_{SV,2} = k_{q,anethole}/k_r$.

Equations 17 and 18 can be rearranged to solve for [ER] and [anethole] then substituted into equation 16 to give:

$$f_{ER} = \frac{k_{q,ER} \frac{\left(\frac{I_0}{I_{ER}} - 1\right)}{K_{SV,1}}}{k_{q,ER} \frac{\left(\frac{I_0}{I_{ER}} - 1\right)}{K_{SV,1}} + k_{q,anethole} \frac{\left(\frac{I_0}{I_{anethole}} - 1\right)}{K_{SV,2}} + k_r}$$
(Eq. 19)

$$f_{ER} = \frac{\left(\frac{I_0}{I_{ER}} - 1\right)}{\frac{\tau_0}{\tau_0}}$$

$$f_{ER} = \frac{\left(\frac{I_0}{I_{ER}} - 1\right)}{\frac{\tau_0}{\tau_0} + \frac{\left(\frac{I_0}{I_{anethole}} - 1\right)}{\tau_0} + \frac{1}{\tau_0}}{\left(\frac{I_0}{I_{ER}} - 1\right)}$$

$$f_{ER} = \frac{\left(\frac{I_0}{I_{ER}} - 1\right)}{\left(\frac{I_0}{I_{ER}} - 1\right) + \left(\frac{I_0}{I_{anethole}} - 1\right) + 1}$$
(Eq. 21)

Using the emission from TPT-co-SMeth_{NL}-co-MMA as I₀, for TPT-SNap_{NL}-SCNP $\left(\frac{I_0}{I_{ER}} - 1\right)$ was equal to 11 and $\left(\frac{I_0}{I_{anethole}} - 1\right)$ was equal to 1. Substituting into equation 21 gave a value of 6/8 or 75%. The fraction of TPT* quenched by anethole is given by:

$$f_{anethole} = \frac{k_{q,anethole} [TPT^*][anethole]}{k_{q,ER} [TPT^*][ER] + k_{q,anethole} [TPT^*][anethole] + k_r [TPT^*]}$$
(Eq. 22)
$$f_{anethole} = \frac{\left(\frac{I_0}{I_{anethole}} - 1\right)}{\left(\frac{I_0}{I_{ER}} - 1\right) + \left(\frac{I_0}{I_{anethole}} - 1\right) + 1}$$
(Eq. 23)

Using the same values as above, $f_{anethole}$ was 1/8 or 12.5% for TPT-SNap_{NL}-SCNP.

Solutions of SCNPs for each crosslinker (pyrene, phenanthrene, naphthalene, and methyl group) were prepared in acetonitrile without added quencher. After the emission of the sample in air was observed, the same sample was purged with nitrogen gas for 25 minutes. The sample emission was then taken for a second time. Each sample was prepared with a TPT concentration of 0.1 mM, based on the weight percent of TPT for each polymer.



Figure S21: Quencing studies performed with (left) TPT-SNap_{NL}-SCNP and (right) TPT-SMeth_{NL}-SCNP with anethole.

The aforementioned emission experiments were performed again but with anethole present as a quencher. These samples were not purged before collecting the emission data. While the concentration of the TPT molecule within the polymers remained the same (0.1 mM) for each, the concentration of anethole increased from 0 to 0.1 mM.



Figure S22: UV-Vis spectral overlay of SCNPs investigated in the quenching studies.

VII. Relevant UV-Vis Spectra for SCNP Reactions



Figure S23: UV-Vis spectral overlay of reaction conditions (blue trace), SCNP (orange trace), *trans*-anethole (purple trace), and isoprene (red trace) in MeCN.



Figure S24: UV-Vis spectral overlay of reaction conditions (blue trace) and the sum of the SCNP, *trans*-anethole, and isoprene individual absorbances (orange trace) in MeCN.

VIII: Substrate Scope

The desired dienophile (0.1 mmol) and diene (0.3 mmol) were mixed with TPT-co-SNap_{NL}-SCNP photocatalyst (3.3-9.9 mol %), and acetonitrile (1 mL; 0.1 M) were added to a one-dram vial. The vial was then placed in between two 440 nm Kessil lamps at 100% intensity and stirred overnight. After the completion of reaction, acetonitrile was evaporated, and the residue was characterized using NMR spectroscopy with trioxane as an internal standard.



Figure S25: ¹H-NMR spectrum of crude 4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl, 99% yield.

¹**H-NMR**: (400 MHz, CDCl₃) δ 7.09 (2H, d, J = 8.6 Hz), 6.84 (2H, d, J = 8.64 Hz), 5.45 (1H, br.s), 3.79 (3H, s), 2.34-2.27 (1H, m), 2.24-2.13 (2H, m), 2.09 (1H, dd, J = 16.56, 3.64 Hz), 1.95-1.767 (2H, m), 1.69 (3H, s), 0.71 (3H, d, J = 6.32 Hz).



Figure S26: ¹H-NMR spectrum of crude 4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'biphenyl, 99% yield.⁷

¹**H-NMR**: (400 MHz, CDCl₃) δ 7.04 (2H, d, *J* = 8.64 Hz), 6.8 (2H, d, *J* = 8.68 Hz), 3.74 (3H, s), 2.3 (1H, td, *J* = 10.62, 5.76 Hz), 2.16-2.03 (3H, m), 1.83-1.76 (3H, m), 1.61 (3H, s), 1.58 (3H, s), 0.66 (3H, d, *J* = 6.12 Hz).



Figure S27: ¹H-NMR spectrum of crude tert-butyl((2',4'-dimethyl-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane, 50% yield.⁸

¹**H-NMR**: (400 MHz, CDCl₃) δ 6.9 (2H, d, *J* = 11.84 Hz), 6.7 (2H, d, *J* = 12.43 Hz), 5.36 (1H, br. S), 2.5-2.35 (1H, m), 2.25-2.15 (2H, m), 2.11-2.06 (3H, m), 1.61 (3H, s), 0.90 (9H, s), 0.62 (3H, br d), 0.19 (3H, s).



Figure S28: ¹H NMR spectrum of crude 2',4',5'-trimethoxy-2,4,6,6-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl, 20% yield.⁹

¹**H-NMR**: (400 MHz, CDCl₃) δ 6.60 (1H, s), 6.5 (1H, s), 5.16 (1H, br. S), 3.84 (3H, s), 3.81 (3H, s), 3.79 (3H, s), 2.87 (1H, d, J = 11.5 Hz), 2.07 (2H, m), 1.9 (1H, s) hidden peak, 1.62 (3H, s), 0.84 (3H, s), 0.75 (3H, s), 0.65 (3H, d, J = 6.09 Hz).



Figure S29: ¹H-NMR spectrum of crude 4'-methoxy-2,4,6,6-tetramethyl-1,2,3,6-tetrahydro-1,1'biphenyl, 99% yield.⁹

¹**H-NMR**: (400 MHz, CDCl₃) δ 6.98 (2H, d, J = 27, 7.17 Hz), 6.77 (2H, d, J = 26.0, 7.2 Hz), 5.14 (1H, br. S), 3.75 (3H, s), 2.15-2.11 (2H, m), 2.04 (1H, dd, J = 17.66, 3.9 Hz), 1.68 (1H, dd, J = 14.66, 1.14 Hz), 1.61 (3H, s), 0.77 (3H, s), 0.72 (3H, s), 0.65 (1H, d, J = 5.96 Hz).



Figure S30: ¹H-NMR spectrum of crude 9-(2,2,4-trimethylcyclohex-3-en-1-yl)-9H-carbazole, 24% yield.⁹

¹**H-NMR**: (400 MHz, CDCl₃) δ 8.08 (2H, d, *J* = 4 Hz,), 7.65 (d, *J* = 8.6 Hz, 1H), 7.48 (1H, br d), 7.42 (1H, br t), 7.34 (1H, br t), 7.21 (2H, m), 5.23 (1H, s), 4.58 (1H, dd, *J* = 13.1, 2.1 Hz,), 2.95 (1H, qd, *J* = 12.43, 5.8 Hz,), 2.26-2.22 (2H, m), 1.92 (1H, m), 1.73 (3H, s), 1.15 (3H, s), 1.03 (3H, s).



Figure S31: ¹H-NMR spectrum of isolated methyl 4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate, 77% yield.

¹**H-NMR**: (400 MHz, CDCl₃) δ 7.07 (2H, d, *J* = 8.62 Hz), 6.77 (2H, d, *J* = 8.79 Hz), 5.43 (1H, br. S), 3.77 (3H, s), 3.40 (3H, s), 2.93 (1H, td, *J* = 10, 5.4 Hz), 2.84 (1H, td, *J* = 10.14, 5.11 Hz), 2.42-2.17 (1H, m), 1.71 (3H, s).



Figure S32: ¹³C-NMR spectrum of isolated methyl 4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate.

¹³**C-NMR**: (100 MHz, CDCl₃) δ 175.8, 158.2, 136.0, 132.1, 128.4, 120.8, 113.8, 55.2, 51.4, 47.0, 42.1, 34.0, 33.8, 23.3.



Figure S33: ¹H-NMR spectrum of crude 4'-methoxy-4-methyl-2-nitro-1,2,3,6-tetrahydro-1,1'biphenyl, 52% yield.⁸

¹**H-NMR**: (400 MHz, CDCl₃) δ 7.08 (2H, d, *J* = 6.45 Hz), 5.43 (1H, br. S), 4.88 (1H, m), 3.71 (3H, s), 3.22 (1H, m), 2.69 (2H, m), 1.69 (3H, s).



Figure S34: ¹H-NMR spectrum of crude 4'-methoxy-4,5-dimethyl-2-nitro-1,2,3,6-tetrahydro-1,1'-biphenyl, 42% yield.¹⁰

¹**H-NMR**: (400 MHz, CDCl₃) δ 7.14 (2H, d, *J* = 8.03 Hz), 6.84 (2H, d, *J* = 8.5 Hz), 4.88 (1H, m), 3.75 (3H, s), 3.37-3.26 (1H, m), 2.88-2.83 (1H, m), 2.69-2.65 (1H, m), 2.46-2.29 (1H, m), 2.34-2.29 (1H, m), 1.64 (3H, s), 1.60 (3H, s).

IX. Polymer Recyclability Studies

Following the standard reaction using isoprene and *trans*-anethole, the solvent was evaporated to afford the desired cyclohexene product, which was analyzed using ¹H-NMR spectroscopy. Yields were calculated with respect to an internal standard. The reaction mixture dissolved in CDCl₃ was charged into cold methanol, whereupon the SCNP precipitated, leaving the remaining organics dissolved. The suspension was centrifuged, yielding a film, which was dried under air. This precipitated polymer was then dissolved in MeCN (10 mg mL⁻¹); a 100 μ L aliquot was diluted to 1 mL and used to record a UV-Vis spectrum. The polymer sample was then concentrated to a film, which was reused for a fresh reaction.



Figure S35: UV-Vis spectroscopic overlay of recovered SCNPs after a first round of recycling (red trace), a second round of recycling (yellow trace), a third round of recycling (purple trace), and a fourth round (blue trace).

The polymer residue was analyzed after reaction using UV-Vis spectroscopy, wherein the TPT chromphore (shoulder at ~410 nm) was found to photobleach over time, even after one recycling attempt.

The observed yields for the reactions represented above were as follows:

- \circ 1st recycle (red trace): 99%
- \circ 2nd recycle (yellow trace): 84%
- \circ 3rd recycle (purple trace): 54%
- 4th recycle (blue trace): 13%

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