Supporting Information

Visible light mediated efficient photoswitching of dimethyldihydropyrenes in thin films for all-photonic logic gate applications and dynamic encryption/decryption capabilities

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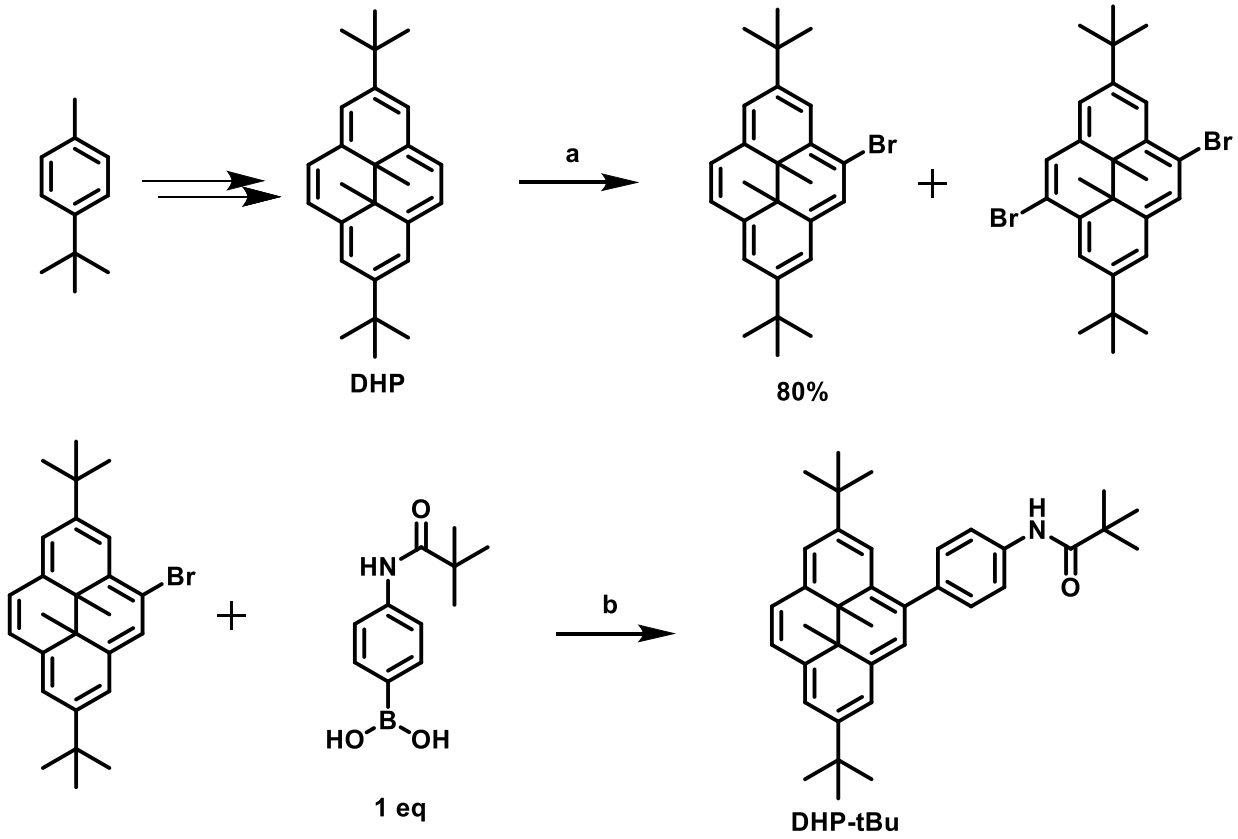
Materials and instruments:

The reagents used in this study were sourced from commercial suppliers and utilized without additional purification unless specified. Standard methods were applied to purify and dry solvents, with tetrahydrofuran (THF) freshly distilled over sodium/benzophenone and anhydrous CaH_2, respectively, before use. All other solvents for synthesis and purification such as DMF, acetonitrile underwent fresh distillation prior to their usage. A dry nitrogen/argon atmosphere was maintained during reactions, employing flame-dried glassware unless otherwise noted. Column chromatography was carried out with silica gel (Merck, 100-200 mesh). Thin-layer chromatography (TLC) was performed on Merck plates (TLC Silica Gel 60 F254) to monitor reactions. Yields reported pertain to the use of chromatographically and spectroscopically pure compounds. Compound structures were characterized through NMR spectroscopy, mass spectrometry, and various spectroscopic techniques as mentioned in the text. ^{1}H NMR spectra were acquired on a 500 MHz Bruker spectrometer, with chemical shifts reported as δ values relative to tetramethylsilane (TMS) for the ^{1}H NMR or the solvent peak. For the ^{13}C NMR, the solvent peaks were utilized for calibration on 125 MHz Bruker spectrometers with complete proton decoupling.

Photoisomerization studies:

The photochemical isomerization studies were performed in acetonitrile for all the compounds at 298 K, unless otherwise indicated. Closed to open photoisomerization reaction of compound DHP-tBu was carried out under 525 nm green light and 640 nm red light source has been used in case of BDHP-tBu and NDHP-tBu for the closed to open photoisomerization. Kessil PR160 series lights have been used for the experiments. The average intensity of PR160 series is 399 mW/cm^2 (measured from 1 cm distance). The reverse isomerization under different light sources have been studied and are indicated in the figure captions. A 1 mL cuvette was kept under ice-cold conditions to minimize the effect of heat. The UV-vis absorbance data were recorded subsequently with a Cary 60 UV-Vis spectrophotometer. The open to closed isomerization were conducted thermally at multiple temperatures using a Peltier module. The open to closed isomerization under the thermal conditions were carried out in the spectrophotometer itself using a Peltier heating system accessory with an accuracy of ± 1 °C.

Synthetic scheme:

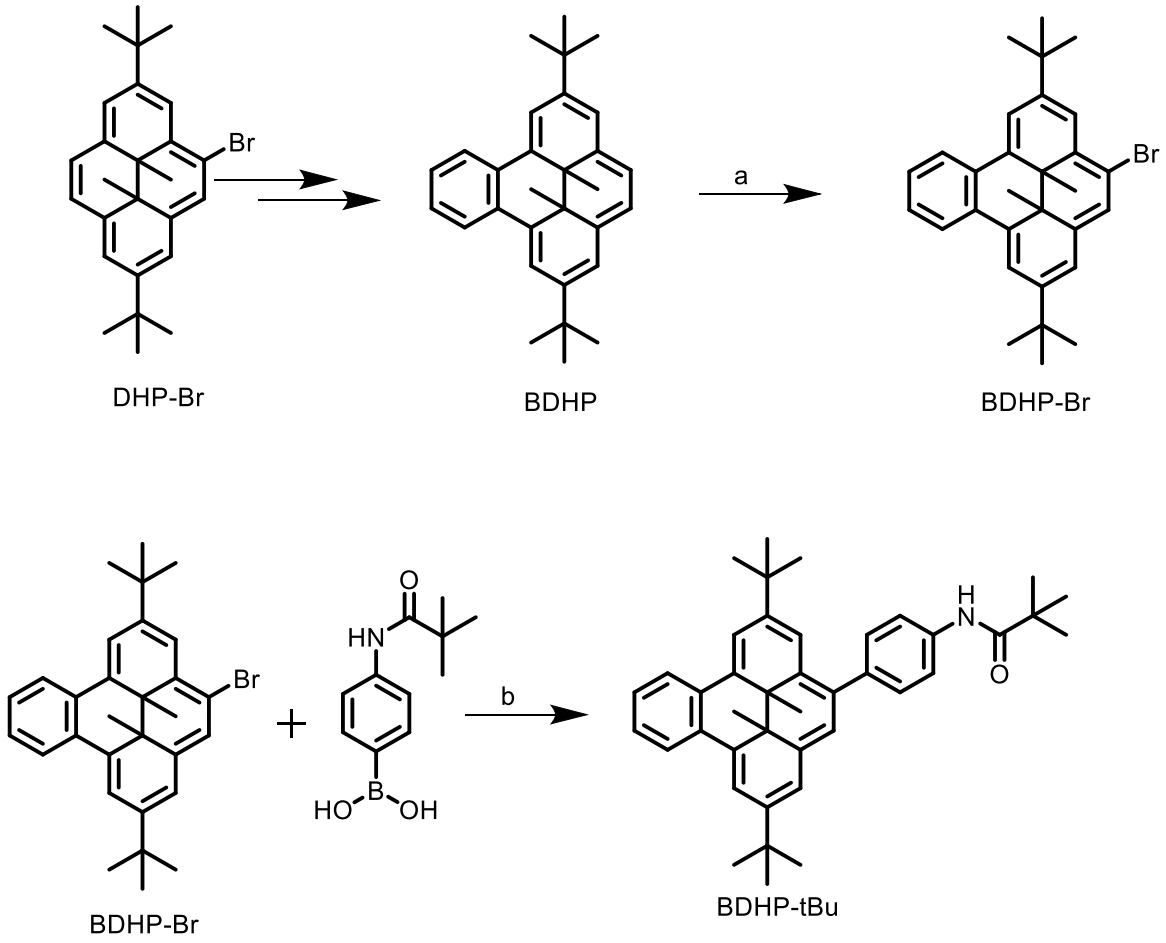


Scheme S1: (a) NBS (1 equiv), CH_2Cl_2, DMF, 0 °C, 2 h; **(b)** $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 equiv), and 4 mL THF:H_2O (3:1), reflux, N_2, 24 h.

The unsubstituted DHP was synthesized from 4-tert-butyltoluene in a seven-step synthesis following the the literature report.[1] The purity of the synthesized compound was confirmed from ^{1}H NMR and ^{13}C NMR data which were consistent with the reported values. Bromination of the DHP was done following the reported procedure to afford the mono-substituted DHP-Br**,** the ^{1}H NMR and ^{13}C data were consistent with the literature.[2]

N-(4-(2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyren-4-yl)phenyl)pivalamide (1). $Pd(PPh_3)_4$ (27 mg, 0.024 mmol) was added to a mixture of DHP-Br (100 mg, 0.236 mmol), (4-pivalamidophenyl)boronic acid (58 mg, 0.26 mmol), K_2CO_3 (36 mg, 0.26 mmol) dissolved in 3 ml THF, 1 ml water and the mixture was purged with nitrogen for 30 minutes. The mixture was stirred for 24 h at 80 °C. After cooling it to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane, and washed with water (2 × 15 mL) and then with brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in vacuum, the residue was purified by column chromatography (silica gel, eluent: 5% ethyl acetate in hexane) to give 86 mg of pure compound **1**

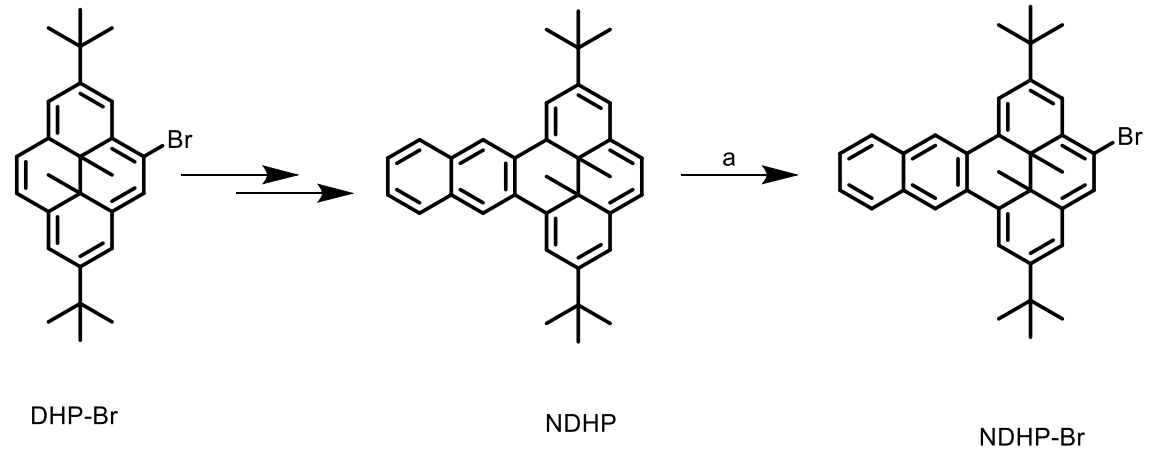
(yield 70%; melting point 193–195 °C); **^{1}H NMR** (500 MHz, Acetone-d_6) δ = 8.80 (s, 1H), 8.72 (s, 1H), 8.67 – 8.61 (m, 3H), 8.53 – 8.49 (m, 3H), 7.98 (d, *J*=8.6, 2H), 7.77 (d, *J*=8.6, 2H), 1.70 (s, 9H), 1.61 (s, 9H), 1.38 (s, 9H), −3.86 (d, *J*=12.6, 6H).**^{13}C{^{1}H} NMR** (100 MHz, Acetone-d_6) δ 177.22, 145.85, 145.52, 139.38, 138.79, 137.49, 135.78, 133.69, 130.77, 130.06, 126.95, 126.87, 125.74, 125.56, 125.37, 120.68, 120.62, 118.32, 117.99, 40.28, 36.64, 36.27, 36.05, 30.90, 30.88, 27.82, 18.24, 18.02. **HRMS (ESI)**: *m/z* (Calc): $C_{37}H_{45}NO$[M+H] 520.3574; found: 520.3581.

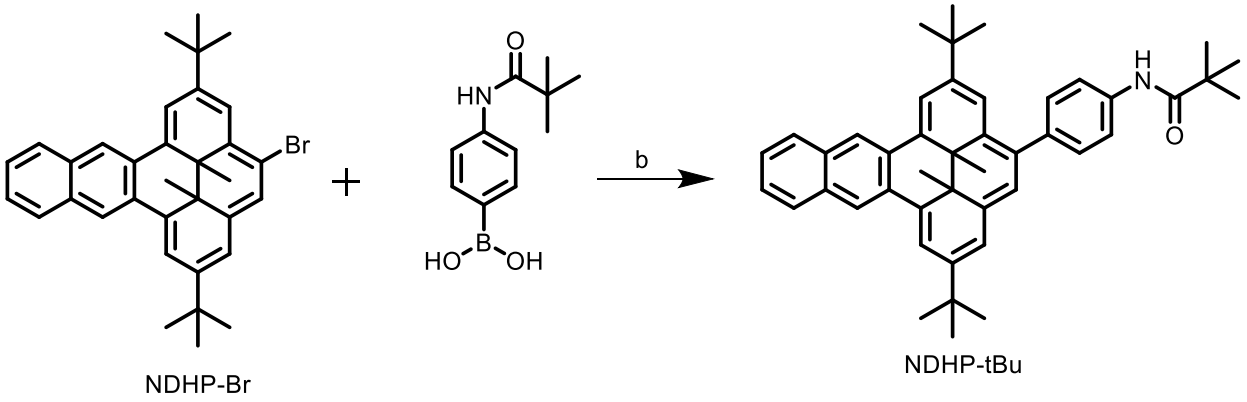


Scheme S2: (a) NBS (1 equiv), CH_2Cl_2, DMF, 0 °C, 2 h; **(b)** $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 equiv), and 4 mL THF:H_2O (3:1), reflux, N_2, 24 h.

The unsubstituted BDHP was synthesized according to the literature report.[3] The purity of the synthesized compound was confirmed by the ^{1}H NMR and ^{13}C NMR data which were consistent with the reported values. Bromination of the BDHP was done following the reported procedure to afford the mono-substituted BDHP-Br.[4]

N-(4-(2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydrobenzo[e]pyren-4-yl)phenyl)pivalamide (2). In a 15 mL pressure tube equipped with a magnetic stir bar, $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) was added to a mixture of BDHP-Br (100 mg, 0.175 mmol), (4-Pivalamidophenyl)boronic acid (47 mg, 0.21 mmol), K_2CO_3 (29 mg, 0.21 mmol) was dissolved in 3 ml THF, 1 ml water and the mixture was purged with nitrogen for 30 minutes. The mixture was stirred for 24 h at 80 °C. After cooling to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane, and washed with water (2 × 15 mL), brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in rotavapor, the residue was purified by column chromatography (silica gel, eluent: 10% ethyl acetate in hexane) to give 78 mg of pure compound **2** (yield 65%; melting point 195–197 °C); **^{1}H NMR** (500 MHz, Acetone-d_6) δ = 8.93 (s, 2H), 8.73 (s, 1H), 8.49 (d, *J*=7.4, 2H), 7.87 (d, *J*=8.3, 2H), 7.70 – 7.59 (m, 3H), 7.57 – 7.45 (m, 3H), 7.26 (s, 1H), 1.53 (s, 9H), 1.44 (s, 9H), 1.35 (s, 9H), -1.44 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, Acetone-d_6) δ 177.22, 145.85, 145.52, 139.38, 138.79, 137.49, 135.85, 135.78, 133.95, 133.69, 130.77, 130.36, 130.06, 126.95, 126.87, 125.74, 125.56, 125.37, 120.68, 120.62, 118.32, 117.99, 40.28, 36.64, 36.27, 36.05, 30.90, 30.88, 27.82, 18.24, 18.02. **HRMS(ESI)**: *m/z* (Calc): $C_{41}H_{47}NO$[M+Na] 592.3658; found: 592.3753





Scheme S3: (a) NBS (1 equiv), CH_2Cl_2, DMF, 0 °C, 2 h; **(b)** $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 equiv), and 4 mL THF:H_2O (3:1), reflux, N_2, 24 h.

The unsubstituted NDHP was synthesized according to the literature report.[3] The purity of the synthesized compound was confirmed from ^{1}H NMR and ^{13}C NMR data which were consistent with the reported values. Bromination of the DHP was done following the reported procedure to afford the mono-substituted NDHP-Br**,** the ^{1}H NMR and ^{13}C data were consistent with the literature.[5]

N-(4-(2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydrodibenzo[de,qr]tetracen-4-yl)phenyl)pivalamide (3).

In a 15 mL pressure tube equipped with a magnetic stir bar, $Pd(PPh_3)_4$ (22 mg, 0.019 mmol) was added to a mixture of NDHP-Br (100 mg, 0.19 mmol), (4-Pivalamidophenyl)boronic acid (51 mg, 0.23 mmol), K_2CO_3 (32 mg, 0.23 mmol) was dissolved in 3 ml THF, 1 ml water and the mixture was purged with nitrogen for 30 minutes. The mixture was stirred for 24 h at 80 °C. After cooling to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane, and washed with water (2 × 15 mL), brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in rotavapor, the residue was purified by column chromatography (silica gel, eluent: 10% ethyl acetate in hexane) to give 77 mg of pure compound **3** (yield 65%; melting point 199–201 °C); **^{1}H NMR** (500 MHz, Acetone-d_6) δ = 9.34 (d, *J*=2.0, 2H), 8.70 (s, 1H), 8.28 (dd, *J*=7.2, 1.4, 2H), 8.17 (dd, *J*=6.3, 3.3, 2H), 7.85 – 7.82 (m, 2H), 7.56 (dd, *J*=6.3, 3.2, 2H), 7.45 – 7.43 (m, 2H), 7.24 (d, *J*=1.2, 1H), 7.04 – 7.02 (m, 1H), 6.81 (s, 1H), 1.47 (s, 9H), 1.38 (s, 9H), 1.34 (s, 9H), -0.40 (s, 6H). **^{13}C{^{1}H}** NMR (125 MHz, Acetone-d_6) δ 177.28, 146.16, 145.87, 139.79, 139.49, 137.26, 136.95, 136.89, 134.80, 133.79, 132.84, 132.78, 130.54, 129.75, 129.43, 129.40, 128.85, 128.82, 126.64, 125.73, 124.18, 123.98, 120.81, 120.78, 118.81, 118.79, 118.41, 40.40, 39.21, 38.58, 36.15, 35.92, 30.58, 30.55, 27.94, 27.87, 20.09, 19.91. **HRMS(ESI)**: *m/z* (Calc): $C_{45}H_{49}NO$[M+H] 620.3887; found: 620.3936

The polymers were synthesized according to the literature report.[6] The purity of the synthesized compound was confirmed from ^{1}H NMR.

PMMA

^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.59 (s, 3H), 1.97 – 1.73 (m, 2H), 1.05 – 0.78 (m, 3H).

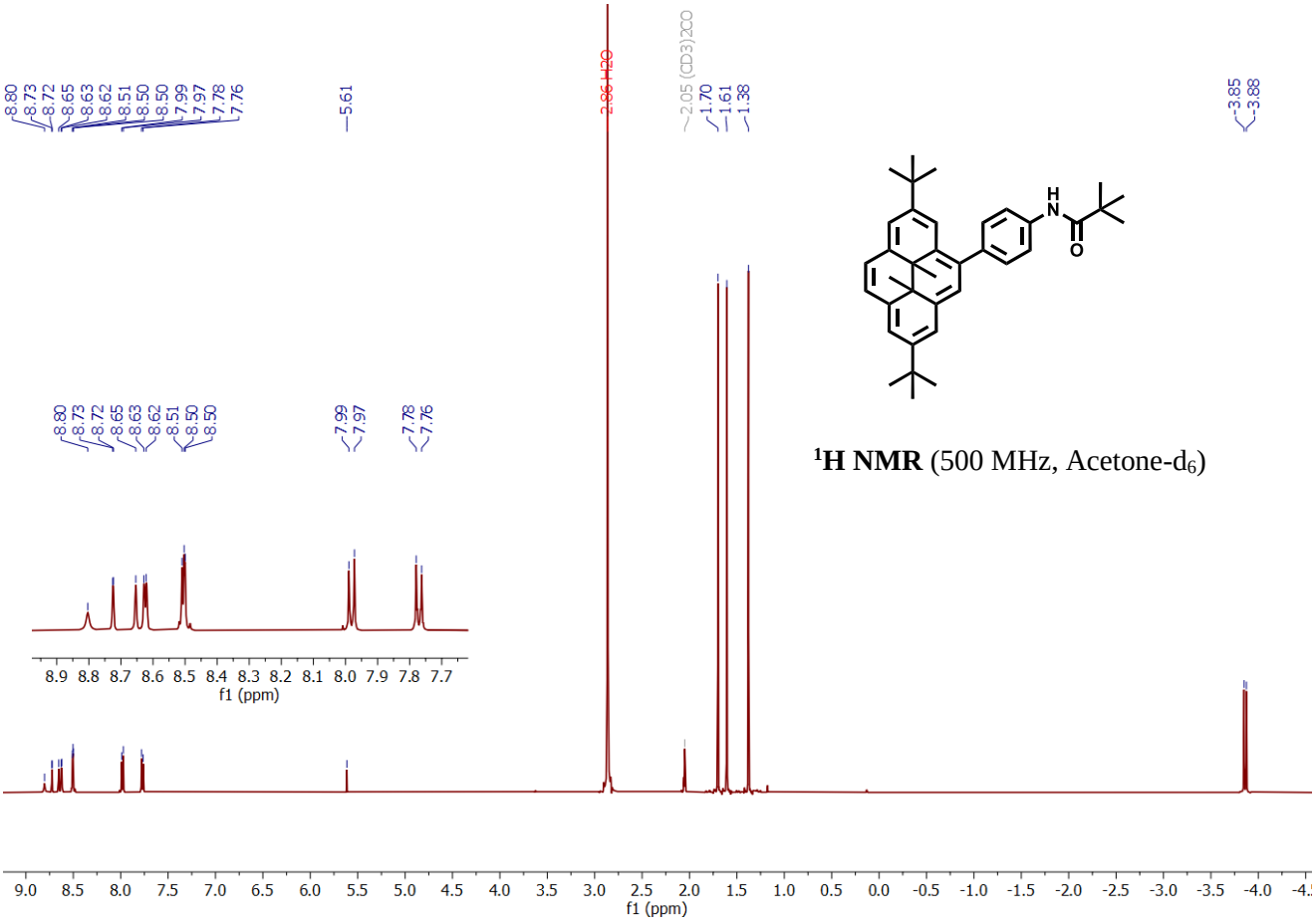
PCMA

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.58 (s, 1H), 2.05 – 0.70 (m, 15H).

PTBMA

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.32 – 1.66 (m, 2H), 1.42 – 1.30 (m, 12H).

^{1}H and ^{13}C NMR spectra:



^{1}H NMR (500 MHz, Acetone-d_6)

Figure S1. ^{1}H NMR spectrum of compound **DHP-tBu.**

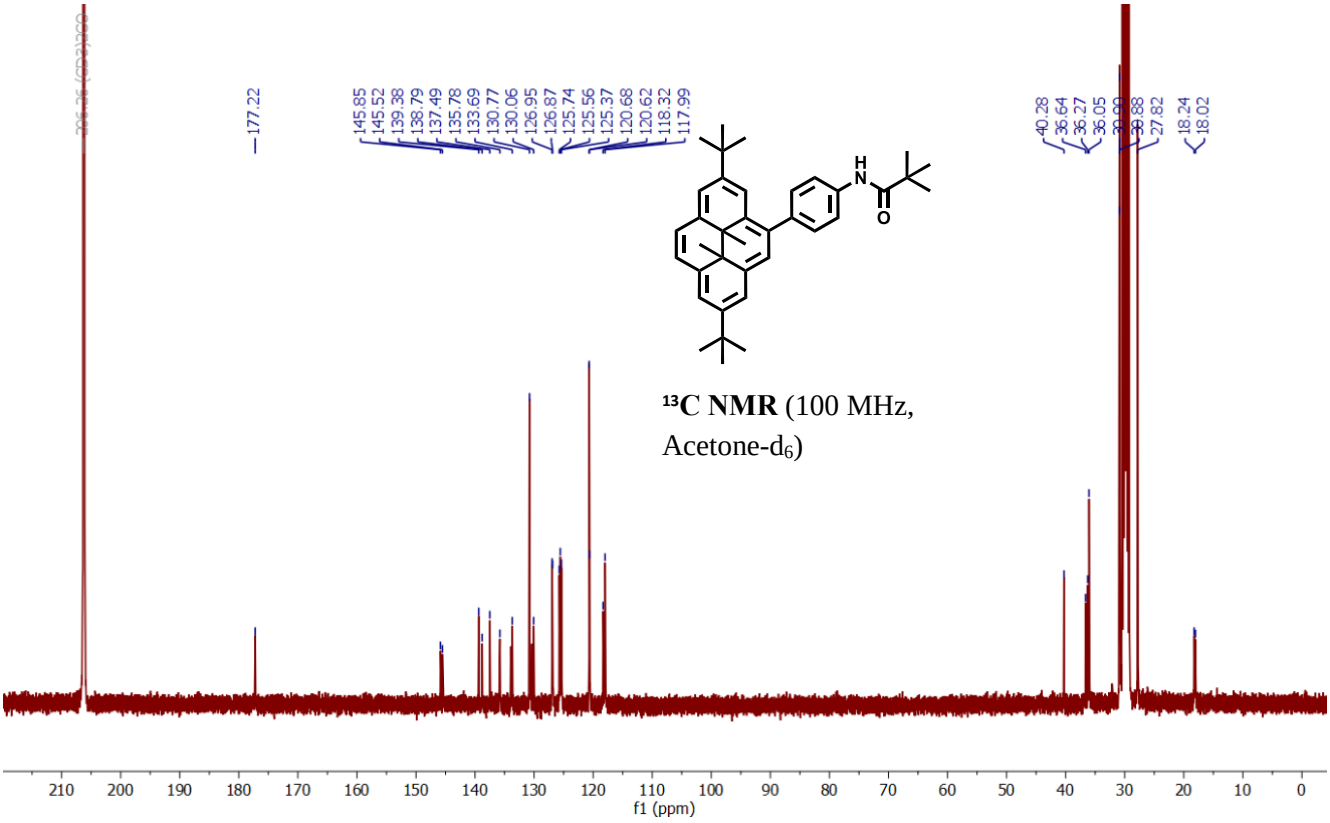
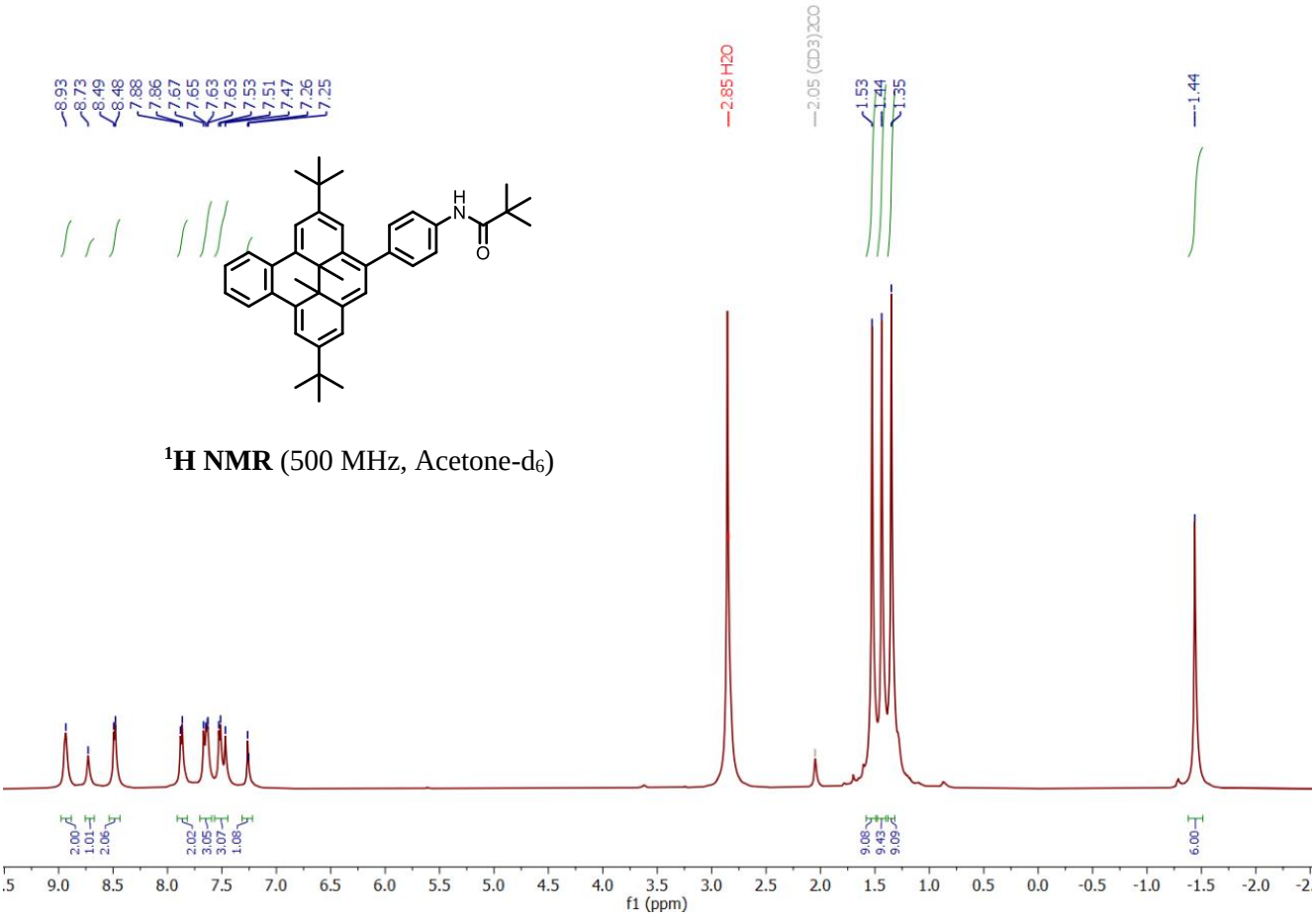


Figure S2. ^{13}C NMR spectrum of compound **DHP-tBu.**



^{1}H NMR (500 MHz, Acetone-d_6)

Figure S3. ^{1}H NMR spectrum of compound **BDHP-tBu.**

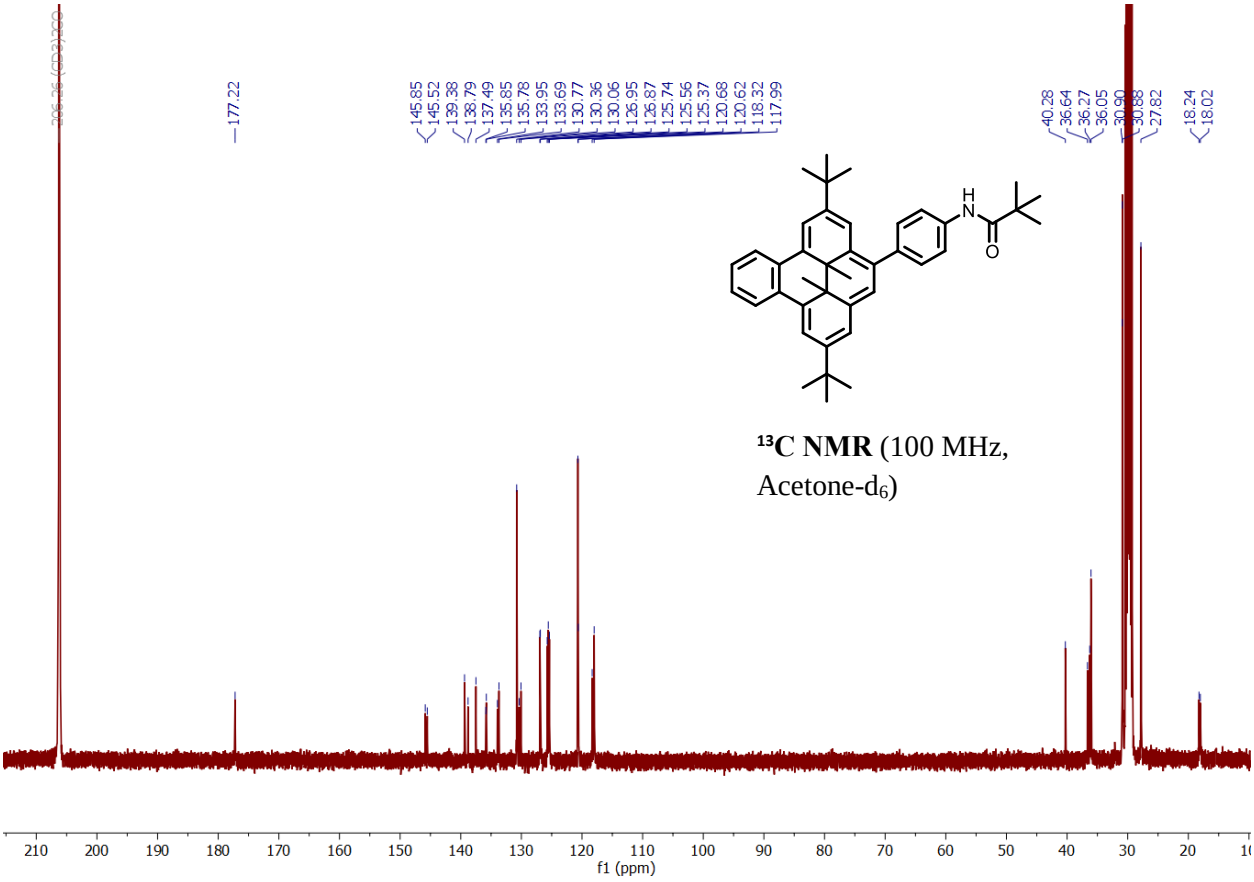


Figure S4. ^{13}C NMR spectrum of compound **BDHP-tBu.**

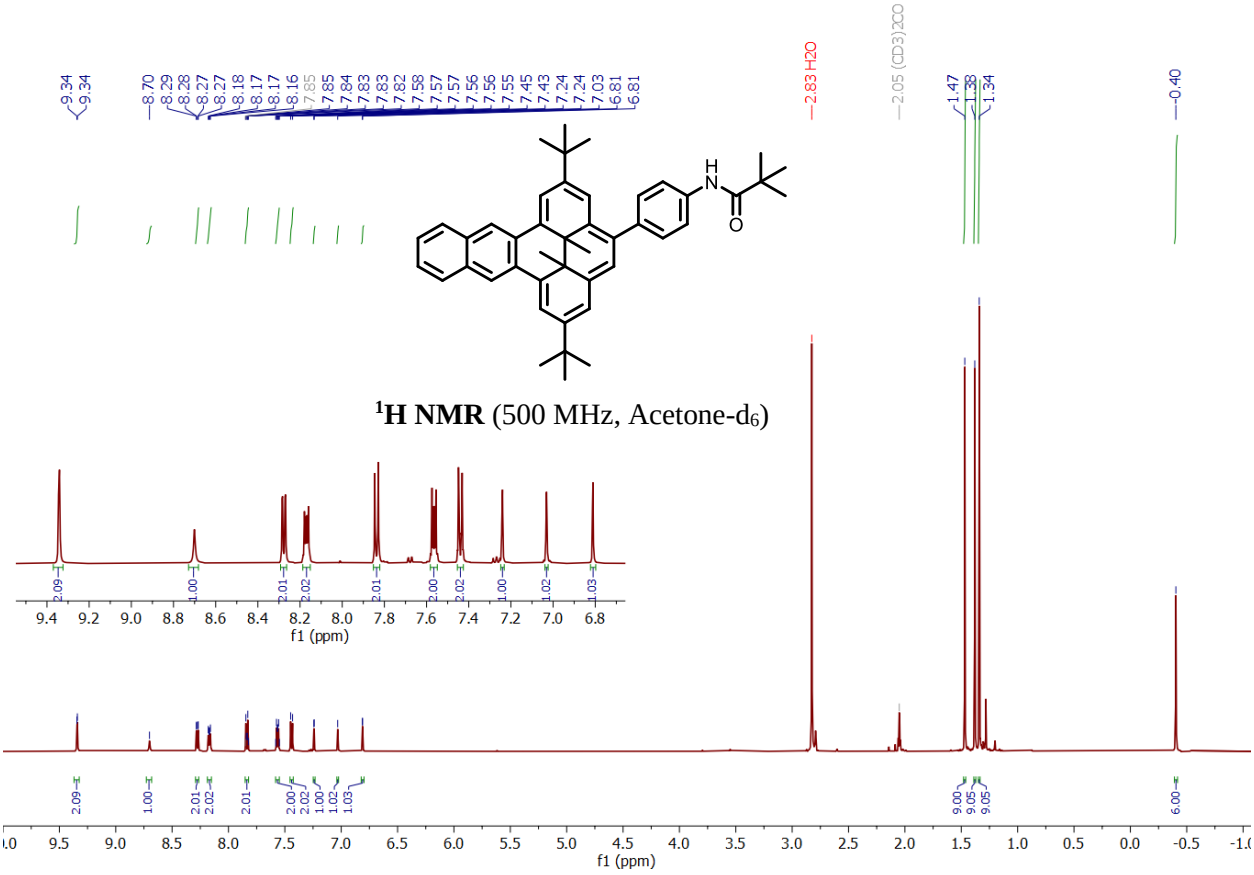


Figure S5. [1]H NMR spectrum of compound **NDHP-tBu.**

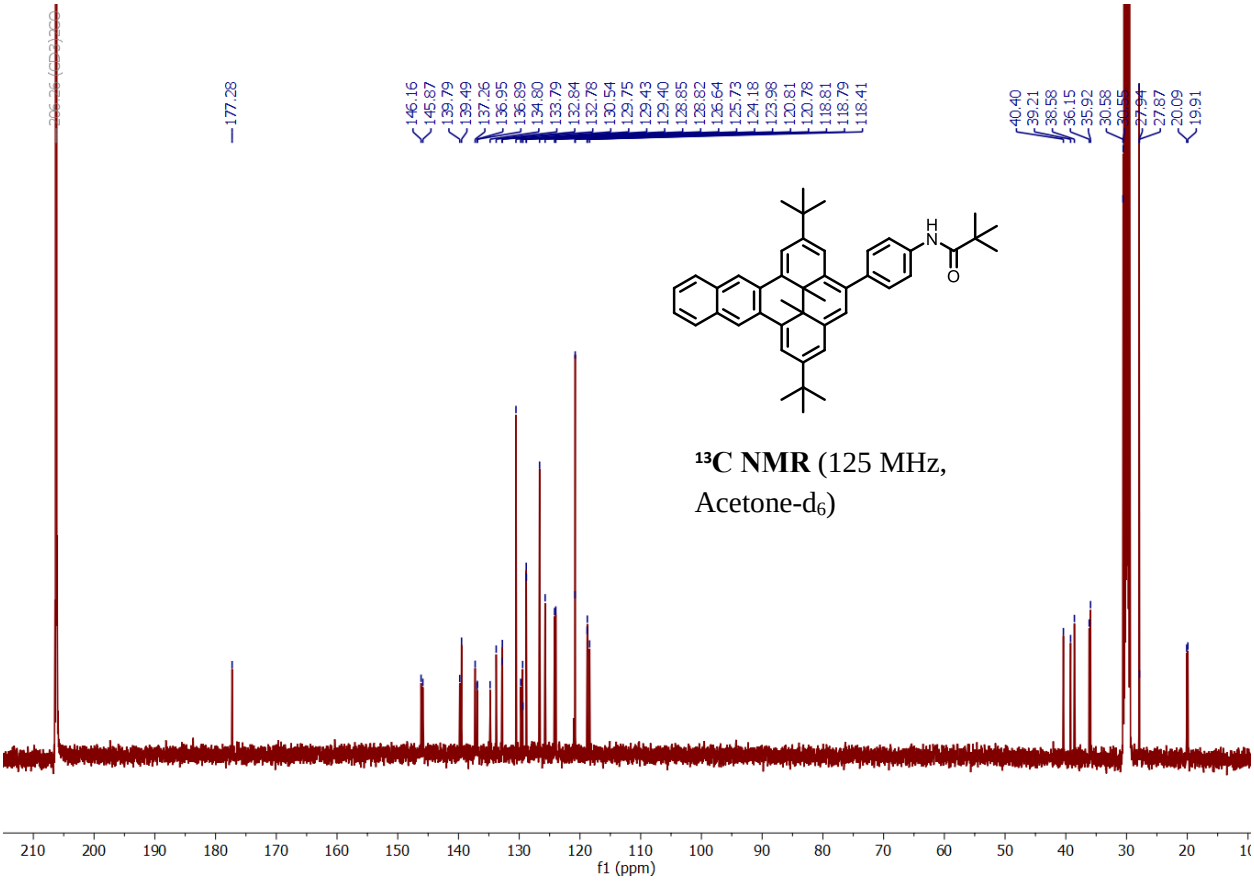


Figure S6. ^{13}C NMR spectrum of compound **NDHP-tBu.**

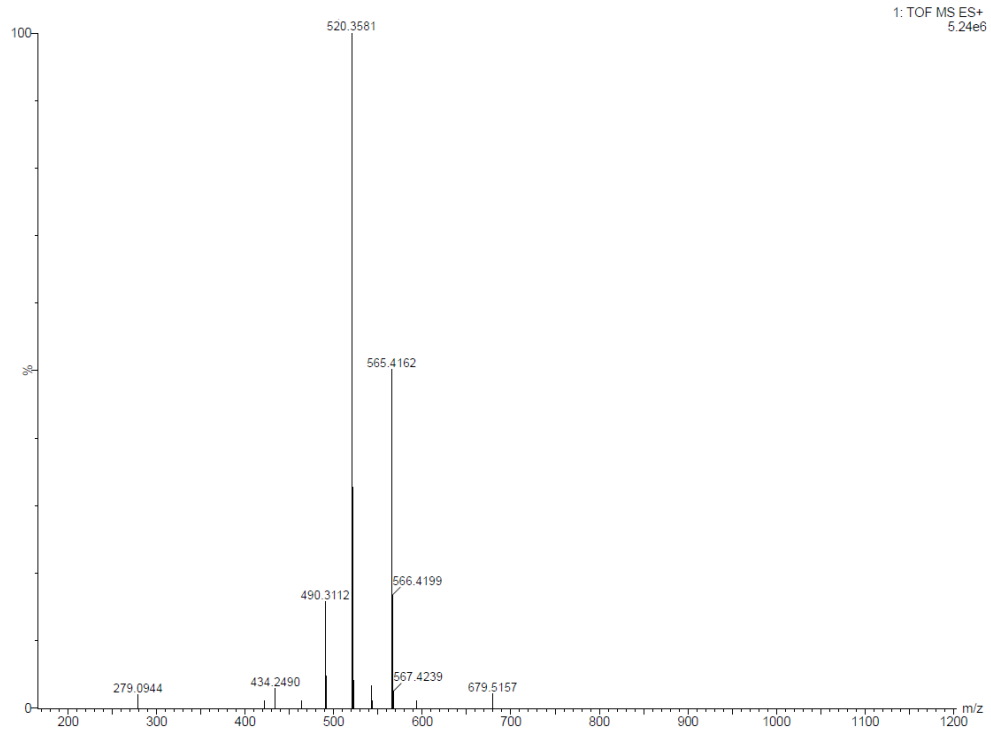


Figure S7. HRMS spectrum of compound **DHP-tBu.**

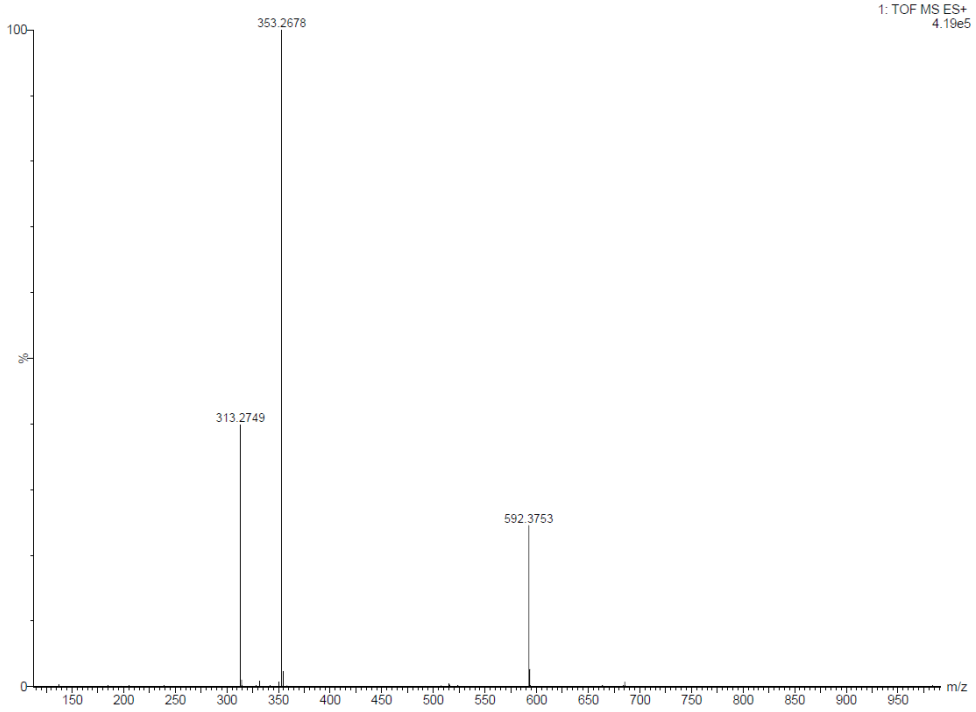


Figure S8. HRMS spectrum of compound **BDHP-tBu.**

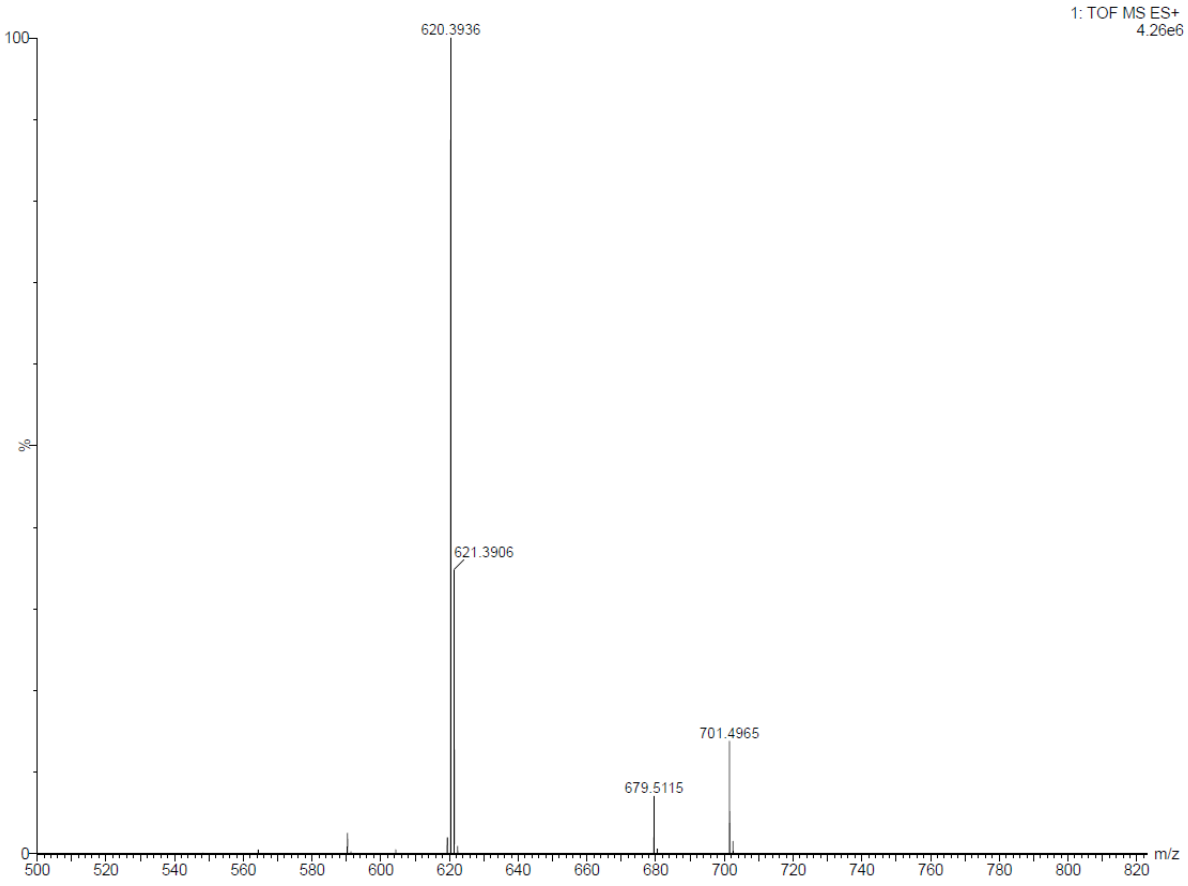


Figure S9. HRMS spectrum of compound NDHP-tBu.

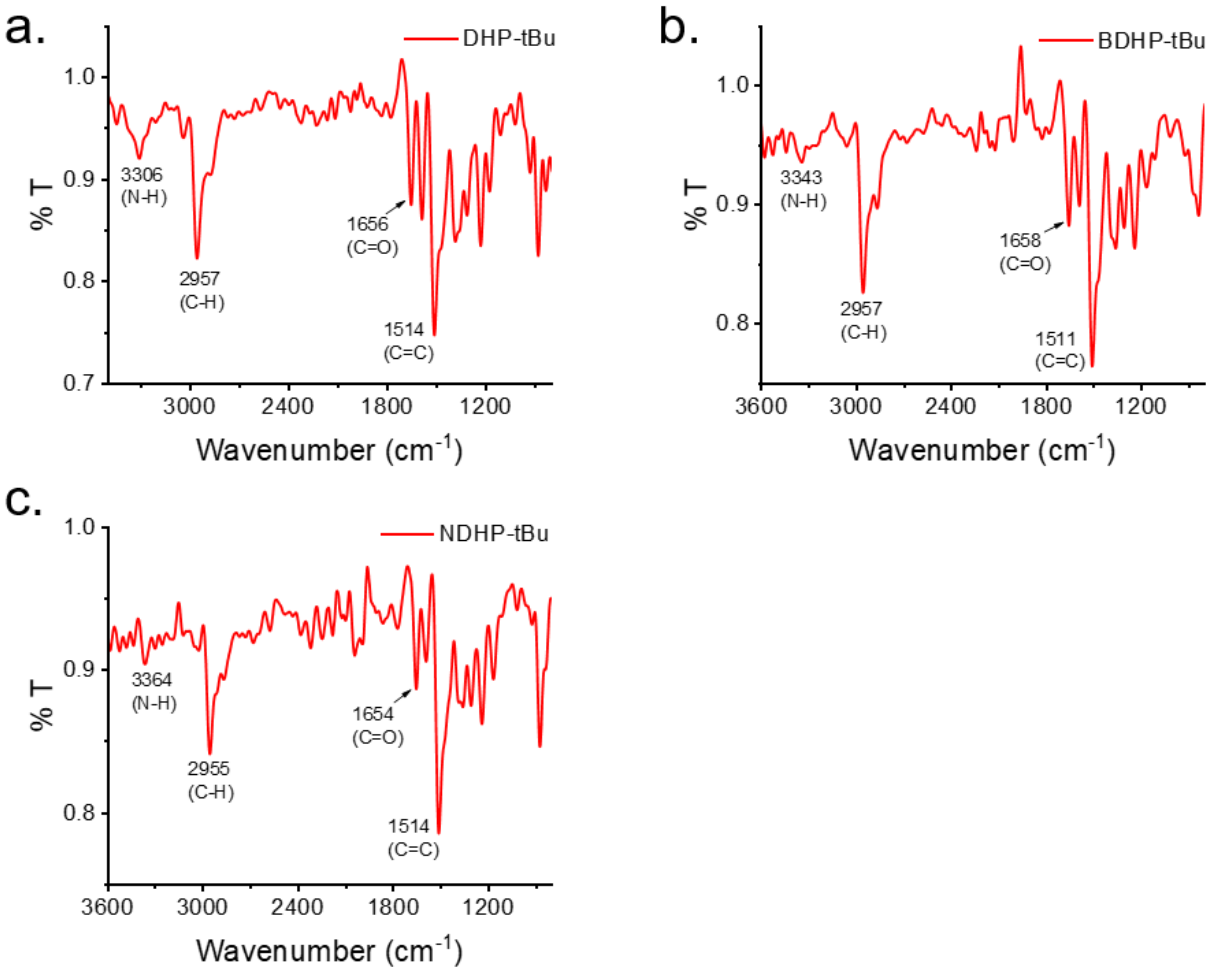


Figure S10. IR spectra of a) **DHP-tBu** b) **BDHP-tBu** and c) **NDHP-tBu.**

^{1}H NMR of the synthesized polymers:

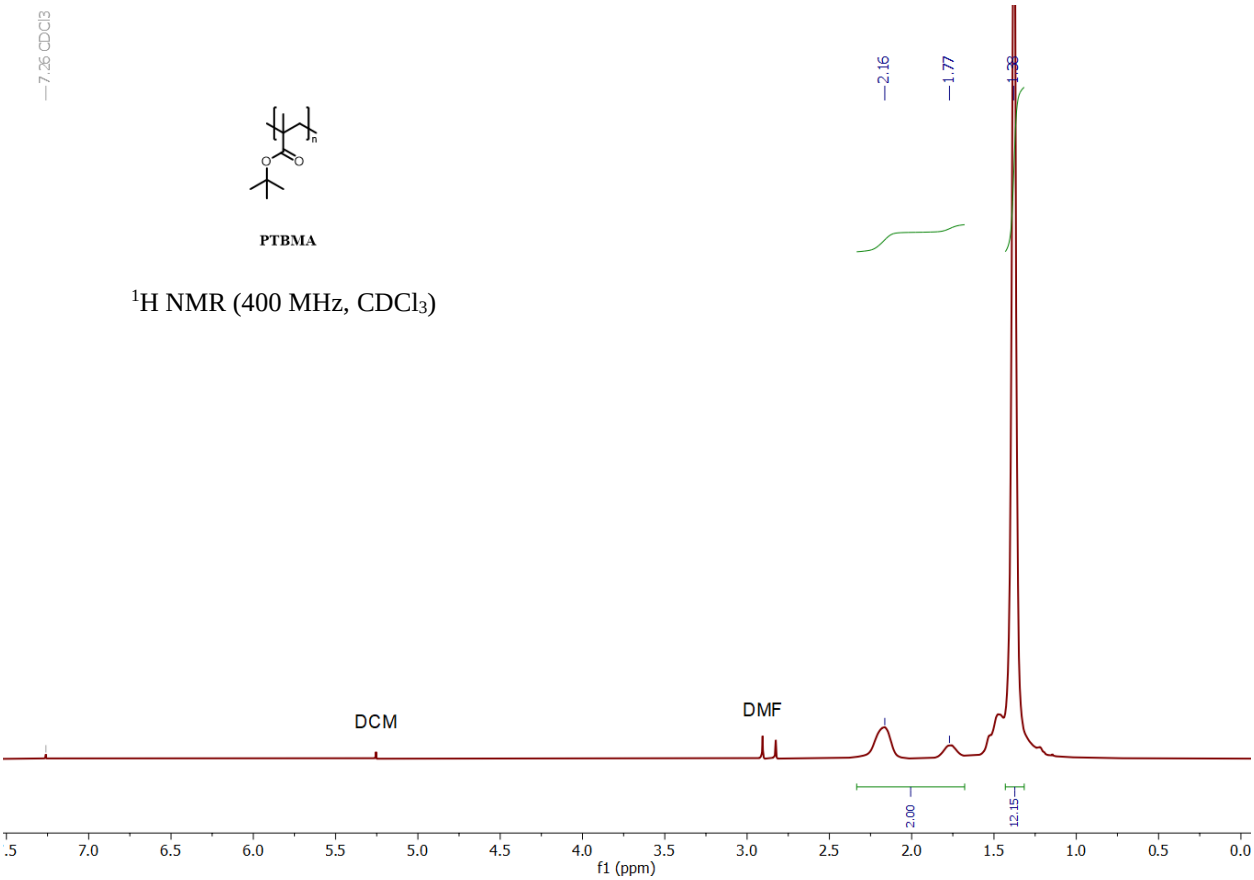


Figure S11. ^{1}H NMR spectrum of compound **PTBMA.**

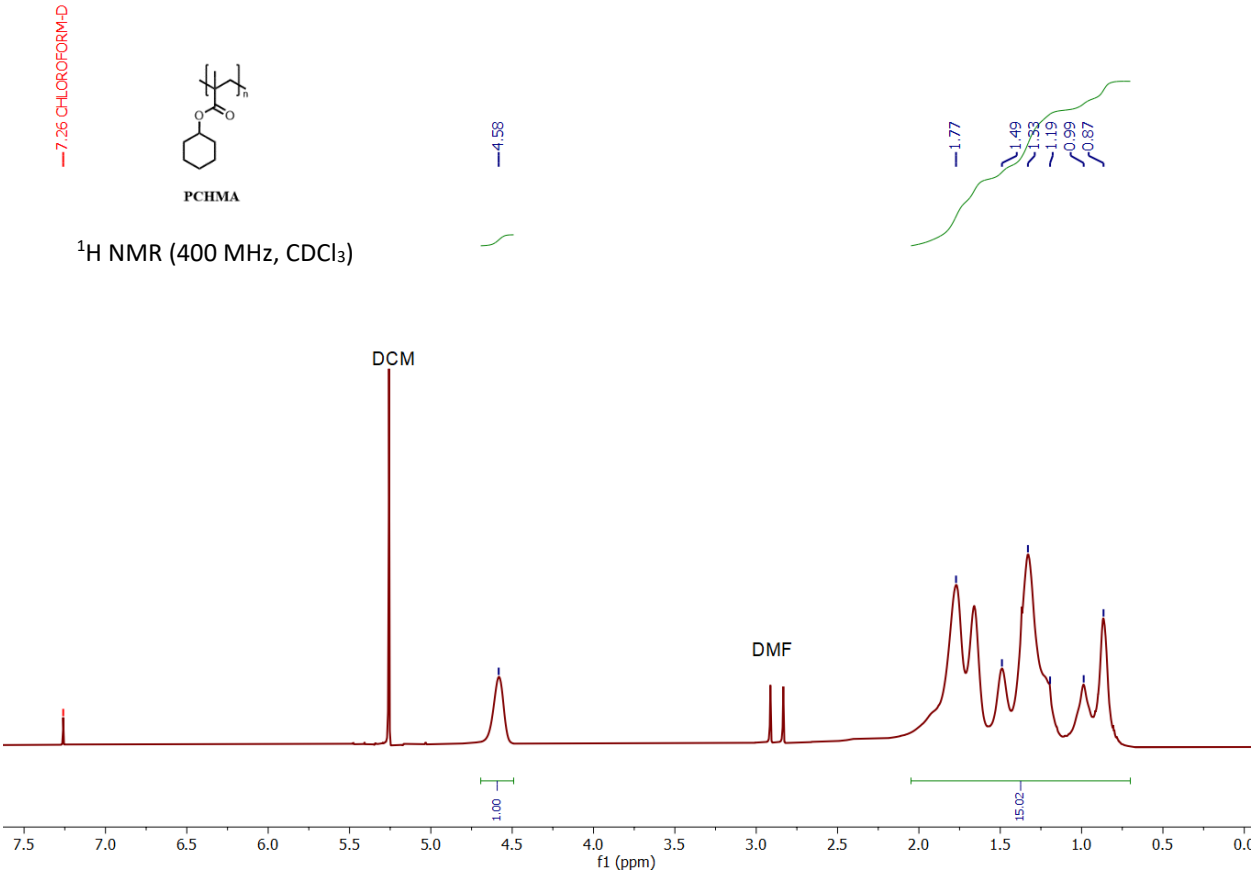


Figure S12. ^{1}H NMR spectrum of compound **PCMA.**

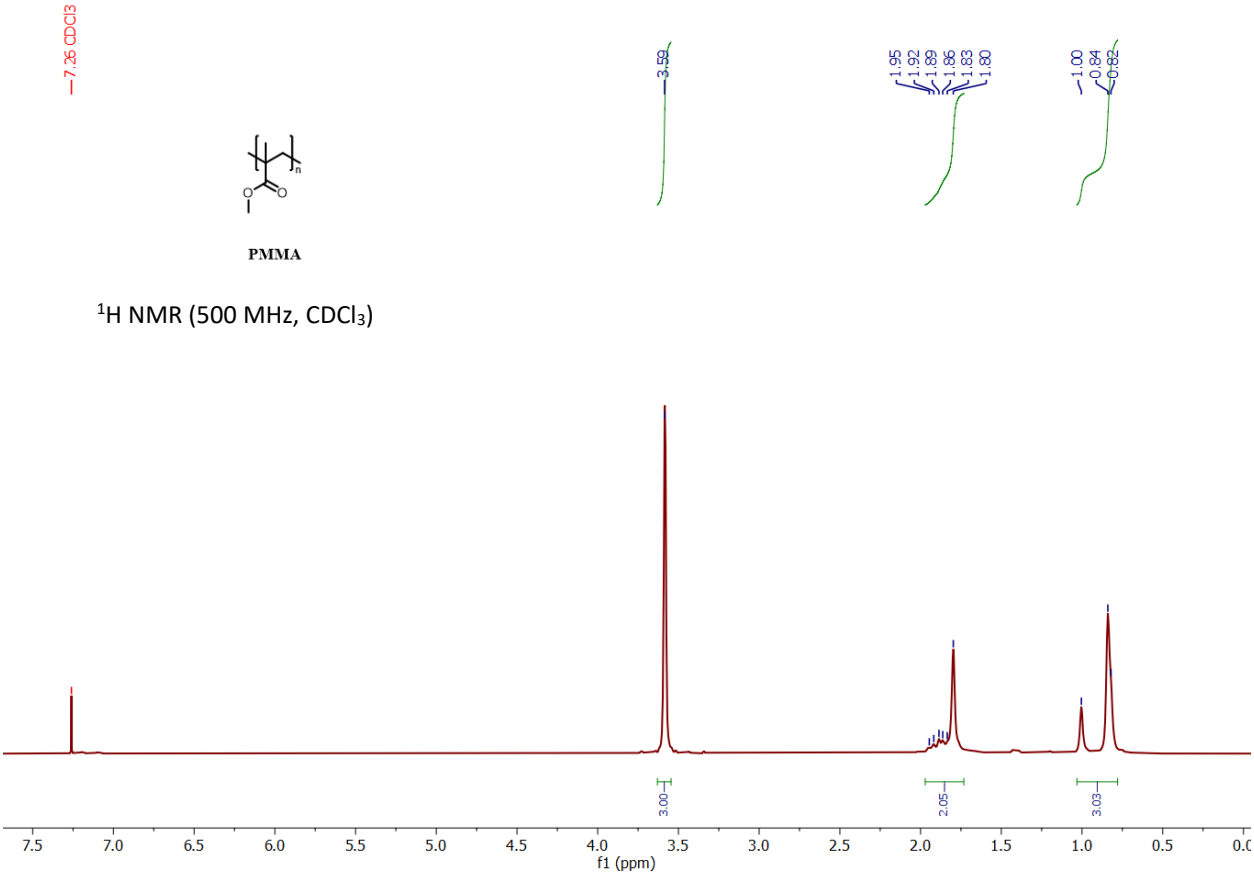


Figure S13. ^{1}H NMR spectrum of compound **PMMA.**

Photoisomerization Studies:

Photoisomerization, the process in which the absorption of photons triggers changes in molecular configuration, was systematically explored in both the solution state and also in thin films. Throughout this work, we subjected the samples to the light exposure, continuously monitoring the changes employing a combination of spectroscopic techniques, including UV-Vis and NMR spectroscopy.

A) Absorption spectra of photoswitching:

The photoisomerization studies were carried out using various light sources, including UV (370 nm, 254 nm), blue (456 nm), green (525 nm), and red (640 nm) Kessil lamps, The average intensity of PR160 series is 399 mW/cm^2 (measured from 1 cm distance) except for 254 nm intensity was 8 mW/cm^2. The experiments were performed in quartz glass cuvettes with a path length of 1 cm and HPLC grade solvents. The photostationary state (PSS) distributions were calculated using the following equation:

$$\chi_{open} = (A_0 - A_{PSS} / A_0) \times 100\%$$

where, χ= Percentage of molecules undergone ring opening at the PSS.

A_0 = Absorbance at initial state; A_{PSS} = Absorbance at PSS

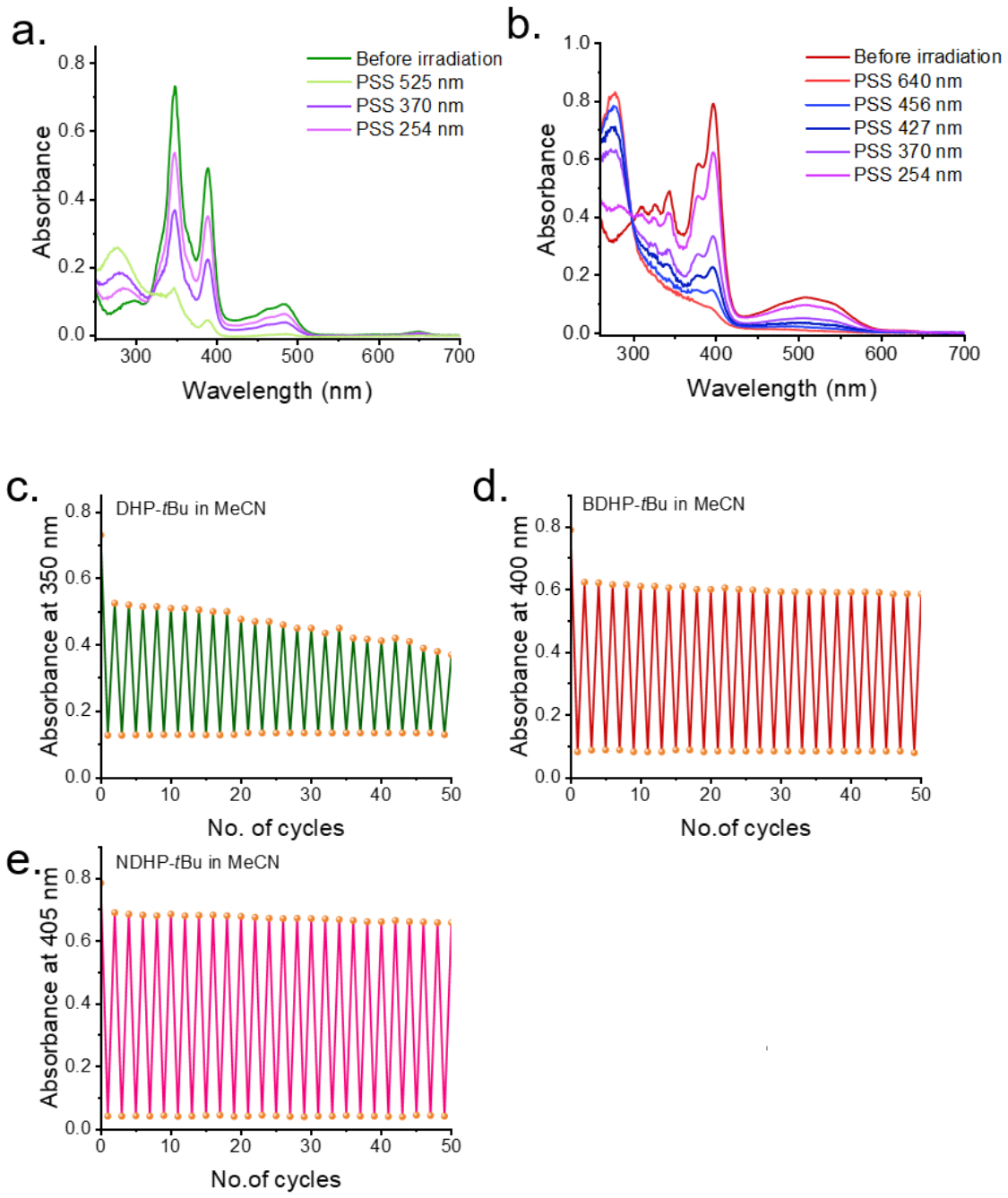


Figure S14. Absorbance spectra of photoisomerization: (a) DHP-tBu (b) BDHP-tBu in acetonitrile solution (10 μM, 298 K). (c) Up to 50 switching cycles for DHP-tBu in MeCN were achieved upon alternate irradiation with 525 nm and 254 nm light. Up to 50 switching cycles for (d) BDHP-tBu and (e) NDHP-tBu in MeCN were achieved upon alternate irradiation with 640 nm and 254 nm light.

B) Arrhenius and Eyring plots:

The freshly prepared solutions of the photochromic compounds were subjected to exposure of light at distinct wavelengths (525 nm or 640 nm) corresponding to their photochemical characteristics until a photostationary state (PSS) rich in the photoisomerized open form was attained. To initiate the reverse reaction, the same samples rich in the opened form of PSS were transferred to a dark setting within a Peltier module (temperature specified in the graphs). Absorbance *vs* time data at each of the temperatures were fitted to exponential plots. The fitted parameters were used to construct the Arrhenius plot that allowed determination of the thermal half-lives of the open forms at 298 K by extrapolation.

the rate constants (*k*) for the thermal reversal were determined using the following equation:

$$[\boldsymbol{CPD}] = [\boldsymbol{CPD}]_{\boldsymbol{0}}\boldsymbol{e}^{-\boldsymbol{kT}}$$

Half-life ($t_{1/2}$)= **0.693/k**.

Arrhenius equation, $\boldsymbol{ln\ k = ln\ A - E_a/RT}$, from the plot of ln *k* vs 1/T, we got, $slope = -E_a/R$ and

Eyring equation, $\boldsymbol{ln\ (k/T) = -\Delta H^{\neq}/RT + ln\ (k_b/h) + \Delta S^{\neq}/R}$, from the plot of ln (*k*/T) vs 1/T, we got

$slope = -\Delta H^{\neq}/R$ and $intercept = \Delta S^{\neq}/R$.

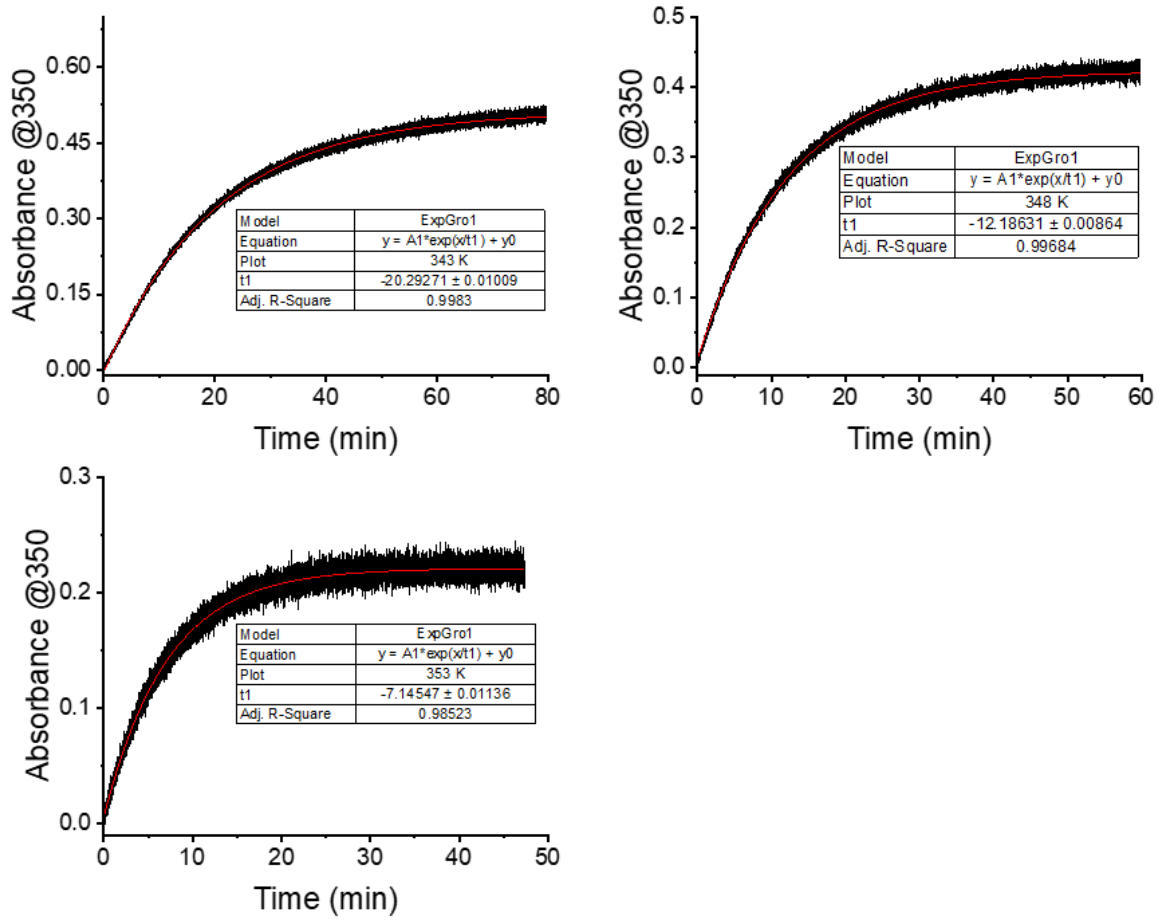


Figure S15. Kinetics plot of DHP-tBu at variable temperatures (343 K, 348 K, and 353 K, respectively) for the open to closed isomer thermal reversal. The absorbance at 350 nm at each temperature was fitted to an exponential fit.

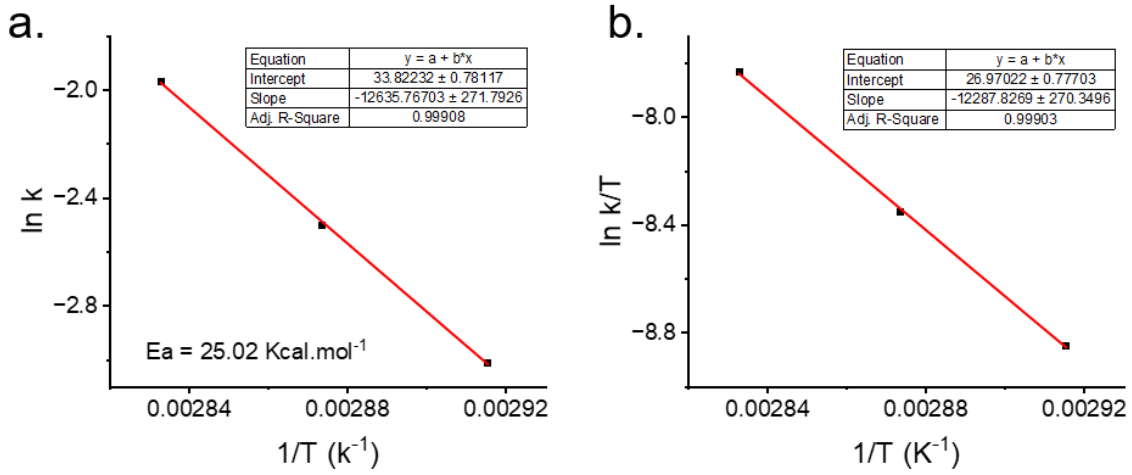


Figure S16. Arrhenius plot and Eyring plot of compound **DHP-tBu**.

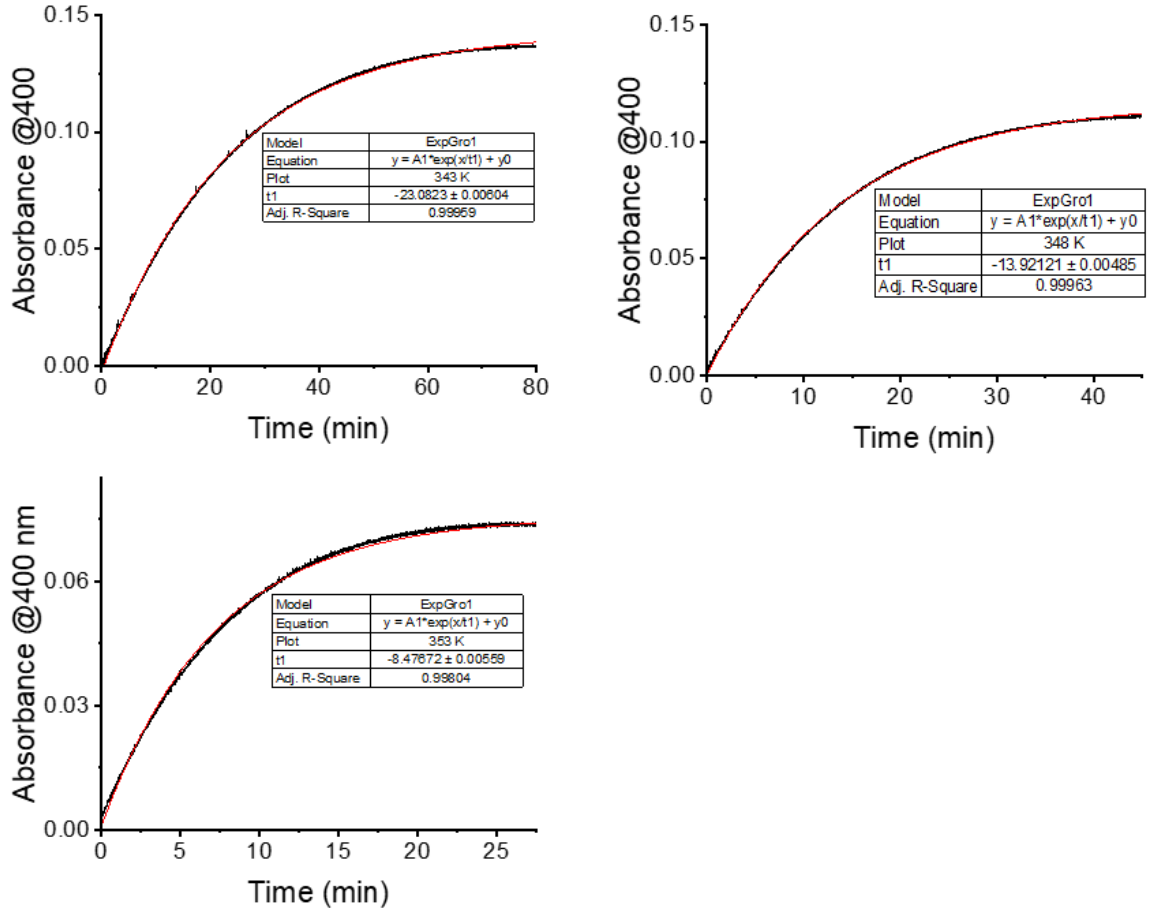


Figure S17. Kinetics plot of **BDHP-tBu** at variable temperatures (343 K, 348 K, and 353 K respectively) for the open to closed isomer thermal reversal. The absorbance at 400 nm at each temperature was fitted to an exponential fit.

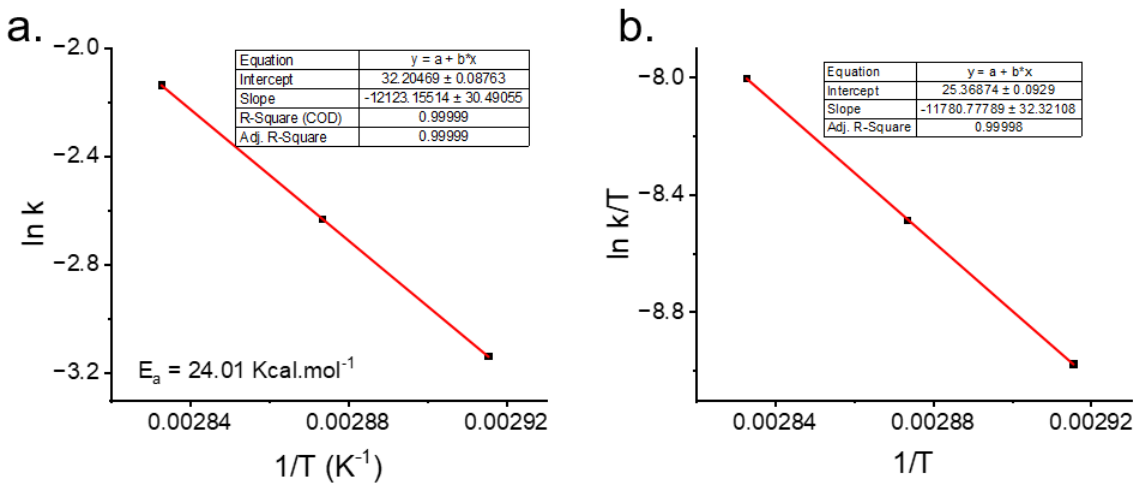


Figure S18. Arrhenius plot and Eyring plot of compound **BDHP-tBu**.

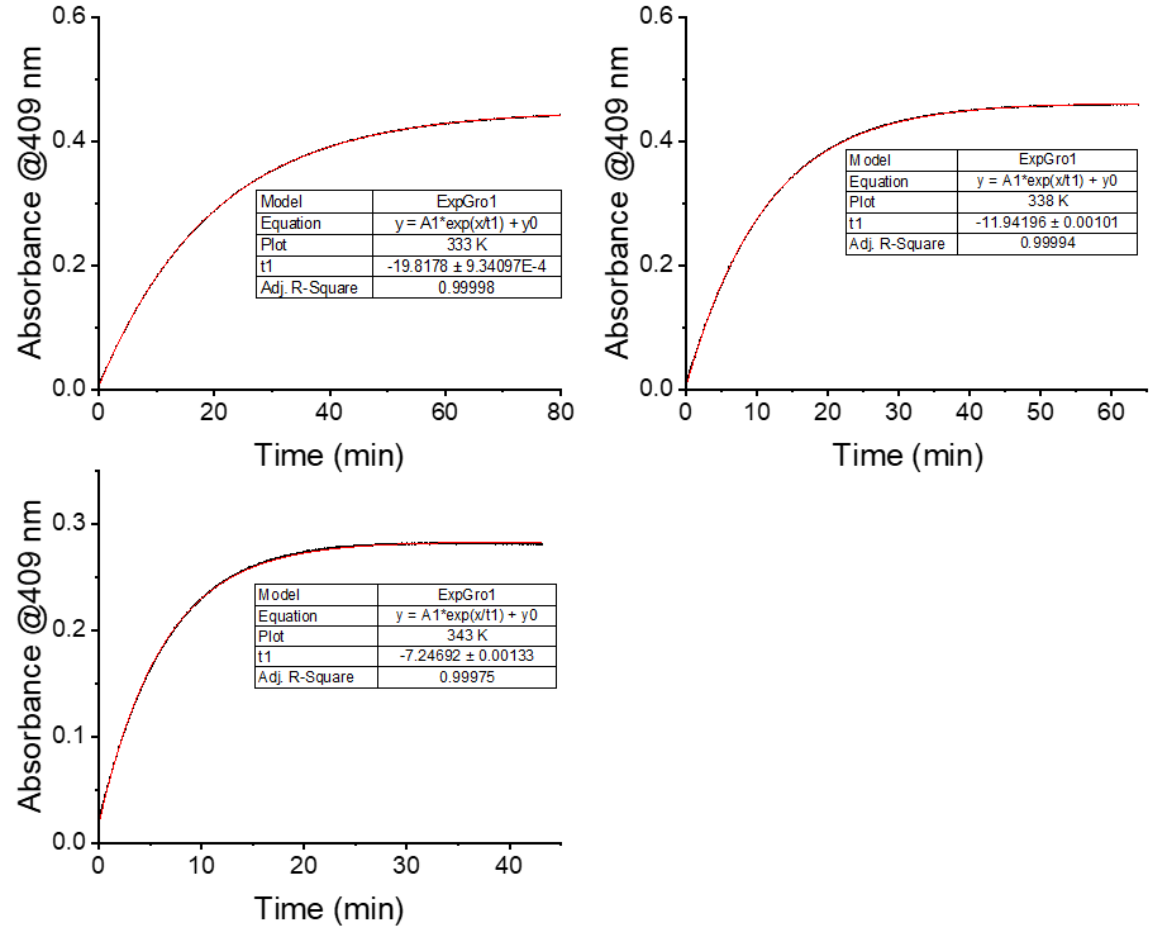


Figure S19. Kinetics plot of **NDHP-tBu** at variable temperatures (333 K, 338 K, 343 K respectively) for

the open to closed isomer thermal reversal. The absorbance at 409 nm at each temperature was fitted to an exponential fit.

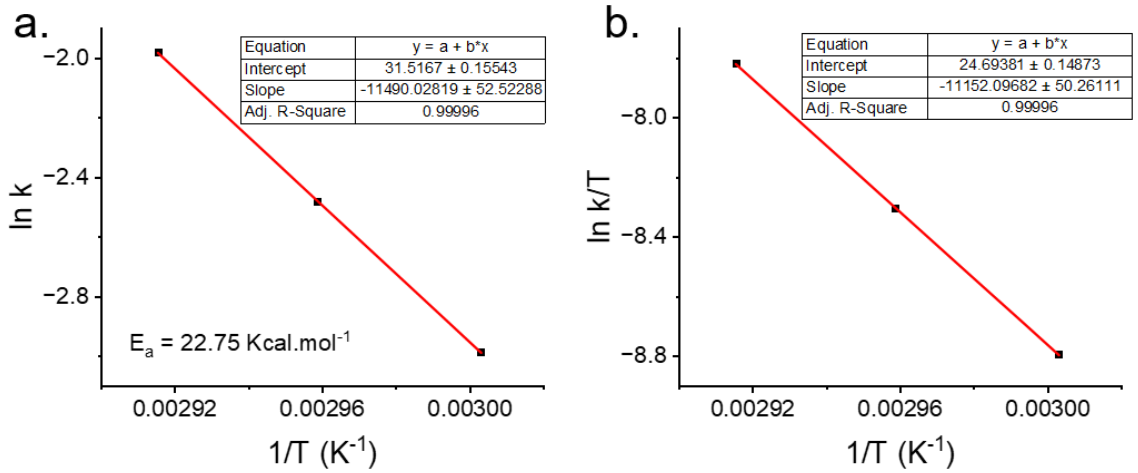


Figure S20. Arrhenius plot and Eyring plot of compound **NDHP-tBu**.

Table S1. Photochemical and thermodynamic properties of the tert-butyl-substituted derivatives (DHP-tBu, BDHP-tBu, NDHP-tBu) in solution (10 μM in acetonitrile).

Compounds	PSS in respective λ's (ring opened isomer)	$PSS_{254\ nm}$ (ring closed isomer)	Activation energy (E_a) for reverse reaction (kcal/mol)	Enthalpy of activation ($\Delta H^{\neq}$) for reverse reaction (kcal/mol)	$t_{1/2}$ (h) at 298K
DHP-tBu	95% with 525 nm	74%	25.02 ± 0.54	24.33 ± 0.54	61 h
BDHP-tBu	99% with 640 nm	84%	24.01 ± 0.06	23.33 ± 0.07	55 h
NDHP-tBu	99% with 640 nm	90%	22.75 ± 0.10	22.08 ± 0.10	14 h

Photoisomerization quantum yield

Quantum yield has been calculated using previously reported method.[7]

The rate of a unidirectional photochemical reaction initiated with monochromatic light is given by:

$$r_{A\rightarrow B} = \frac{q_{in}\Phi_{A\rightarrow B}}{V}\left(1 - 10^{-\varepsilon_A[A]l}\right) \qquad (1)$$

In our case, since the value of absorbance of the compounds DHP-tBu (at 525 nm), BDHP-tBu and NDHP-tBu (at 640 nm, wavelength at which the quantum yield was measured) was much less than 0.4, Taylor series expansion of the exponential function and subsequent truncation at the linear term was carried out leading to a first-order rate equation (2). This equation can be further expressed in terms of the quantum yield and the observed first-order rate constant, photon flux and other known measurable quantities for the sample (see below) leading to equation (3):

$$r_{A\rightarrow B} = q_{in}\Phi_{A\rightarrow B}\varepsilon_A l\, V\,[A] \qquad (2)$$

$$\Phi_{A\rightarrow B} = \frac{k\,V}{q_{in}\varepsilon_A l\, ln\,10} \qquad (3)$$

Where Φ = quantum yield; k= rate constant (obtained from the exponential fit of a graph of A vs. time); V = sample volume; ε_A= molar extinction coefficient; l = pathlength; and q = molar photon flux.

Molar photon flux:

$$q_{in} = \frac{P\lambda}{hcN_A} \qquad (4)$$

where P = power (of the laser); λ = pump wavelength; h = Planck's constant; c = speed of light; and N_A = Avogadro's number.

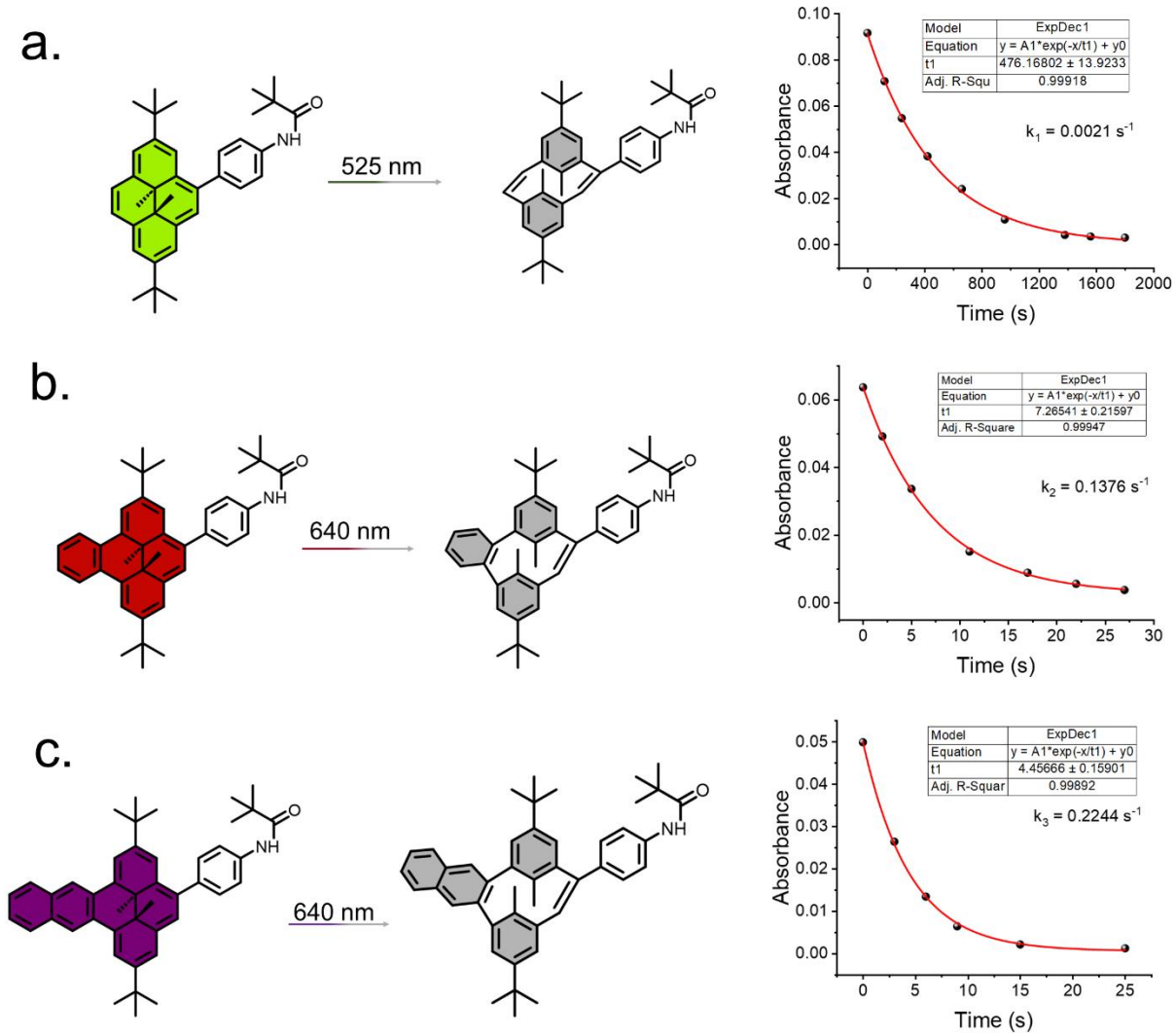


Figure S21. Kinetics for ring opening photoisomerization of a) DHP-tBu b) BDHP-tBu and c) NDHP-tBu, used for quantum yield calculations (fitted to an exponential fit to get *k*).

Table S2. Estimation of quantum yield for the forward photoisomerization of in acetonitrile.

Compound	Wavelength (λ)(nm)	Extinction coefficient (ε_A) at λ ($Lmol^{-1}cm^{-1}$)	Rate constant (k) s^{-1}	Photon Flux (q_{in}) (10^{-6})	Quantum yield (Φ) (10^{-2})
DHP-tBu	525	2500	0.0021	0.878	0.042
BDHP-tBu	640	4100	0.1376	1.07	1.36
NDHP-tBu	640	5700	0.2244	1.07	1.60

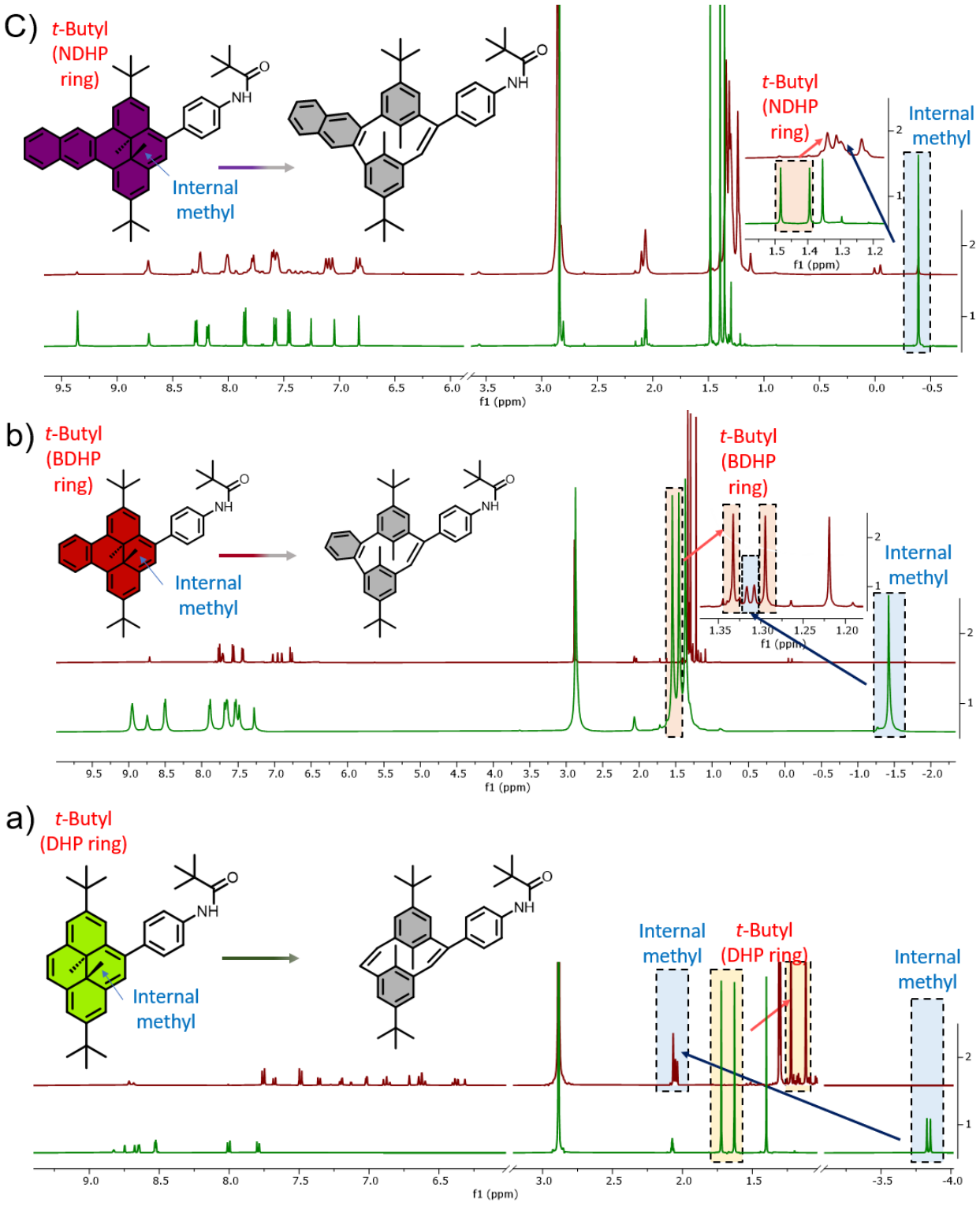

c)
t-Butyl (NDHP ring)
Internal methyl
t-Butyl (NDHP ring)
Internal methyl
f1 (ppm)
b)
t-Butyl (BDHP ring)
Internal methyl
t-Butyl (BDHP ring)
Internal methyl
f1 (ppm)
a)
t-Butyl (DHP ring)
Internal methyl
Internal methyl
t-Butyl (DHP ring)
Internal methyl
f1 (ppm)

Figure S22. ^{1}H NMR spectra of a) DHP-tBu, b) BDHP-tBu and c) NDHP-tBu before irradiation (red) and after irradiation (525 nm for 50 min in case of DHP-tBu and 640 nm for 10 min for the other two derivatives). All spectra acquired in Acetone-d6 with 50 mM compounds. The chemical shifts in the negative region disappeared upon photoisomerization as the ring opening accompanies loss of aromaticity. Also, a significant change of chemical shift in the aromatic region have been observed.

Sample preparation for thin film studies:

Quartz slides (30 x 25 mm) were sonicated in isopropanol and acetone and dried. Meanwhile, a polymer and compound composite has been prepared with 0.5%, 1%, 2.5%, 5% and 10 % (w/w%) compounds. Then, this composite was dissolved in the required amount of chloroform and hexane mixture (1:1). When the mixture had dissolved completely. The mixture was spin-coated (750 rpm for 60 seconds) on the quartz slide and then kept for 60 minutes at 50 ℃ to evaporate off any residual solvent. The protocol consistently yielded films of adequate thickness, smoothness, and uniformity.

Table S3. Film preparation solution concentrations:

Compounds	Polymers	Compounds in 100 mg of composite mixture (polymer + compound) (w/w%)	Concentration (chloroform: hexane 1:1)
DHP-tBu/BDHP-tBu/NDHP-tBu	PTBMA/PCMA/PMMA	0.5	100 mg per 0.5 ml
		1	100 mg per 1 ml
		2.5	100 mg per 2.5 ml
		5	100 mg per 5 ml
		10	100 mg per 10 ml

Photoisomerization in thin films:

The experimental procedure of photoisomerization studies in thin films is quite similar to solution state studies. Here, the prepared films are analyzed using UV-vis spectroscopic technique. First, the absorption spectrum of the film is recorded in the dark to get the spectrum of the closed isomer (DHP-tBu, BDHP-tBu, NDHP-tBu). Then, the film is irradiated with the desired wavelength of a light source to induce the photoisomerization process. The change in the UV absorbance spectra have been monitored with regular intervals of time until it reaches a photostationary state (PSS). Similarly, the reverse isomerization can also be monitored by following the same procedure, starting with the corresponding open isomers.

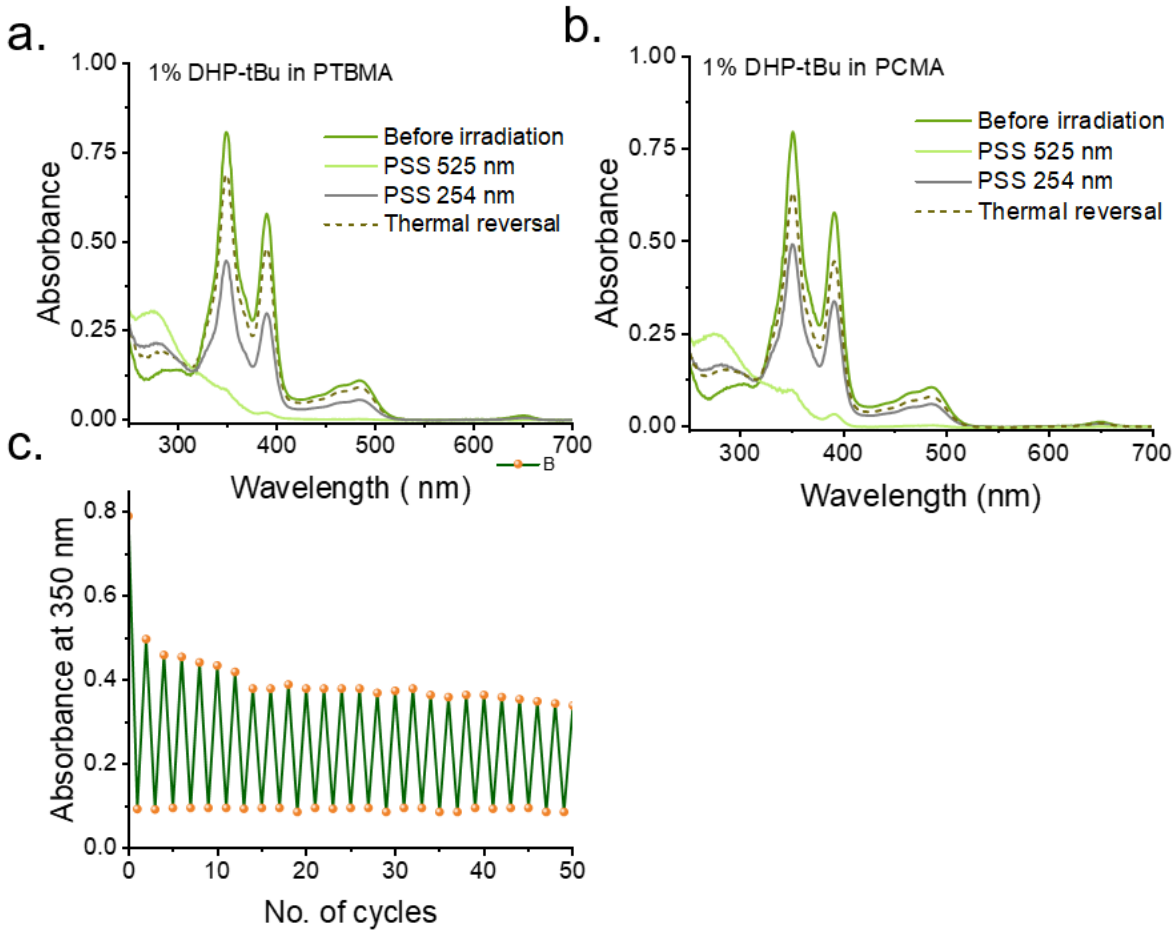


Figure S23. Absorption spectra of DHP-tBu at 298 K in (a) PTBMA (b) PCMA with several PSS distribution upon exposure to a light. The spectra after the thermal reversal at 65°C has been shown with the dotted line. (c) Up to 50 switching cycles for DHP-tBu in PMMA upon alternate irradiation with 525 nm and 254 nm light.

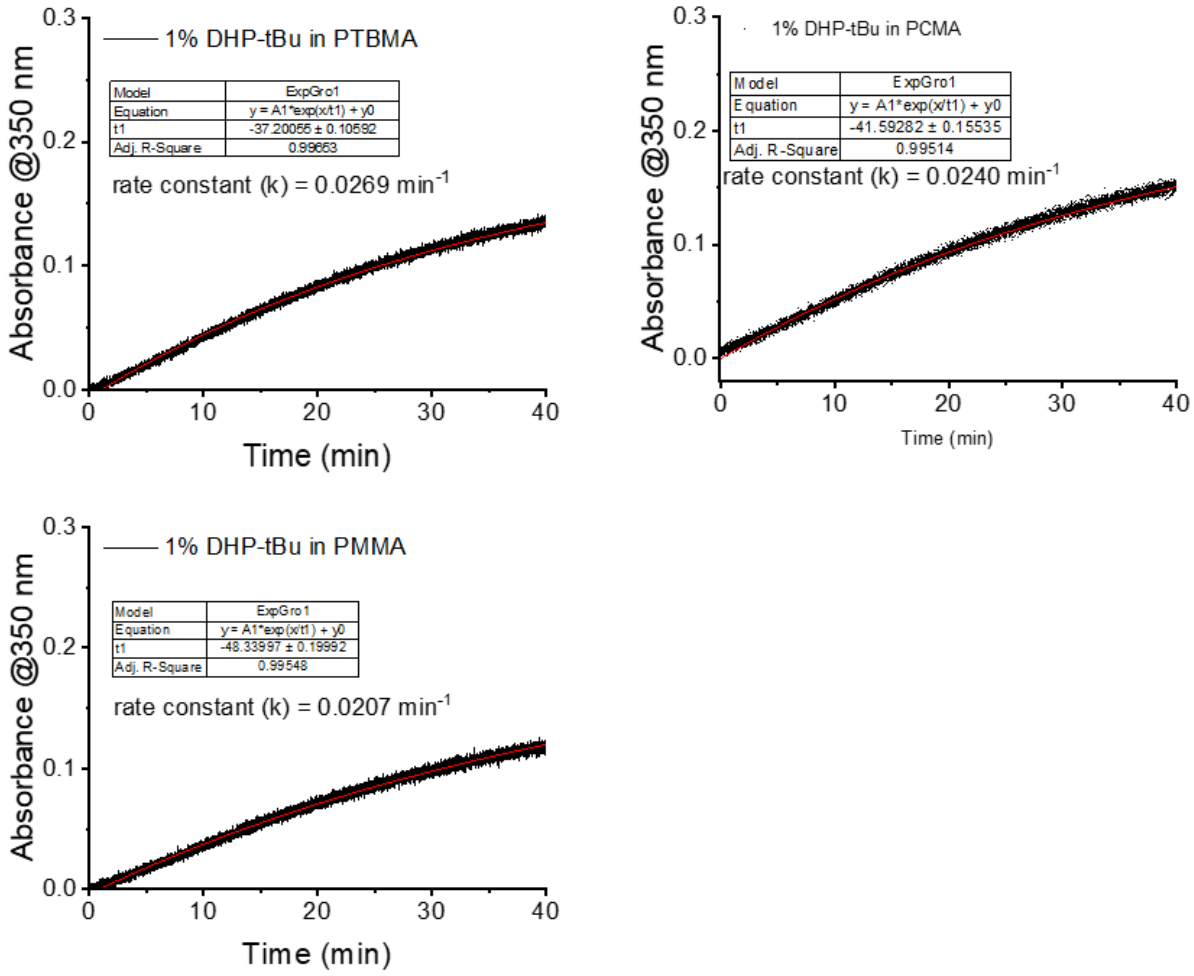


Figure S24. Kinetics plot of DHP-tBu at 338 K for the open to closed isomer thermal reversal different polymer matrix. The absorbance at 350 nm at each temperature was fitted to an exponential fit to get k.

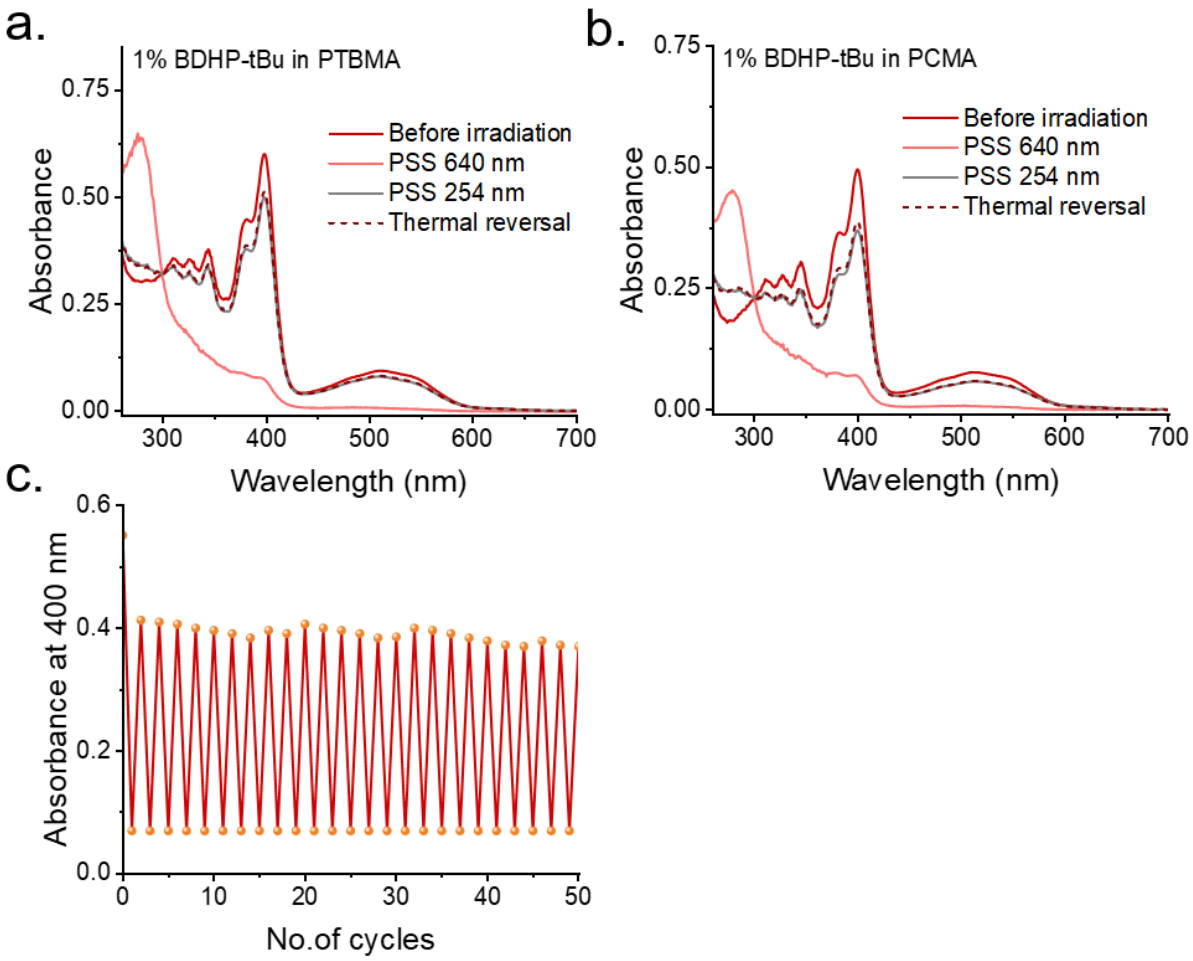


Figure S25. Absorption spectra of BDHP-tBu at room temperature in (a) PTBMA (b) PCMA with several PSS distribution upon exposure to a light. The spectra after the thermal reversal at 65°C has been shown with the dotted line. c) Up to 50 switching cycles for BDHP-tBu in PMMA upon alternate irradiation with 640 nm and 254 nm light.

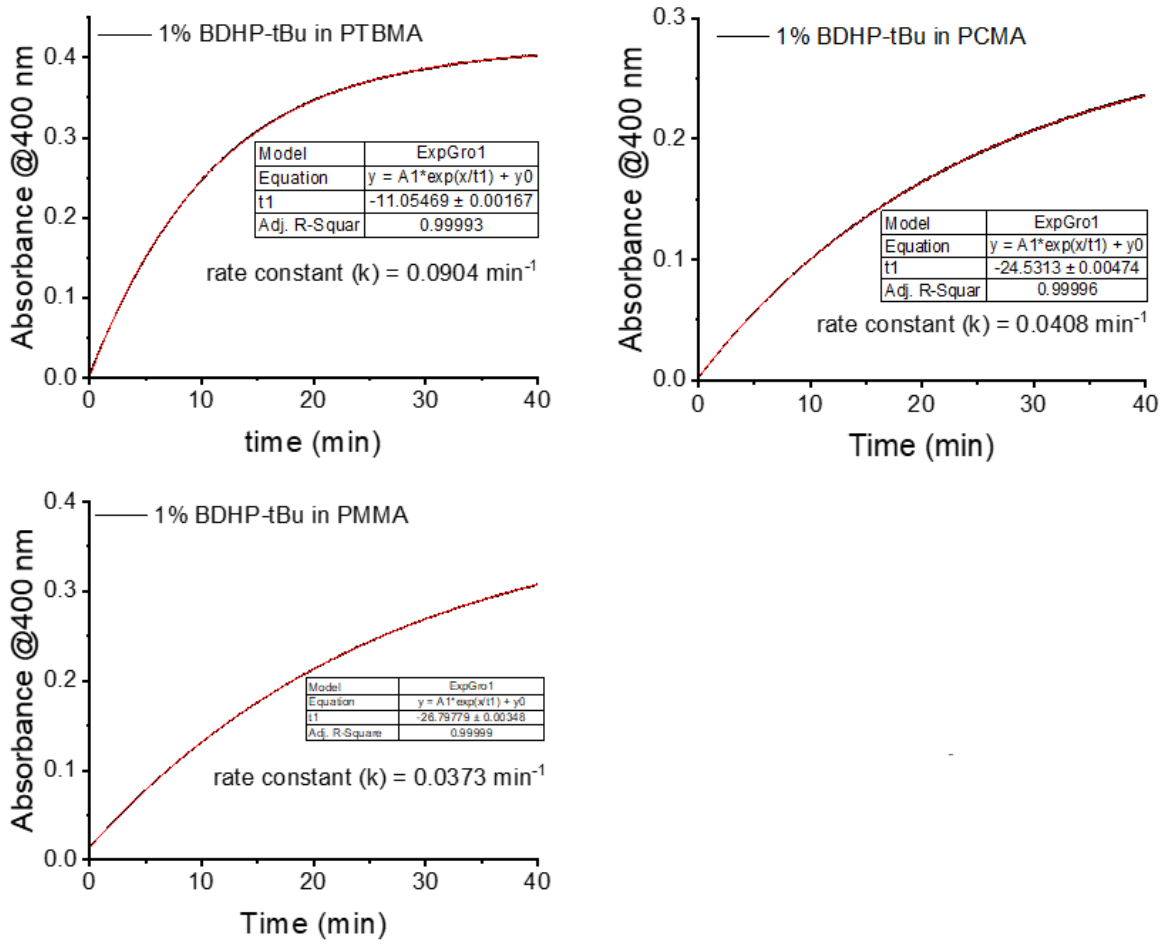


Figure S26. Kinetics plot of BDHP-tBu at 338 K for the open to closed isomer thermal reversal different polymer matrix. The absorbance at 400 nm at each temperature was fitted to an exponential fit to get *k*.

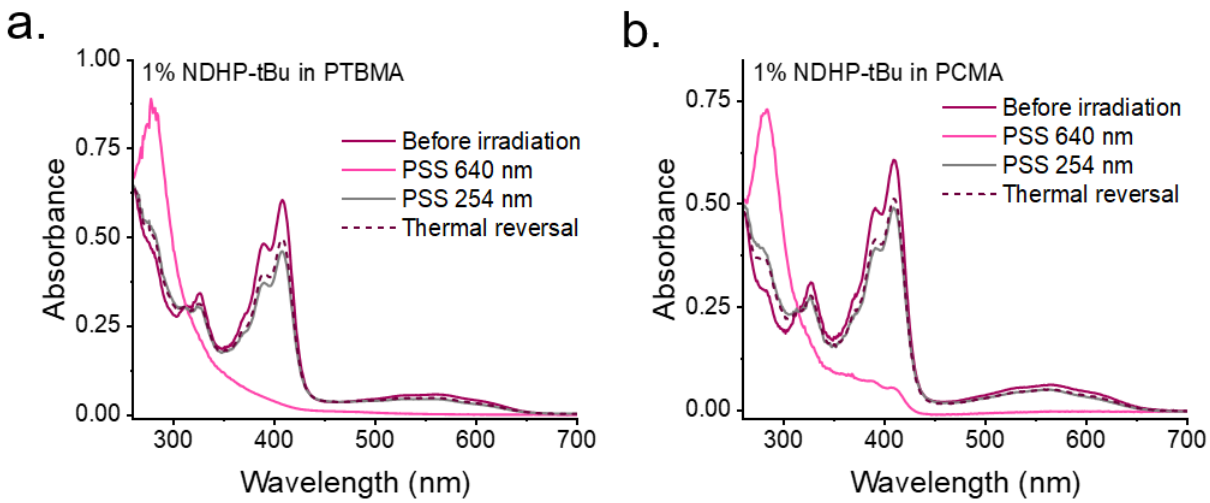


Figure S27. Absorption spectra of NDHP-tBu at room temperature in (a) PTBMA (b) PCMA with several PSS distribution upon exposure to a light. The spectra after the thermal reversal at 65°C has been shown with the dotted line.

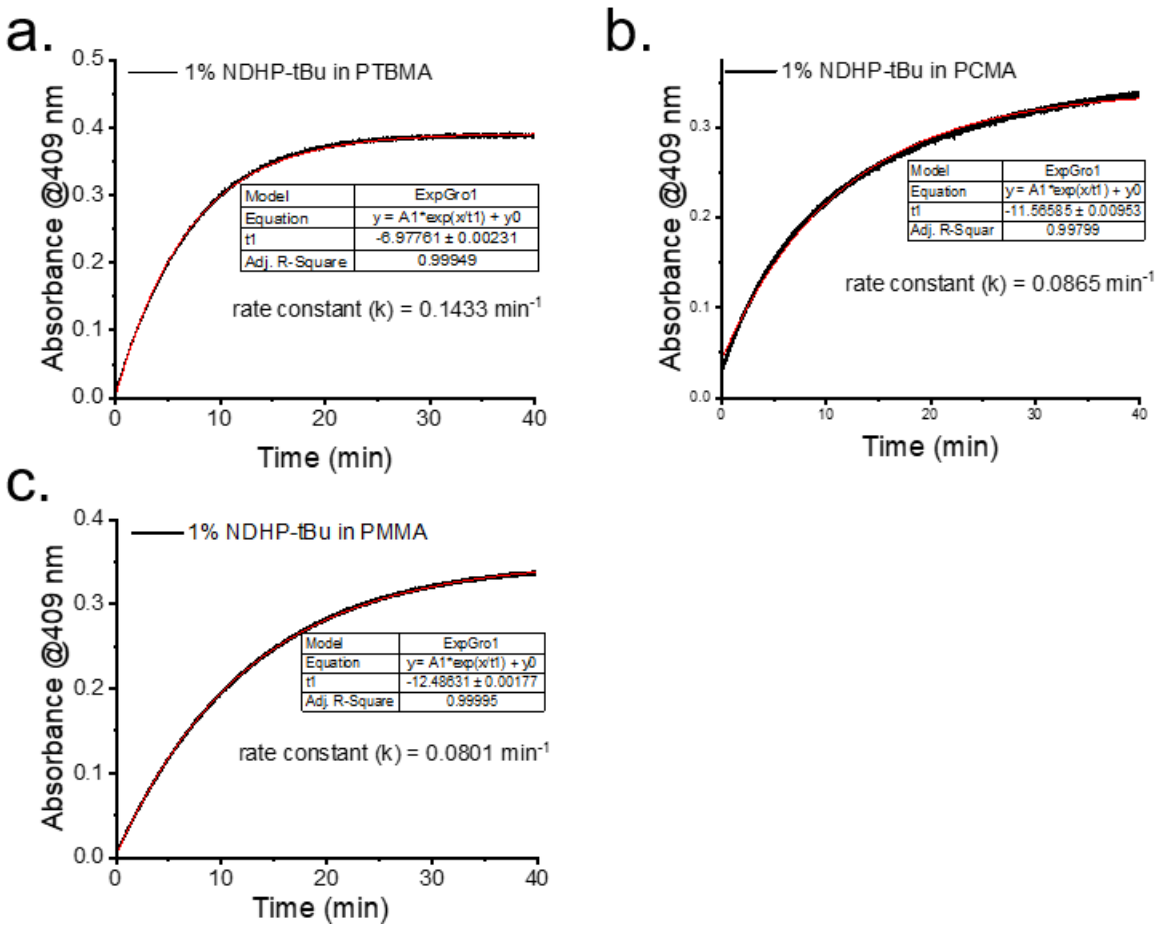


Figure S28. Kinetics plot of NDHP-tBu at 338 K for the open to closed isomer thermal reversal in different polymer matrix. The absorbance at 409 nm at each temperature was fitted to an exponential fit to get the *k*.

Table S4. Photochemical properties of the tert-butyl-substituted derivatives (DHP-tBu, BDHP-tBu, NDHP-tBu) in spin coated thin films.

Compounds	Polymer matrix	PSS of opened form (closed to open). 525 nm for DHP-tBu and 640 nm for other two derivative.	PSS of closed form (open to closed) with 254 nm	rate constants (k) (min^{-1}) for the thermal reversal at 338 K	Goodness of fit value (R^2)	$t_{1/2}$ (min) at 338K
DHP-tBu	PTBMA	95	60	0.0269	0.996	25.8
	PCMA	93	68	0.0240	0.995	28.9
	PMMA	88	62	0.0207	0.995	33.5
BDHP-tBu	PTBMA	89	83	0.0904	0.999	11.1
	PCMA	86	74	0.0408	0.999	17.0
	PMMA	88	75	0.0373	0.999	18.6
NDHP-tBu	PTBMA	94	77	0.1433	0.999	4.8
	PCMA	91	81	0.0865	0.997	8.1
	PMMA	92	73	0.0801	0.999	8.7

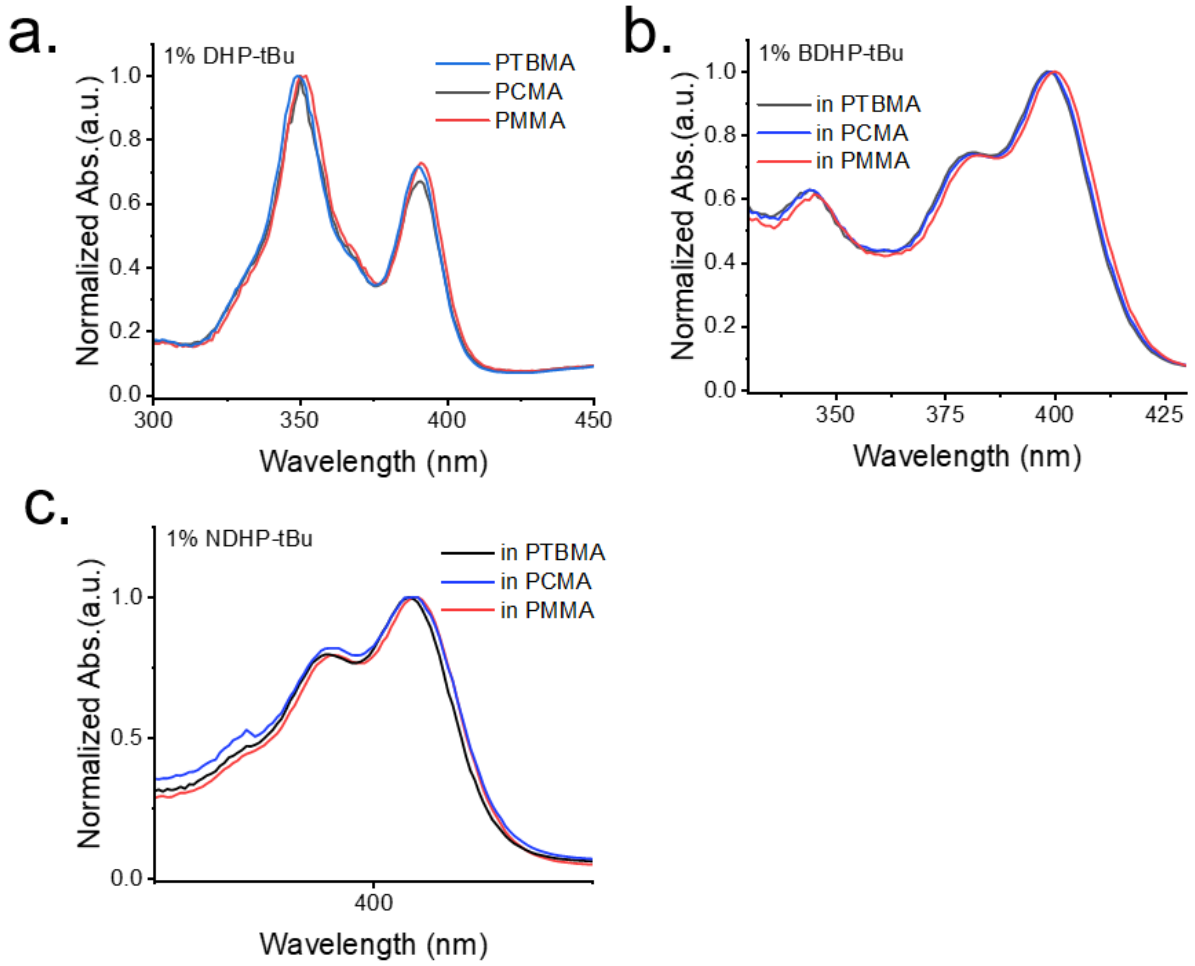


Figure S29. A zoomed in normalized absorption spectra of a) DHP-tBu b) BDHP-tBu c) NDHP-tBu at room temperature in PTBMA, PCMA and PMMA environment, showing minimal change in absorption specta.

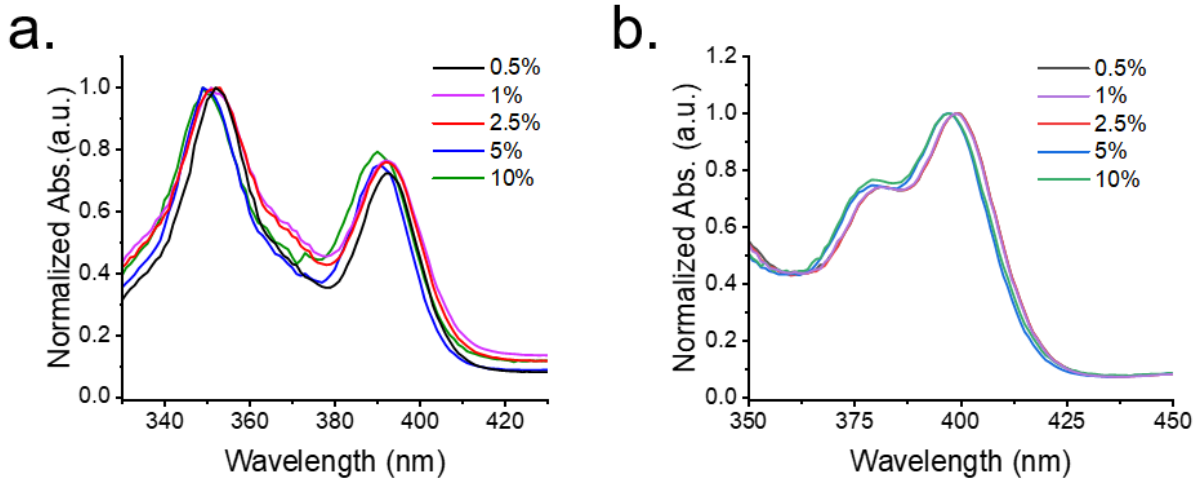


Figure S30. A zoomed in normalized absorption spectra of a) DHP-tBu b) BDHP-tBu at room temperature in different % (w/w) loading of sample in PMMA environment, showing a small blue shift of λ_{max}.

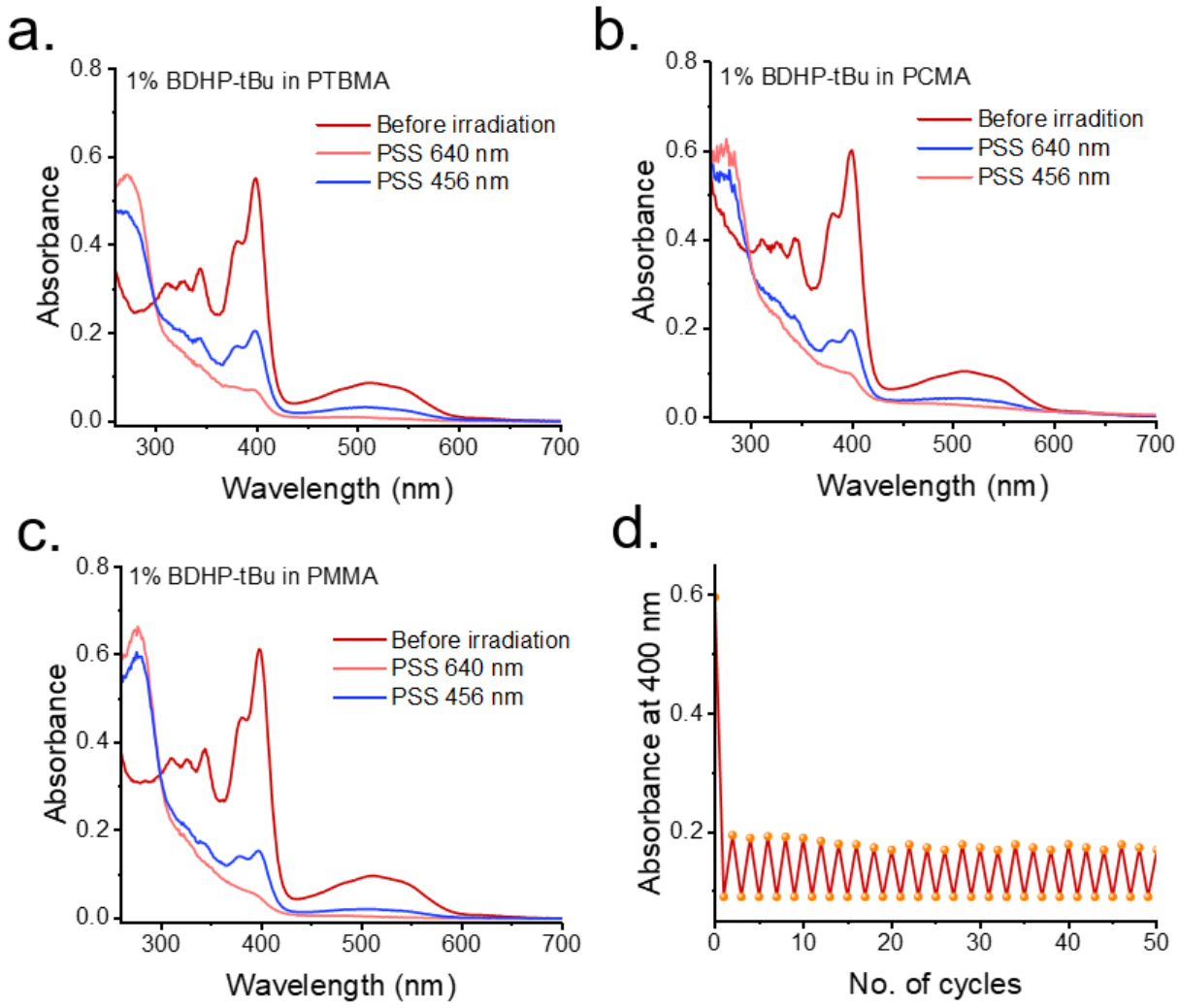


Figure S31. Absorption spectra of BDHP-tBu in (a) PTBMA (b) PCMA and c) PMMA with several PSS distribution upon exposure to visible light only. d) Up to 50 switching cycles for BDHP-tBu in PTBMA upon alternate irradiation with 640 nm and 456 nm light.

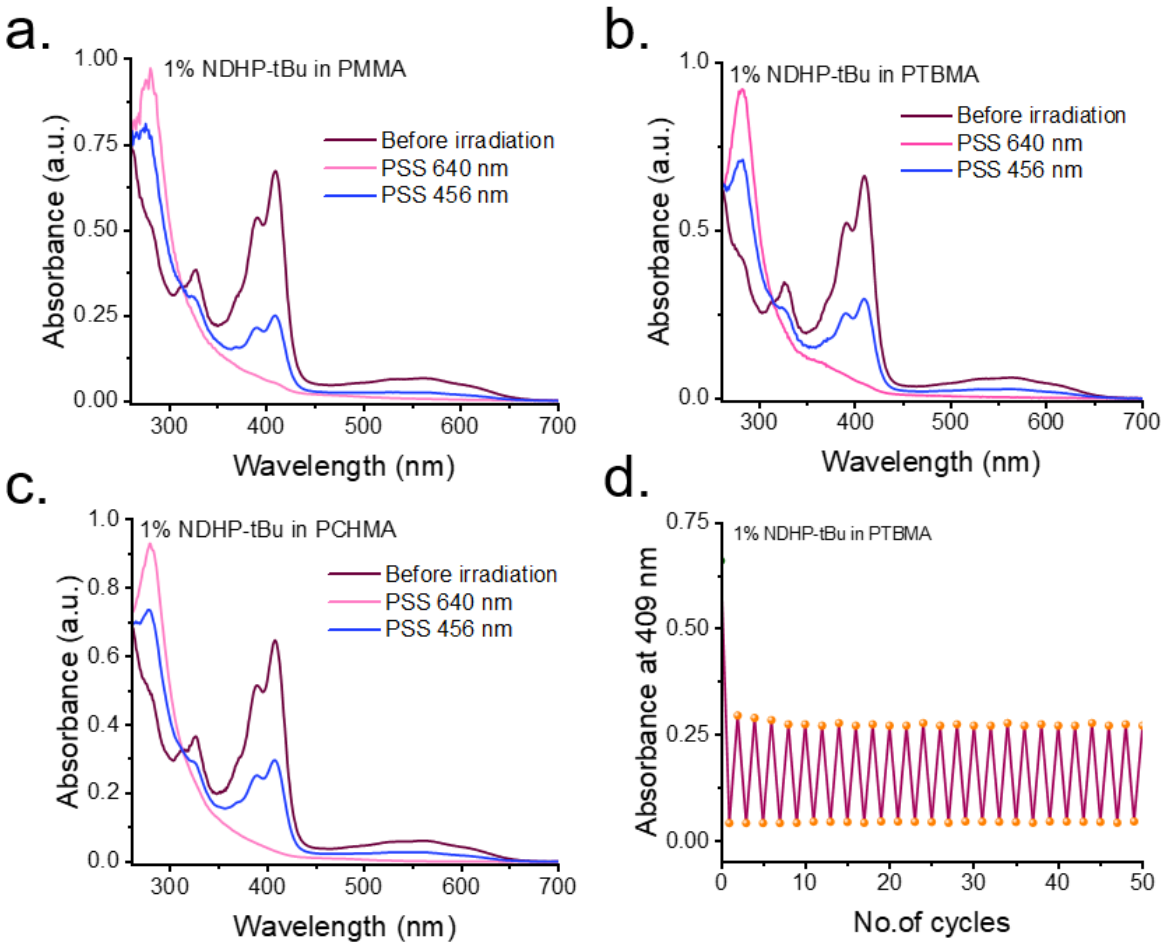


Figure S32. Absorption spectra of NDHP-tBu in (a) PTBMA (b) PCMA and c) PMMA with several PSS distribution upon exposure to visible light only. d) Up to 50 switching cycles for NDHP-tBu in PTBMA upon alternate irradiation with 640 nm and 456 nm light.

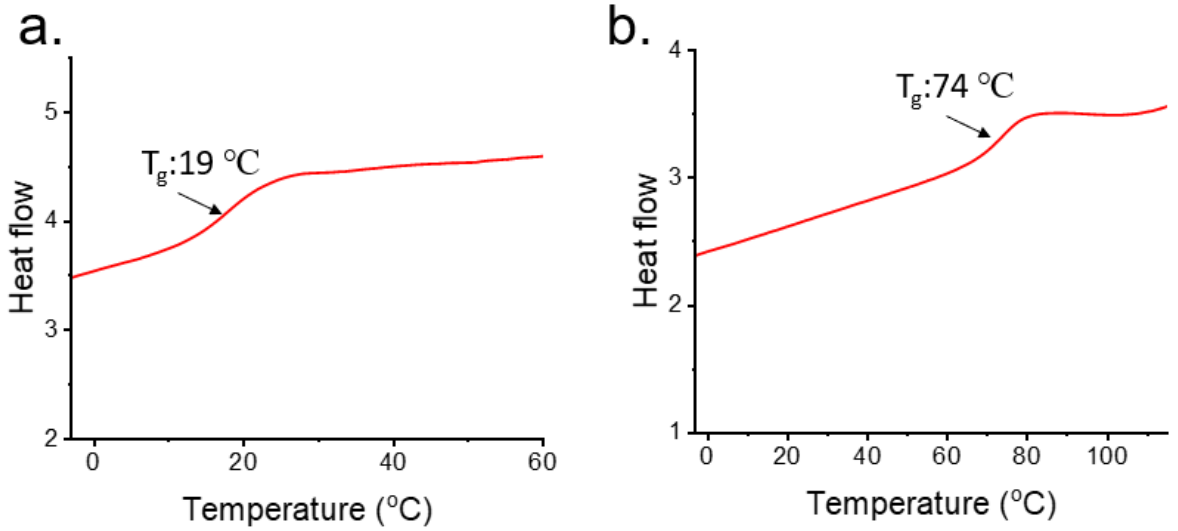


Figure S33. DSC curves of (a) PTBMA (b) PCMA at a heating rate of 5 °C/min.

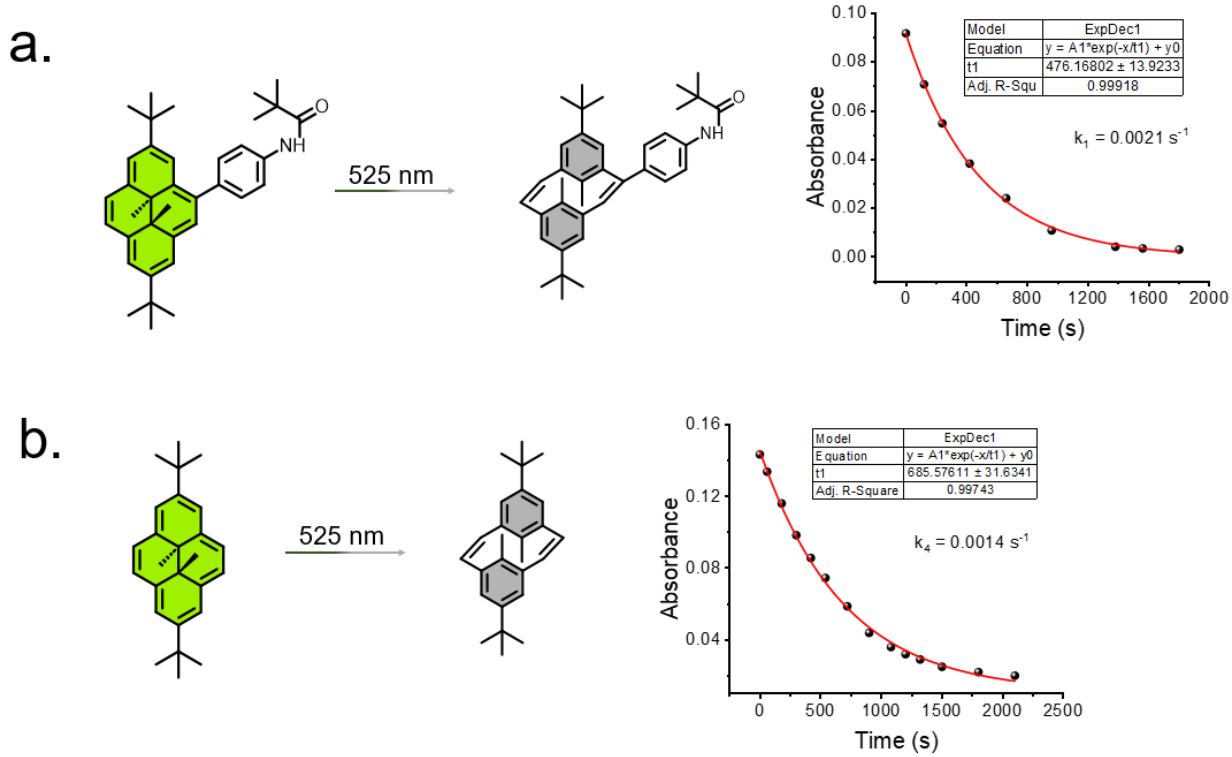


Figure S34. Kinetics for ring opening photoisomerization of a) DHP-tBu b) DHP in acetonitrile under identical conditions (fitted to an exponential fit to get *k*).

k_1/k_4=1.5;

From the result of photochemical ring opening using 10 μM solution in acetonitrile, it is clear that the photochemical ring opening of DHP-tBu (with pivaloyl group protected 4-aminophenyl substituent) is 1.5 times faster compared to DHP (without any substitution) under identical conditions.

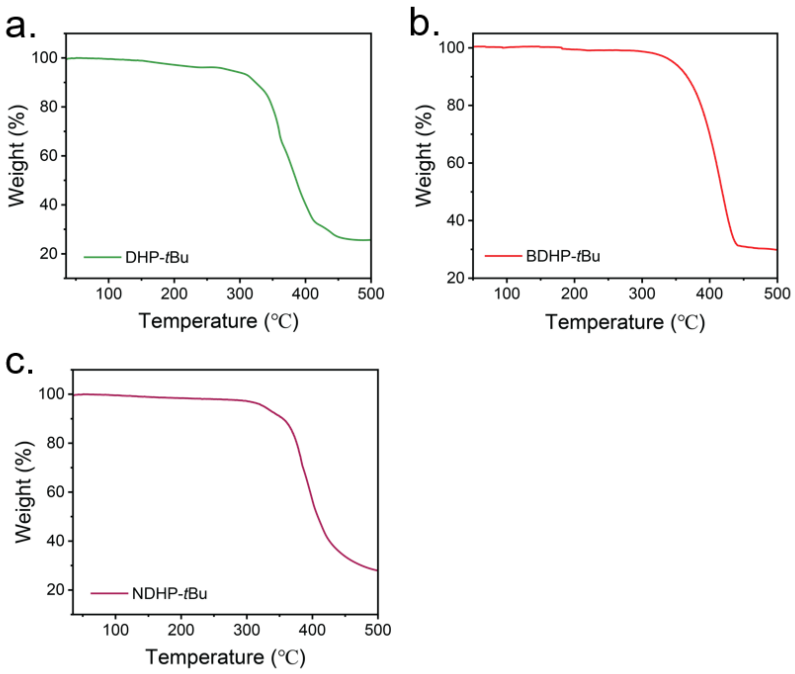


Figure S35. Thermal analysis of (a) DHP-tBu (b) BDHP-tBu and (c) NDHP-tBu, TGA plots showing the decomposition of the sample after 350 °C.

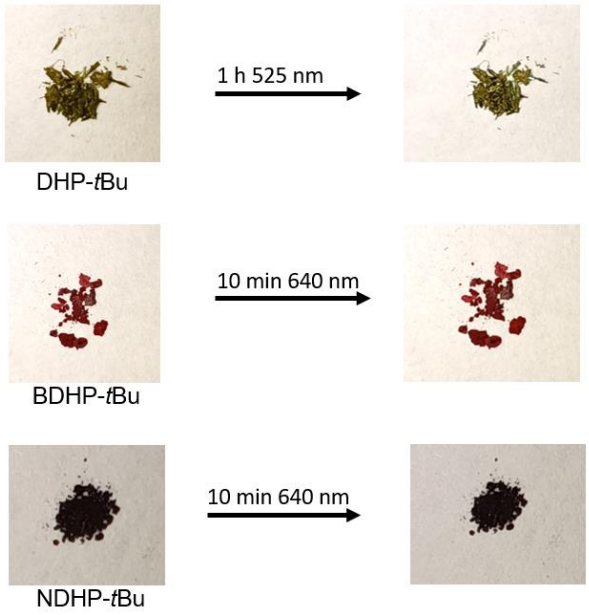


Figure S36. Snapshots taken before and after exposure to light on the solid samples. To compare our results with pure solid-state photoswitching, we conducted tests with prolonged irradiation in the solid state but did not observe any significant color change. This suggests that the polymer matrix provides a suitable environment for achieving fast and efficient photoswitching in thin films.

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