Electronic Supporting Information

Rhodamine-installed Polynorbornenes: Molecular Design, Structure and Stimuli-Responsive Properties

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1. **Materials:** Materials were used as received: 2-(4-Diethylamino-2-hydroxybenzoyl)benzoic acid (98%, TCI America), resorcinol (1,3-benzene diol, 99%, Sigma Aldrich), trifluoroacetic acid (TFA, 99%, Sigma Aldrich), ethanolamine (98%, Sigma Aldrich), anhydrous ethanol (99.5%, Sigma Aldrich), 5-norbornene-2-carboxylic acid (NBCOOH, mixture of *endo*- and *exo*-isomers, 98%, Sigma Aldrich), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC, 98%, Proteochem), hydroxybenzotriazole (HOBt, 97%, Sigma Aldrich), 11-bromoundecanoic acid (99%, Sigma Aldrich), potassium carbonate (K₂CO₃, 99%, Sigma Aldrich), anhydrous dimethylformamide (DMF, 99%, Acros Organics), dry methylene chloride (CH₂Cl₂, DCM, 99.8%, Acros Organics), anhydrous tetrahydrofuran (THF, 99.8%, Acros Organics), triethylamine (99.5%, Sigma Aldrich), pyridine (99.8%, Acros Organics), 2nd Generation Grubbs Catalyst ((H₂IMes)(pyr)₂(Cl)₂RuCHPh (mG2), 98%, AK Scientific), ethyl vinyl ether (EVE, 99%, Acros Organics). Rhodamine molecule, HO-Rh-OH, was synthesized using a literature protocol¹.
2. Synthesis of Monomers:

2.1 Monomer 1 (NB-Rh-OH):

Rhodamine HO-Rh-OH (500 mg, 1.16 mmol), HOBT (235 mg, 1.74 mmol), EDC (356 mg, 1.86 mmol) and 5-norbornene-2-carboxylic acid (177 mg, 1.28 mmol) were dissolved in DMF (10–12 mL) in a round-bottom flask equipped with a stir bar. The reaction mixture was cooled to 0 °C on an ice bath. Triethylamine (5–6 mL) was added dropwise to the chilled solution under continuous stirring and the reaction mixture turned turbid. Then, the reaction mixture was allowed to gradually warm to room temperature, stirred for 12 h at ambient T, and precipitate formation was observed. This reaction mixture was diluted with distilled water, transferred to a separatory funnel and extracted using CH₂Cl₂ (3 × ~10 mL). The combined organic phase was then treated with brine to remove residual DMF, dried over anhydrous sodium sulfate (Na₂SO₄) and the volume of reaction mixture was reduced using a rotary evaporator. The crude product was purified using column chromatography in which a silica column was packed with mixture of hexane isomers and 3-5 mL of triethylamine. The product was eluted by gradually increasing the polarity of the eluent up to 1:1 ethyl acetate:hexane. The fractions were monitored by TLC; the colorless main band was collected to provide, after removal of the solvent using rotary evaporation, Monomer 1 (NB-Rh-OH) as a white-colored powder in 50% yield (320 mg). HR-MS (ESI+, CH₃OH): m/z calculated
2.2 Monomer 2 (NB-Rh-NB):  

Scheme S2: Representative synthesis of Monomer 2

Prepared as described for Monomer 1 (NB-Rh-OH), except that the stoichiometric ratio of rhodamine HO-Rh-OH to 5-norbornene-2-carboxylic acid was changed to 1:2. Thus, HO-Rh-OH (500 mg, 1.16 mmol), 5-norbornene-2-carboxylic acid (353 mg, 2.56 mmol), EDC (712 mg, 3.72 mmol) and HOBT (471 mg, 3.48 mmol) were dissolved in DMF (15 mL), and triethylamine (7 mL). The workup was similar to Monomer 1. The product was then eluted from the triethylamine-treated silica gel with a 2:3 ethyl acetate:hexanes (isomers) mixture to provide, after removal of the solvent using rotary evaporation, Monomer 2 (NB-Rh-NB) as a white-colored powder in 40% yield (311 mg). HR-MS (ESI+, CH₃OH): m/z calculated for C₄₂H₄₃O₆N₂⁺ [M+H]⁺: 671.3110, found 671.3139. ¹H NMR of Monomer 2 is presented in Figure S2 on Page S15.
2.3 Monomer 3 (NB-(CH$_2$)$_{10}$-Rh-OH):

![Scheme S3](image)

Scheme S3: Representative synthesis of Monomer 3

In Step 1, pure 5-norbornene-2-carboxylic acid (5.0 g, 36 mmol) was converted to its potassium salt by reacting it with potassium carbonate (K$_2$CO$_3$, 5.0 g, 36 mmol) at 80 °C for 15–20 min. In Step 2, the potassium salt of 5-norbornene-2-carboxylic acid thus obtained was reacted with 11-bromoundecanoic acid (8.27 g, 31.2 mmol) dissolved in DMF (130 mL) for 48 h at 100 °C. After this time, a precipitate formation was observed. The volume of the reaction mixture was reduced by rotary evaporation. The reaction mixture was diluted with distilled water, transferred to a separatory funnel and extracted using CH$_2$Cl$_2$ (3 x ~130 mL). The combined organic phase was then treated with brine to remove residual DMF. The collected organic phase was then washed once with 1M HCl, dried over anhydrous sodium sulfate and the volume was reduced by rotary evaporation. The crude product was purified using column chromatography (silica gel) with a 3:7 mixture of ethyl acetate:hexanes to provide, after removal of the solvent using rotary evaporation, NB-(CH$_2$)$_{10}$-COOH as a faint yellowish oily product in 84% yield (7.69 g). $^1$H NMR of intermediate product NB-(CH$_2$)$_{10}$-COOH is presented in Figure S3 on Page S16.
The intermediate product NB-(CH$_2$)$_{10}$-COOH (4.84 g, 15 mmol) was dissolved in DMF (175 mL) together with HO-Rh-OH (6.03 g, 14 mmol), EDC (4.22 g, 22 mmol), HOBT (2.84 g, 21 mmol) and reacted by addition of triethyl amine (87.5 mL) at ice temperatures. The volume of the reaction mixture was reduced by rotary evaporation. The workup and purification of the reaction was carried out as described for the preparation of Monomer 1 (NB-Rh-OH). The product Monomer 3 (NB-(CH$_2$)$_{10}$-Rh-OH) was obtained as a colorless viscous semi-solid in 40% yield (4.12 g). HR-MS (ESI+, CH$_2$Cl$_2$): m/z chemical formula: C$_{45}$H$_{55}$O$_7$N$_2$+: calculated for [M+H]$^+$: 735.3998, found: 735.3954. $^1$H NMR of Monomer 3 is presented in Figure S4 on Page S17.

2.4 Monomer 4 (NB-(CH$_2$)$_{10}$-Rh-(CH$_2$)$_{10}$-NB):

\[
\begin{align*}
\text{Scheme S4: Representative synthesis of Monomer 4} \\
\text{The intermediate product NB-(CH$_2$)$_{10}$-COOH was used and similar synthesis procedure as Monomer 3 was followed except that the stoichiometric ratio of rhodamine HO-Rh-OH to NB-(CH$_2$)$_{10}$-COOH was changed to 1:2. The intermediate product NB-(CH$_2$)$_{10}$-COOH (5 g, 15.5 mmol) was dissolved in DMF (131.8 mL) together with HO-Rh-OH (3.0 g, 7.0 mmol), EDC (4.29 g, 22.4 mmol), HOBT (2.83 g, 21 mmol) and reacted by addition of triethyl amine (65.9 mL) at ice temperatures. The volume of the reaction mixture was reduced by rotary evaporation. The workup and purification of the reaction was carried out as described for the preparation of Monomer 1 (NB-Rh-OH). The product Monomer 4 (NB-(CH$_2$)$_{10}$-Rh-(CH$_2$)$_{10}$-NB) was obtained as a colorless viscous semi-solid in 45% yield (3.27 g). HR-MS (ESI+, CH$_2$Cl$_2$): m/z chemical}
\end{align*}
\]
formula: C₆₄H₈₃O₁₀N₂⁺: calculated for [M+H]⁺: 1039.912, found: 1039.908. ¹H NMR of Monomer 4 is presented in Figure S5 on Page S18.
3. Polymerization of monomers:

Ring-opening metathesis polymerization (ROMP) of Monomers 1, 2, 3 and 4 yield Polymer 1, Polymer 2, Polymer 3 and Polymer 4 respectively.

3.1 Synthesis of Polymer 1 (P(NB-Rh-OH)) is shown below:

![Scheme S5: Representative synthesis of Polymer 1](image)

Modified Grubbs second generation catalyst (5.46 mg, 7.5 × 10^{-3} mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) and added to a 50 mL round bottom flask equipped with a magnetic stir bar and rubber septum. Nitrogen was purged for 10 min through the round bottom flask with a needle pierced in the septum for the outlet. Monomer 1 NB-Rh-OH (150 mg, 0.27 mmol) dissolved in dry CH$_2$Cl$_2$ (5 mL) was then added to the catalyst solution and the polymerization was carried out for 1 hr at room temperature. The polymerization was terminated by adding excess ethyl vinyl ether (EVE, 1 mL). The polymer reaction mixture was concentrated to about 1 mL by purging nitrogen as described before and the polymer was precipitated in excess diethyl ether (20 mL) under constant stirring, followed by decantation and centrifugation. The supernatant was discarded and the polymer was dried in vacuum oven at ambient temperatures overnight to yield a white colored powder. $^1$H NMR of Polymer 1 is presented in Figure S15 on Page S26, GPC curve is presented.
3.2 Synthesis of Polymer 2 (P(NB-Rh-NB)) is shown below:

Modified Grubbs second generation catalyst (5.45 mg, \(7.5 \times 10^{-3}\) mmol) was dissolved in CH₂Cl₂ (5 mL) and added to a 50 mL round bottom flask equipped with a magnetic stir bar and rubber septum. Nitrogen was purged for 10 min through the round bottom flask with a needle pierced in the septum for the outlet. Monomer 2 NB-Rh-NB (150 mg, 0.22 mmol) dissolved in dry CH₂Cl₂ (5 mL) was then added to the catalyst solution and the polymerization was carried out for 1 hr at room temperature. The polymerization was terminated by adding excess ethyl vinyl ether (EVE, 1 mL). The polymer reaction mixture was concentrated to about 1 mL by purging nitrogen as described before and the polymer was precipitated in excess methanol (20 mL) under constant
stirring, followed by decantation and centrifugation\textsuperscript{2}. The supernatant was discarded and the polymer was dried in vacuum oven at ambient temperatures overnight to yield a white colored powder. \textsuperscript{1}H NMR of Polymer 2 is shown in Figure S16 on Page S27, IR spectra is shown in Figure S19 on Page S30, TGA is shown in Figure S22 on Page S33, DSC cooling curve is presented in Figure 2 on Page 12 in the main manuscript, DSC heating curve is presented in Figure S23 on page S34, XRD data is presented in Figure S28 on Page S41 and 2D WAXS is given in Figure S29 on Page S42.

3.3 Synthesis of Polymer 3 (P(NB-(CH\textsubscript{2})\textsubscript{10}-Rh-OH)) is shown below:

**Scheme S7**: Representative synthesis of Polymer 3

Modified Grubbs second generation catalyst (5.45 mg, 7.5 \times 10^{-3} \text{ mmol}) was dissolved in THF (5 mL) and added to a 50 mL round bottom flask equipped with a magnetic stir bar and rubber septum. Nitrogen was purged for 10 min through the round bottom flask with a needle pierced in the septum for the outlet. Monomer 3 NB-(CH\textsubscript{2})\textsubscript{10}-Rh-OH (150 mg, 0.2 mmol) dissolved in dry THF (5 mL) was then added to the catalyst solution and the polymerization was carried out for
10 min at room temperature. The polymerization was terminated by adding excess ethyl vinyl ether (EVE, 1 mL). The polymer reaction mixture was concentrated to about 1 mL by purging nitrogen as described before and the polymer was precipitated in excess cold hexane (20 mL) under constant stirring, followed by decantation and centrifugation\(^3\). The supernatant was discarded and the polymer was dried in vacuum oven at ambient temperatures overnight to yield a whitish grey colored powder. \(^1\)H NMR of Polymer 3 is given in Figure S17 on page S28, GPC curve is presented in Figure S21 on Page S32, TGA is given in Figure S22 on page S33, DSC cooling curve is given in Figure 2 on page 12 in the main paper, DSC heating curve is given in Figure S23 on page S34, XRD pattern is given in Figure S28 on page S41, 2D WAXS is given in Figure S29 on page S42 and mechanochromic behavior is shown in Figure S24 on page S36.

3.4 Synthesis of Polymer 4 (P(NB-(CH\(_2\)\(_{10}\)-Rh-(CH\(_2\)\(_{10}\)-NB)) is shown below:

![Scheme S8](image)

**Scheme S8**: Representative synthesis of Polymer 4

Modified Grubbs second generation catalyst (5.45 mg, 7.5 \times 10\(^{-3}\) mmol) was dissolved in THF (5 mL) and added to a 50 mL round bottom flask equipped with a magnetic stir bar and rubber
Nitrogen was purged for 10 min through the round bottom flask with a needle pierced in the septum for the outlet. Monomer 4 NB-(CH\(_2\))\(_{10}\)-Rh-(CH\(_2\))\(_{10}\)-NB (150 mg, 0.14 mmol) dissolved in dry THF (5 mL) was then added to the catalyst solution and the polymerization was carried out for 10 mins at room temperature. The polymerization was terminated by adding excess ethyl vinyl ether (EVE, 1 mL). The polymer reaction mixture was concentrated to about 1 mL by purging nitrogen as described before and the polymer was precipitated in excess cold hexane (20 mL) under constant stirring, followed by decantation and centrifugation\(^3\). The supernatant was discarded and the polymer was dried in vacuum oven at ambient temperatures overnight to yield a whitish green colored powder. \(^1\)H NMR of Polymer 4 is given in Figure S18 on Page S29, IR spectra is given in Figure S20 on Page S31, TGA is given in Figure S22 on Page S33, DSC cooling curve is given in Figure 2 on Page 12 in the main manuscript, DSC heating curve is given in Figure S23 on page S34, XRD pattern is given in Figure S28 on Page S41, 2D WAXS is given in Figure S29 on Page S42.
Characterization results:

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91–7.88 (m, 1H), 7.46–7.43 (m, 2H), 7.03–7.00 (m, 1H), 6.91 (dd, $J = 2.3$, 1.4 Hz, 1H), 6.68 (d, $J = 8.6$ Hz, 1H), 6.63 (dt, $J = 8.6$, 2.0 Hz, 1H), 6.49 (d, $J = 8.9$ Hz, 1H), 6.35 (d, $J = 2.6$ Hz, 1H), 6.31 (dd, $J = 8.9$, 2.6 Hz, 1H), 6.24 (dt, $J = 5.5$, 2.7 Hz, 1H), 6.03 (dt, $J = 5.9$, 3.1 Hz, 1H), 4.00 (td, $J = 5.8$, 1.7 Hz, 1H), 3.43 (dddt, $J = 7.2$, 4.9, 3.8, 1.7 Hz, 2H), 3.37–3.23 (m, 8H), 3.19 (dt, $J = 9.3$, 3.8 Hz, 2H), 2.96 (s, 1H), 2.03–1.95 (m, 1H), 1.59 (s, 1H), 1.52–1.46 (m, 2H), 1.34 (dt, $J = 8.3$, 1.6 Hz, 1H), 1.15 (t, $J = 7.0$ Hz, 7H)

Figure S1. $^{1}$H NMR (CDCl$_3$, 400 MHz) spectrum of Monomer 1 (NB-Rh-OH) at room temperature.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (dt, $J=6.1$, 1.9 Hz, 1H), 7.46–7.39 (m, 2H), 7.03–6.96 (m, 1H), 6.92–6.90 (m, 1H), 6.68–6.57 (m, 2H), 6.44 (dd, $J=8.9$, 1.7 Hz, 1H), 6.36 (d, $J=2.5$ Hz, 1H), 6.28 (dt, $J=8.9$, 2.6 Hz, 2H), 6.05 (ddt, $J=19.6$, 5.8, 2.8 Hz, 2H), 5.81 (dt, $J=5.9$, 3.1 Hz, 1H), 3.84–3.52 (m, 2H), 3.45–3.26 (m, 7H), 3.18 (dt, $J=8.3$, 3.8 Hz, 1H), 2.96 (s, 1H), 2.90 (s, 1H), 2.82 (d, $J=5.9$ Hz, 1H), 2.72 (dt, $J=8.8$, 3.8 Hz, 1H), 1.98 (ddd, $J=12.3$, 9.3, 3.7 Hz, 2H), 1.77 (s, 1H), 1.54–1.46 (m, 2H), 1.41 (dd, $J=8.4$, 1.6 Hz, 1H), 1.34 (d, $J=8.2$ Hz, 2H), 1.31–1.22 (m, 2H), 1.14 (t, $J=7.0$ Hz, 7H).

**Figure S2** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Monomer 2 (NB-Rh-NB) at room temperature.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.87 (s, 1H), 6.18 (ddd, $J = 8.8, 5.7, 3.1$ Hz, 1H), 6.11 (qd, $J = 5.8, 2.8$ Hz, 1H), 5.91 (dd, $J = 5.7, 2.9$ Hz, 1H), 4.15–3.92 (m, 4H), 3.27–3.14 (m, 1H), 3.05–2.85 (m, 3H), 2.30 (dt, $J = 21.5, 7.5$ Hz, 4H), 1.90 (tdd, $J = 12.2, 8.3, 3.7$ Hz, 2H), 1.60 (hept, $J = 7.1$ Hz, 8H), 1.48–1.19 (m, 26H).

**Figure S3** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Monomer 3 intermediate product NB-(CH$_2$)$_{10}$-COOH at room temperature.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, $J = 5.6, 3.1$ Hz, 1H), 7.43 (dd, $J = 5.6, 3.1$ Hz, 2H), 7.05 – 6.98 (m, 1H), 6.66 (d, $J = 2.4$ Hz, 1H), 6.52 – 6.33 (m, 5H), 6.29 – 6.21 (m, 1H), 6.19 – 6.14 (m, 1H), 5.90 (dd, $J = 5.8, 2.8$ Hz, 1H), 4.09 – 3.93 (m, 3H), 3.76 (t, $J = 6.5$ Hz, 2H), 3.34 (dq, $J = 21.6, 7.0$ Hz, 7H), 3.19 (d, $J = 4.2$ Hz, 1H), 2.96 – 2.85 (m, 2H), 2.28 (dt, $J = 15.6, 7.5$ Hz, 1H), 2.08 (t, $J = 7.5$ Hz, 2H), 1.88 (ddd, $J = 12.3, 9.3, 3.7$ Hz, 1H), 1.63 – 1.53 (m, 5H), 1.46 (t, $J = 7.2$ Hz, 2H), 1.40 (ddt, $J = 9.4, 7.2, 2.6$ Hz, 2H), 1.32 – 1.18 (m, 16H), 1.15 (t, $J = 7.0$ Hz, 7H)

**Figure S4** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Monomer 3 (NB-(CH$_2$)$_{10}$-Rh-OH) at room temperature.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.88 (m, 1H), 7.45 – 7.42 (m, 2H), 7.03 – 6.95 (m, 2H), 6.68 – 6.58 (m, 2H), 6.43 (dd, $J = 8.8$, 2.0 Hz, 1H), 6.36 (d, $J = 2.7$ Hz, 1H), 6.28 (dd, $J = 8.9$, 2.4 Hz, 1H), 6.16 (dd, $J = 5.7$, 3.2 Hz, 1H), 6.10 (qd, $J = 5.6$, 2.8 Hz, 1H), 5.90 (dd, $J = 5.8$, 2.8 Hz, 1H), 4.08 – 3.95 (m, 5H), 3.78 (td, $J = 6.3$, 5.5, 2.2 Hz, 2H), 3.42 – 3.28 (m, 7H), 3.19 (d, $J = 4.2$ Hz, 2H), 3.03 – 2.85 (m, 4H), 2.52 (t, $J = 7.5$ Hz, 1H), 2.26 (t, $J = 7.6$ Hz, 1H), 2.08 (t, $J = 7.5$ Hz, 2H), 1.88 (ddt, $J = 15.8$, 9.1, 3.9 Hz, 2H), 1.71 (p, $J = 7.4$ Hz, 1H), 1.58 (d, $J = 13.1$ Hz, 9H), 1.52 – 1.44 (m, 3H), 1.43 – 1.37 (m, 4H), 1.37 – 1.19 (m, 29H), 1.15 (t, $J = 7.0$ Hz, 6H)

**Figure S5.** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Monomer 4 (NB-(CH$_2$)$_{10}$-Rh-(CH$_2$)$_{10}$-NB).
Figure S6: Kinetics of Polymerization for Monomers 1, 2, 3 and 4. Monomers 1 and 2 take longer time as compared to Monomers 3 and 4.
Figure S7. UV-vis absorbance of Monomer 1 before and after addition of 10 µL TFA to 10⁻⁴ M solution of Monomer 1. Emergence of peak at 535 nm on addition of TFA indicating ring-opening of spirolactam ring in Monomer 1. Molar absorptivity of Monomer 1 = 6 x 10² L/mol cm.

Figure S8. UV-vis absorbance of Monomer 2 before and after addition of 10 µL TFA to 10⁻⁴ M solution of Monomer 2. Emergence of peak at 535 nm on addition of TFA indicating ring-opening of spirolactam moiety in the monomer. Molar absorptivity of Monomer 2 = 45 x 10² L/mol cm.
Figure S9. UV-vis absorbance of Monomer 3 before and after addition of 10 μL TFA to 10^{-4} M solution of Monomer 3. Emergence of peak at 535 nm on addition of TFA indicating ring-opening of the spirolactam moiety. Molar absorptivity of Monomer 3 = 30 \times 10^2 \text{ L/mol cm}.

Figure S10. UV-vis absorbance of Monomer 4 before and after addition of 10 μL TFA to 10^{-4} M solution of Monomer 4. Emergence of peak at 535 nm on addition of TFA indicating ring-opening of spirolactam moiety. Molar absorptivity of Monomer 4 = 5 \times 10^2 \text{ L/mol cm.}
Figure S11. Representative of thermogravimetric analysis of Monomers 1-4 and HO-Rh-OH. The decomposition temperature is presented in the inset table.
**Figure S12.** DSC of HO-Rh-OH and Monomers 1, 2, 3 and 4. The monomers are amorphous. Melting transition temperature and liquid crystalline transition temperatures, indicative of semicrystalline and liquid crystalline features, respectively, were absent.
Figure S13. Mechanochromic, photochromic and thermochromic behavior of dye HO-Rh-OH. The dye showed a very significant color change from white to dark pink on abrasion and heating. On the contrary, the dye showed a very light pink color on exposure to UV light for 10 mins. Solid state UV-vis Absorbance of the dye heated at 215 °C showed an absorption peak at 550 nm.
Figure S14: Photochromic, mechanochromic and thermochromic behaviors of Monomers 1-4. Monomers 1-4 show a faint orangish color on exposure to UV light for 10 min which is a less intense color change compared to their polymer analogs. Mechanochromic behavior: Monomer 1 does not show any color change, Monomer 2 shows a faint orangish red color, Monomer 3 and Monomer 4 show a faint pink color change. Thermochromic behavior: Monomers 1-4 do not show a color change.
4. Characterization of Polymers:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (s, 1H), 7.40 (s, 2H), 6.94 (d, $J$ = 28.6 Hz, 2H), 6.62 (s, 2H), 6.50 – 6.16 (m, 3H), 5.41 (d, $J$ = 54.7 Hz, 2H), 3.98 (s, 1H), 3.25 (q, $J$ = 36.5, 33.6 Hz, 8H), 3.01 – 2.69 (m, 1H), 2.53 (s, 1H), 2.32 – 1.72 (m, 3H), 1.60 (s, 4H), 1.41 (s, 1H), 1.31 – 1.21 (m, 1H), 1.11 (s, 5H).

**Figure S15.** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Polymer 1 at room temperature.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (s, 1H), 7.46 (d, $J = 34.2$ Hz, 1H), 6.67 (d, $J = 247.1$ Hz, 5H), 5.29 (s, 4H), 3.06 (d, $J = 201.0$ Hz, 8H), 2.26 – 1.51 (m, 5H), 1.11 (d, $J = 18.1$ Hz, 5H).

**Figure S16.** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of Polymer 2 at room temperature. The peaks are broad as it is a partially crosslinked polymer structure.
$^1$H NMR (400 MHz, THF) $\delta$ 7.88 – 7.81 (m, 1H), 7.49 – 7.41 (m, 2H), 7.03 (d, $J = 2.1$ Hz, 2H), 6.74 (d, $J = 2.7$ Hz, 2H), 6.54 – 6.36 (m, 3H), 5.62 – 5.17 (m, 2H), 4.14 – 3.86 (m, 3H), 3.40 (q, $J = 7.4$ Hz, 4H), 3.23 (qd, $J = 9.5, 9.0, 3.3$ Hz, 5H), 3.00 – 2.83 (m, 2H), 2.60 – 2.43 (m, 4H), 1.67 – 1.57 (m, 4H), 1.49 – 1.26 (m, 17H), 1.17 (t, $J = 7.0$ Hz, 7H).

Figure S17. $^1$H NMR (C$_4$D$_8$O, 400 MHz) spectrum of Polymer 3 at room temperature.
$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.95 – 7.85 (m, 1H), 7.54 – 7.48 (m, 2H), 7.09 – 6.97 (m, 2H), 6.71 (d, $J = 9.7$ Hz, 2H), 6.54 – 6.31 (m, 3H), 5.58 – 5.14 (m, 5H), 4.20 – 3.88 (m, 6H), 3.79 (qd, $J = 10.2$, 6.0, 5.5 Hz, 2H), 3.38 (d, $J = 7.2$ Hz, 6H), 3.19 (d, $J = 17.1$ Hz, 2H), 3.02 – 2.72 (m, 4H), 2.57 (t, $J = 7.5$ Hz, 3H), 2.30 (t, $J = 7.4$ Hz, 2H), 2.04 (dtt, $J = 42.8$, 20.5, 7.6 Hz, 7H), 1.76 (p, $J = 8.1$, 7.7 Hz, 4H), 1.64 (d, $J = 12.3$ Hz, 11H), 1.32 (t, $J = 14.5$ Hz, 41H), 1.19 (t, $J = 7.0$ Hz, 9H)

**Figure S18.** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectrum of Polymer 4 at room temperature. The peaks are broad because of the partially crosslinked polymer structure.
Figure S19. Comparing the ATR-IR of Monomer 2 and Polymer 2. The stretching vibration peak of $=\text{CH}$ at 3060 cm$^{-1}$ has disappeared on polymerization.
Figure S20. Comparing the ATR-IR of Monomer 4 and Polymer 4. The stretching vibration peak of $\equiv$CH at 3060 cm$^{-1}$ has disappeared on polymerization.
Figure S21. GPC traces of non-crosslinked Polymer 1 and Polymer 3.
Figure S22. TGA of Polymers 1-4. Partially crosslinked Polymer 2 and Polymer 4 showed higher degradation temperature than non-crosslinked Polymer 1 and Polymer 3.
Figure S23. Second heating curves of Polymers 1-4.
Table S1. Summary of mechanochromic behavior of Polymers 1-4 upon abrasion

|                | Color change                      | Reversibility of mechanochromic behavior |
|----------------|-----------------------------------|------------------------------------------|
| Polymer 1      | Gray white to very light pink     | Results inconclusive                      |
| Polymer 2      | White to red                      | Partly reversible upon heat treatment    |
| Polymer 3      | Gray to light pink                | Reversible upon heat treatment           |
| Polymer 4      | White to dark pink/purple         | Completely reversible upon heat treatment|
| Pristine HO-Rh-OH | White to dark pink             | Not reversible                           |
Figure S24. Photographs of reversible mechanochromic properties of Polymer 1 and Polymer 3.
Figure S25. Example method used for quantifying colorimetric intensity of Polymers 1 and 2 before and after abrasion using ImageJ software. The value 255 is considered as pure white according to the gray scale. Multimodal distribution of populations of ring closed and open before and after abrasion points to the different population of SP rings within polymer chains.
Figure S26. Example method used for quantifying colorimetric intensity of Polymers 3 and 4 before and after abrasion using ImageJ software. The value 255 is considered as pure white according to the gray scale.
Figure S27. Photographs of piezochromic behavior of Polymers 1-4 when applied with 500 MPa pressure.

Table S2. Summary of piezochromic behavior of Polymers 1-4

| Polymer  | Color change                     |
|----------|----------------------------------|
| Polymer 1| Gray white to no color change    |
| Polymer 2| White to red                     |
| Polymer 3| Gray to light pink               |
| Polymer 4| White to dark pink/purple        |
Table S3. Summary of Photochromic behavior:

| Polymer    | Color change                  | Reversibility of photochromic behavior |
|------------|-------------------------------|---------------------------------------|
| Polymer 1  | Gray white to very light orange | Partly reversible upon heat treatment |
| Polymer 2  | White to light orangish red    | Partly reversible upon heat treatment |
| Polymer 3  | Gray to light orange           | Reversible upon heat treatment        |
| Polymer 4  | White to dark red/purple       | Completely reversible upon heat treatment |
| Pristine HO-Rh-OH | White to light pink               | Not reversible                       |

Table S4. Summary of Thermochromic behavior

| Polymer    | Color change                  | Reversibility of thermochromic behavior |
|------------|-------------------------------|---------------------------------------|
| Polymer 1  | Gray white to blackish brown  | Degraded without color change, NA     |
| Polymer 2  | White to brown                | Not reversible                        |
| Polymer 3  | Gray to blackish brown        | Degraded without color change, NA     |
| Polymer 4  | White to bright red           | Not reversible                        |
| Pristine HO-Rh-OH | White to dark pink               | Not reversible                       |
Figure S28. XRD pattern of Polymer 2, Polymer 3 and Polymer 4 when compressed at 500 MPa. Polymer 1 didn’t form a film at 500 MPa. Polymer 3 and Polymer 4 have spacers in the polymer architecture and give more resolved peaks as compared to Polymer 2 that does not have a spacer in the polymer architecture suggesting motional decoupling is important for orientation.
Figure S29. 2D WAXS data of Polymer 2, Polymer 3 and Polymer 4. (1), (2) and (3) for Polymer 3 stands for different positions of the same sample of Polymer 3 recorded for 2D WAXS. 2D WAXS of Polymer 2 shows a continuous whole ring suggesting that it is isotropic whereas 2D WAXS of Polymer 3 and Polymer 4 shows a discontinuous ring suggesting better order due to the presence of methylene spacers in the polymer architectures that impart motional decoupling. Also, the ring looks more diffused in Polymer 3 and Polymer 4 due to the presence of methylene spacers making it more amorphous and flexible.
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