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Photoswitching topology in polymer networks with metal–organic cages as crosslinks

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Supporting information for:

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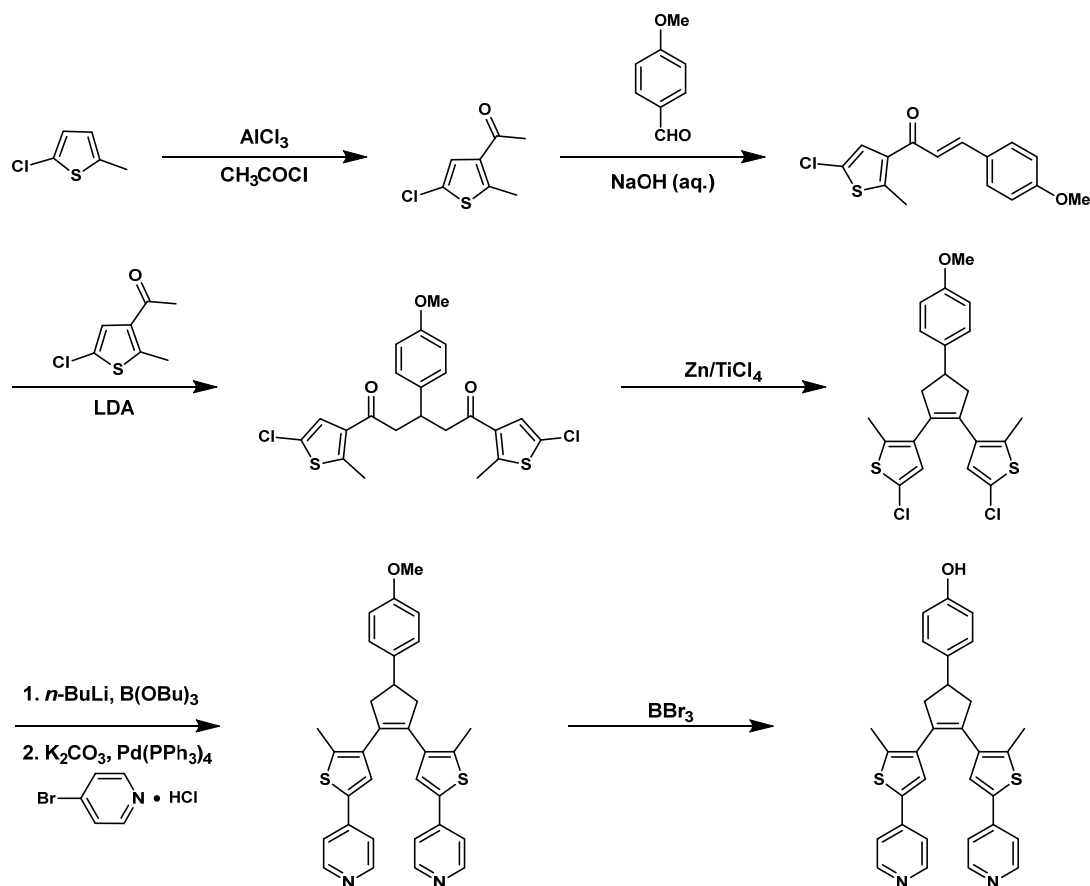
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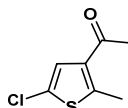
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Synthesis of ligands and polymer ligands



Scheme S1. Synthetic route for the phenol-containing photochromic bis-pyridine ligand



1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one

12.57 g AlCl_3 (94.2 mmol) was placed in an oven-dried flask. The flask was evacuated and refilled with nitrogen three times. 5.36 mL acetyl chloride (75.1 mmol) and 140 mL DCM was then added and the mixture was cooled to 0 °C. In a separate flask, 10 g 2-chloro-5-methylthiophene (75.4 mmol) was dissolved in 60 mL DCM and then slowly cannulated to the flask under 0 °C. The reaction was allowed to stir under 0 °C for 2 hours, after which time 80 mL ice-water was added to quench the reaction. The organic layer was separated and washed with saturated NaHCO_3 (aq.) and brine, dried over Na_2SO_4 , and concentrated. The crude mixture was purified using silica column chromatography (gradient, hexane to 4% ethyl acetate/hexane). (80% yield)

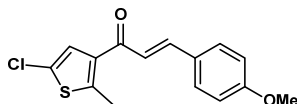
Note: The purified product contains 9% regioisomer, which can be separated in the

following steps.

HRMS (m/z) calculated for $C_7H_8ClOS^+$ ($[M+H]^+$): 174.9984; found: 174.9976

1H -NMR (500 MHz, $CDCl_3$) δ : 7.15 (s, 1H), 2.65 (s, 3H), 2.45 (s, 3H).

^{13}C -NMR (126 MHz, $CDCl_3$) δ : 193.05, 147.59, 135.28, 127.37, 125.14, 29.77, 15.99.



1-(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one

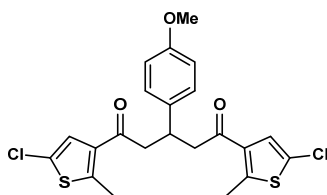
4.8 g 1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one (27.5 mmol) and 3.3 g 4-methoxybenzaldehyde (24.2 mmol) was dissolved in 80 mL ethanol. 14.4 mL 10% NaOH (aq.) solution was then added. The mixture was stirred at room temperature for 1.5 hours, during which time a yellow solid precipitated out from the solution. 30 mL water was added and the solution was neutralized with 1 M HCl (aq.). Ethanol was then removed by rotary evaporation and the product was extracted with ethyl acetate three times. The organic phase was combined and washed with water and brine, dried over Na_2SO_4 , and concentrated. The crude product was purified using silica column chromatography (gradient, hexane to 3% ethyl acetate/hexane). (68% yield)

Note: A certain amount of 4-methoxybenzaldehyde might co-elute with the product, making it difficult to separate. Therefore, the residual 4-methoxybenzaldehyde in the collected fraction was quantified from 1H -NMR, carried out to the next step. It has been confirmed that the 4-methoxybenzaldehyde can be separated in the next step.

HRMS (m/z) calculated for $C_{15}H_{14}ClO_2S^+$ ($[M+H]^+$): 293.0403; found: 293.0406

1H -NMR (500 MHz, $CDCl_3$) δ : 7.69 (d, $J = 15.6$ Hz, 1H), 7.57 (d, $J = 8.7$ Hz, 2H), 7.24 (s, 1H), 7.09 (d, $J = 15.6$ Hz, 1H), 6.94 (d, $J = 8.7$ Hz, 2H), 3.87 (s, 3H), 2.70 (s, 3H).

^{13}C -NMR (126 MHz, $CDCl_3$) δ : 193.79, 158.25, 147.88, 135.55, 134.94, 128.34, 126.75, 125.30, 114.02, 55.26, 48.05, 36.01, 15.98.



1,5-bis(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)pentane-1,5-dione

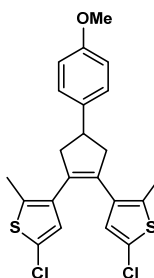
To 4.06 g 1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one (23.2 mmol) under N₂ was added 86 mL THF and cooled to -25 °C (using 7:3 water/MeOH cooling bath with dry ice). 12.48 mL (25.0 mmol) lithium diisopropylamide solution (2.0 M in THF/heptane/ethylbenzene) was then added. The mixture was allowed to stir at -25 °C for 10 minutes. 5.5 g of 1-(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (21.1 mmol) in 45 mL THF was then added. The reaction was allowed to stir at -25 °C for 30 minutes, then at room temperature for another 40 minutes. The reaction was quenched with H₂O. THF was removed via rotary evaporation and then the aqueous phase was extracted with DCM three times. The organic phase was combined, washed with brine, dried over Na₂SO₄ and concentrated. The crude product was purified using silica column chromatography (gradient, hexane to 3% ethyl acetate/hexane). (57% yield)

Note: The 1-(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one used in the reaction contains 10.4% (wt.) 4-methoxybenzaldehyde from the previous step, the amount of which was determined from ¹H-NMR. When calculating reaction stoichiometry, the amount of 1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one needed to consume 4-methoxybenzaldehyde was taken into account.

HRMS (*m/z*) calculated for C₂₂H₂₁Cl₂O₃S₂⁺ ([M+H]⁺): 467.0309; found: 467.0328

¹H-NMR (500 MHz, CDCl₃) δ: 7.20 (s, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.87 (p, *J* = 7.9 Hz, 1H), 3.79 (s, 3H), 3.20 (dd, *J* = 16.5, 6.9 Hz, 2H), 3.06 (dd, *J* = 16.5, 7.0 Hz, 2H), 2.59 (s, 6H).

¹³C-NMR (126 MHz, CDCl₃) δ: 185.65, 161.73, 146.90, 144.38, 136.43, 130.24, 127.37, 126.80, 125.37, 121.96, 114.43, 55.44, 15.80.



3,3'-(4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene)

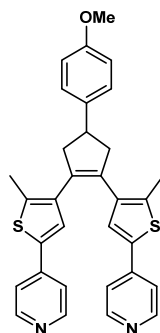
To 1.68 g Zn powder (25.7 mmol) under N₂ was added 30 mL THF and cooled to 0 °C. 1.41 mL TiCl₄ (12.9 mmol) was slowly added and the mixture was then refluxed for 1 hour, yielding a blue-black suspension. The mixture was allowed to cool to 0 °C, and 0.52 mL (6.46 mmol) pyridine was slowly added, stirred for 10 mins. 2.0 g 1,5-bis(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)pentane-1,5-dione (4.28 mmol) in 10 mL THF was added slowly to the suspension, reacted for 1.5 hours in the absence of light under reflux. After cooling to room temperature, the mixture was diluted with 100 mL diethyl ether, washed with 1 M HCl (aq.) and then saturated NH₄Cl (aq.), dried over Na₂SO₄ and concentrated. The crude product was purified using silica column chromatography (gradient, hexane to 3% ethyl acetate/hexane). (68% yield)

Note: Zn was activated with 1 M aq. HCl for 15 min, filtered, rinsed with EtOH and Et₂O, vacuum dried under 80°C for overnight, and stored in a glove box under N₂ atmosphere.

HRMS (*m/z*) calculated for C₂₂H₂₁Cl₂OS₂⁺ ([M+H]⁺): 435.0411; found: 435.0397

¹H-NMR (500 MHz, CDCl₃) δ: 7.25 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.63 (s, 2H), 3.83 (s, 3H), 3.63 (p, *J* = 7.8 Hz, 1H), 3.16 (dd, *J* = 14.2, 8.6 Hz, 2H), 2.86 (dd, *J* = 14.3, 6.9 Hz, 2H), 1.95 (s, 6H).

¹³C-NMR (126 MHz, CDCl₃) δ: 157.98, 138.26, 134.45, 133.63, 133.36, 127.70, 126.59, 125.39, 113.94, 55.33, 46.36, 41.84, 14.29.



4,4'-((4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dipyridine

To 1.26 g 3,3'-(4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene) (2.89 mmol) under nitrogen was added 12 mL THF. 2.54 mL (6.35 mmol) *n*-BuLi solution (2.5 M in hexane) was added slowly at room temperature and stirred for 30 minutes at room temperature to obtain a dark purple solution. 2.34 mL (8.67 mmol) tributyl borate was then added in one portion and stirred for 1 hour at room temperature to obtain an orange solution.

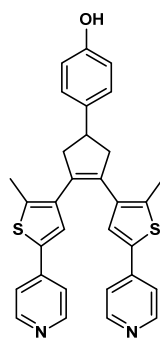
In a separate flask, under nitrogen atmosphere, to 1.24 g 4-bromopyridine hydrochloride (6.38 mmol) and 200 mg Pd(PPh₃)₄ (0.17 mmol) was added 25 mL THF. The mixture was stirred for 10 minutes. 9.4 mL 2.0 M Na₂CO₃ (aq.) solution and 10 drops of ethylene glycol was then added. The two-phase mixture was stirred under N₂ bubbling at room temperature for 15 minutes before the temperature was raised to 40 °C. The prepared orange solution was then slowly added at 40 °C. The reaction was refluxed for 2 hours in the absence of light.

After the reaction was finished, water was added and extracted with Et₂O for three times. The organic phase was combined, washed with water and brine, dried over Na₂SO₄ and concentrated. The crude product was purified using silica column chromatography (gradient, DCM to 3% MeOH/DCM). (72% yield)

HRMS (*m/z*) calculated for C₃₂H₂₉N₂OS₂⁺ ([M+H]⁺): 521.1721; found: 521.1702

¹H-NMR (500 MHz, CDCl₃) δ: 8.56 (d, *J* = 6.3 Hz, 4H), 7.36 (d, *J* = 6.2 Hz, 4H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.26 (s, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.73 (p, *J* = 7.9 Hz, 1H), 3.30 (dd, *J* = 14.4, 8.8 Hz, 2H), 3.00 (dd, *J* = 14.4, 7.2 Hz, 2H), 2.08 (s, 6H).

^{13}C -NMR (126 MHz, CDCl_3) δ : 158.04, 150.27, 141.23, 138.27, 137.59, 136.86, 136.71, 133.72, 127.73, 126.18, 119.30, 113.95, 55.33, 46.53, 41.98, 14.77.



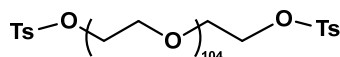
4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol

Under nitrogen atmosphere, to 270 mg 4,4'-((4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dipyridine (0.52 mmol) was added 10 mL DCM and cooled to $-78\text{ }^{\circ}\text{C}$. 2.6 mL (2.6 mmol) BBr_3 solution (1.0 M in DCM) was added dropwise, and the solution was stirred for 30 minutes at $-78\text{ }^{\circ}\text{C}$. The reaction temperature was then raised to room temperature, stirred overnight. The reaction was quenched with water and extracted with DCM three times. The crude product was dried over Na_2SO_4 , concentrated, purified using silica column chromatography (gradient, DCM to 5% MeOH/DCM). (60% yield)

HRMS (m/z) calculated for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{OS}_2^+$ ($[\text{M}+\text{H}]^+$): 507.1565; found: 507.1561

^1H -NMR (500 MHz, CDCl_3) δ : 8.55 (d, $J = 6.3\text{ Hz}$, 4H), 7.39 (d, $J = 6.3\text{ Hz}$, 4H), 7.27 (s, 2H), 7.23 (d, $J = 8.5\text{ Hz}$, 2H), 6.87 (d, $J = 8.5\text{ Hz}$, 2H), 3.69 (p, $J = 7.9\text{ Hz}$, 1H), 3.30 (dd, $J = 14.3, 8.6\text{ Hz}$, 2H), 2.97 (dd, $J = 14.5, 6.5\text{ Hz}$, 2H), 2.08 (s, 6H).

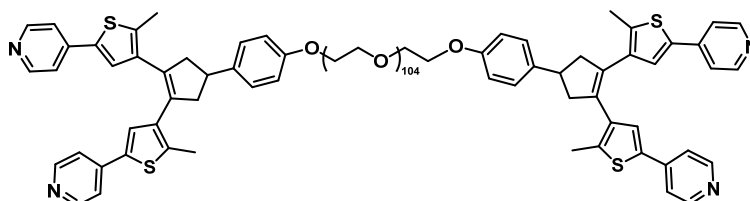
^{13}C -NMR (126 MHz, CDCl_3) δ : 155.33, 149.84, 141.66, 137.86, 137.60, 136.84, 136.62, 133.77, 127.77, 126.43, 119.48, 115.65, 46.63, 41.86, 14.79.



Poly(ethylene glycol) (average Mn 4600) bis(tosylate)

In a 20 mL glass vial, 2 g (0.43 mmol) PEG (average Mn 4600) and 0.25 mL triethylamine (1.79 mmol) was dissolved in 2 mL DCM and cooled to 0 °C. 0.32 g 4-toluenesulfonyl chloride (1.68 mmol) in 1 mL DCM was slowly added at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. The reaction was then diluted with 50 mL DCM, washed with water and brine, dried over Na₂SO₄ and concentrated. The crude product was dissolved in minimum amount of ethyl acetate and precipitated in cold diethyl ether to achieve the product (85% yield).

¹H-NMR (500 MHz, DMSO-*d*₆) δ: 7.79 (d, J = 8.0 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H), 4.10 (t, J = 4.4 Hz, 4H), 3.51 (s, 421H), 2.42 (s, 6H).

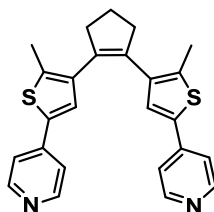


Polymer ligand (PL)

Poly(ethylene glycol) (average Mn 4600) bis(tosylate), 4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol and Cs₂CO₃ were rigorously dried in vacuum oven before reaction. In a 20 mL glass vial, 313 mg 4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol (0.62 mmol) was dissolved in 5 mL DMF, to which 302 mg Cs₂CO₃ (0.93 mmol) was added. The mixture was stirred at 80 °C for 1 hour, before 1 g poly(ethylene glycol) (average Mn 4600) bis(tosylate) (0.20 mmol) dissolved in 5 mL DMF was added. The mixture was allowed to stir at 80 °C for two days in the absence of light. The reaction was quenched with water, extracted with DCM for three times, washed with water and brine, dried over Na₂SO₄ and concentrated to remove DMF. The crude product was dissolved in a minimum amount of ethyl acetate and precipitated in cold diethyl ether for multiple times (typically three to four times) until TLC shows no residual 4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol in the precipitant. The product was obtained as light brown powder. (70% yield)

^1H -NMR (500 MHz, CDCl_3) δ : 8.51 (d, $J = 5.2$ Hz, 8H), 7.36 (d, $J = 5.3$ Hz, 8H), 7.27 (d, $J = 8.9$ Hz, 4H), 7.24 (s, 4H), 6.90 (d, $J = 8.5$ Hz, 4H), 4.13 (t, $J = 5.0$ Hz, 4H), 3.64 (s, 428H), 3.27 (dd, $J = 14.9, 8.5$ Hz, 4H), 2.96 (dd, $J = 14.6, 7.2$ Hz, 4H), 2.05 (s, 12H).

Note: One proton peak from the cyclopentene is overlapped with PEG proton peaks.



1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene was synthesized following a reported procedure¹. The spectroscopic characterizations are consistent with the original report.

HRMS (m/z) calculated for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{S}_2^+$ ($[\text{M}+\text{H}]^+$): 415.1303; found: 415.1299

^1H -NMR (500 MHz, CDCl_3) δ : 8.55 (d, $J = 6.3$ Hz, 4H), 7.36 (d, $J = 6.2$ Hz, 4H), 7.23 (s, 2H), 2.87 (t, $J = 7.5$ Hz, 4H), 2.13 (p, $J = 7.6$ Hz, 2H), 2.03 (s, 6H).

^{13}C -NMR (126 MHz, CDCl_3) δ : 150.28, 141.29, 137.29, 137.09, 136.66, 134.80, 126.27, 119.27, 38.48, 22.99, 14.68.

Reversible photo-switching of model compound

1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene (o-L) was synthesized as a model ligand to study the photo-switching properties of non-fluorinated DTE bis-pyridine ligand.

The reversible photo-switching process was first studied with UV-vis spectroscopy. 3 mL o-L solution (0.0429 mM in CH₃CN) was transferred to a quartz cuvette and measured with UV-vis spectroscopy. The solution in cuvette was then irradiated with UV light and monitored by UV-vis spectroscopy. As shown in Fig. S1, a broad peak rapidly emerged in the visible wavelength upon UV irradiation, indicating the UV-induced ring-closure reaction. The peak was centered at 545 nm, which is the reason why green light was chosen as the source of visible light irradiation. UV-vis shows that the ring-closure reaction reaches completion after 90 seconds. The solution of c-L in cuvette was then irradiated with green light and studied similarly with UV-vis spectroscopy. Fig. S1 shows that the intensity of the broad peak in the visible wavelength slowly decreases and completely disappears after 45 minutes of irradiation, indicating the completion of the visible-light induced ring-opening reaction. The relatively slow switching rate for the ring-opening reaction is attributed to the smaller quantum yield of c-L compared with o-L.

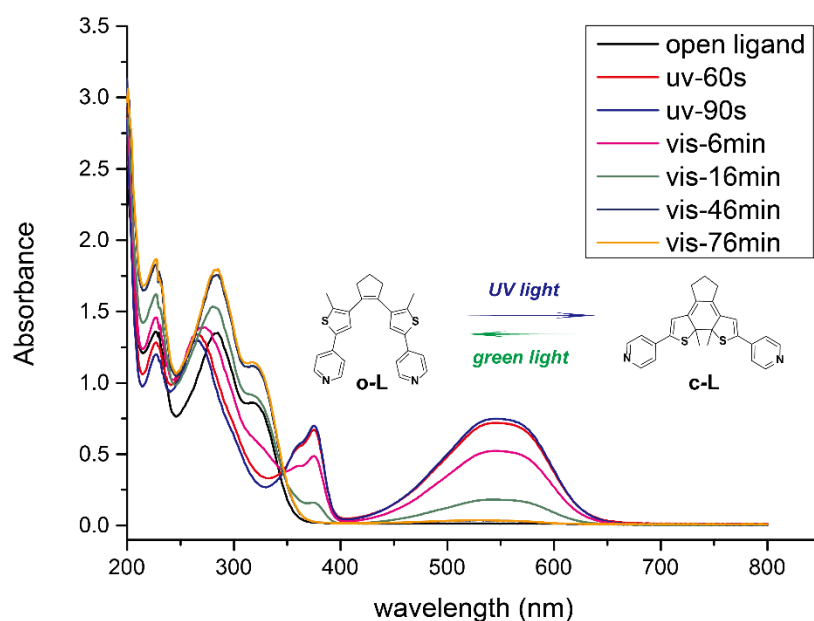


Figure S1. Reversible photo-switching of model ligand monitored by UV-vis spectroscopy

A series of o-L and c-L CH₃CN solutions in different concentrations were prepared and measured with UV-vis spectroscopy. The path length of the used quartz cuvette was 1 cm. The absorbance of o-L at 300 nm was plotted against concentration to determine the molar extinction coefficient of o-L, which was shown in Fig. S2 to be 22512 L • mol⁻¹ • cm⁻¹ at 300 nm. The absorbance of c-L at 550 nm was plotted against concentration to determine the molar extinction coefficient of c-L, which was shown in Fig. S3 to be 9316.3 L • mol⁻¹ • cm⁻¹ at 550 nm.

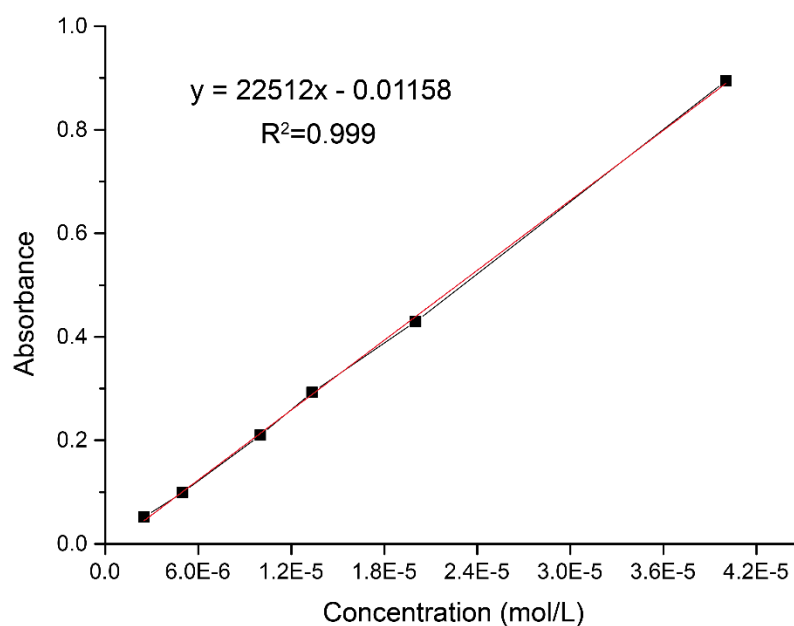


Figure S2. Absorbance at 300 nm vs. o-L concentration

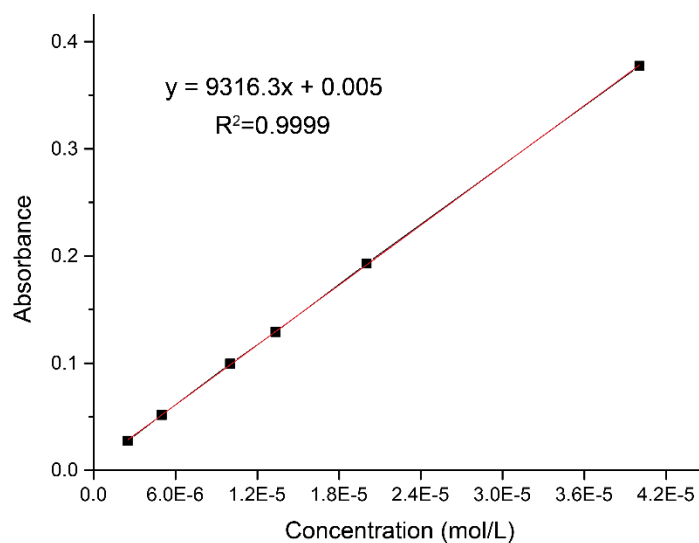


Figure S3. Absorbance at 550 nm vs. c-L concentration

Solution self-assembly of o-L with Pd²⁺

In the fluorinated DTE bis-pyridine ligand case studied by Clever and coworkers², they observed two sets of sharp and well-split ligand-based resonances from ¹H-NMR under the same self-assembly conditions as we used, which was attributed to the formation of a 3:1 mixture of Pd₃(o-L)₆ and Pd₄(o-L)₈ complexes. In our case, although ¹H-NMR clearly indicates the formation of a single self-assembly species, the fragments corresponding to Pd₄(o-L)₈ were also detected in ESI-MS (Fig. S4), indicating the presence of trace amount of Pd₄(o-L)₈ complex with our ligand as well.

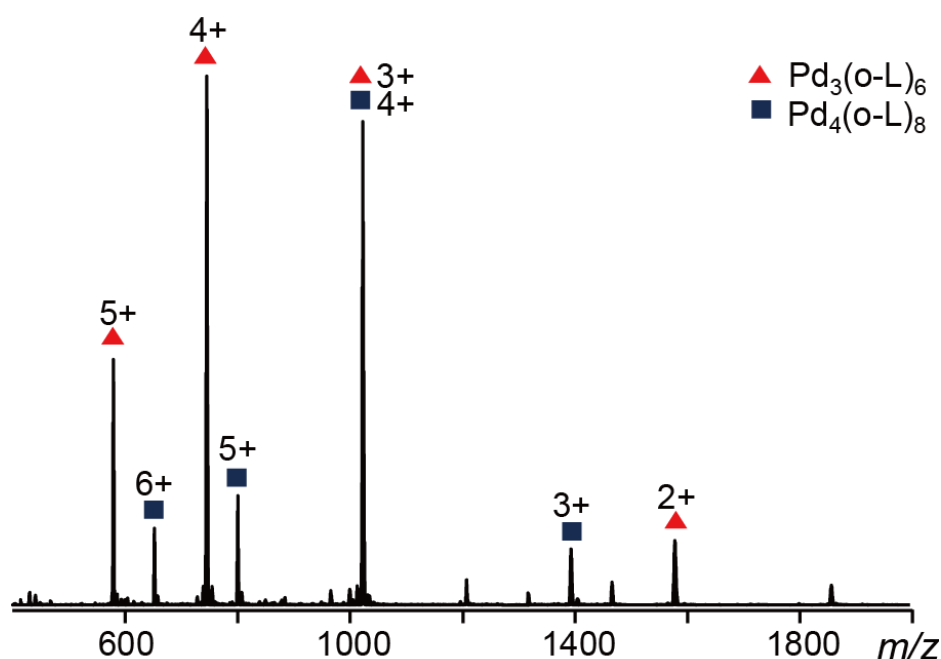


Figure S4. The presence of Pd₄(o-L)₈ complex indicated by ESI-MS

End-to-end distance of PEG (MW = 4600)

Root-mean square polymer end-to-end distance (R_0) can be theoretically calculated by the following equation:

$$R_0 = bN^\nu$$

b is the Kuhn length of polymer, N is the number of Kuhn segments, ν is an exponent factor which depends on the solvent condition ($\nu = 0.5$ in ideal solvent, $\nu = 0.58$ in good solvent).

For PEG, the Kuhn length (b) is equal to 0.76 nm. The number of Kuhn segments (N) in PEG-4600 can be calculated as follows³:

$$N = \frac{nl \cos(\frac{\theta}{2})}{b}$$

where n is the number of bonds in the chain (equal to the degree of polymerization (DP) multiplied by 3), l is the average bond length (0.147 nm), and $\theta = 180^\circ - 109.4^\circ = 70.6^\circ$. So, for PEG-4600, $N = 49.5$.

Therefore, in θ solvent, $R_0 = bN^{0.5} = 5.35$ nm; in good solvent, $R_0 = bN^{0.58} = 7.31$ nm.

Experimentally, R_0 of the polymer linker can be calculated by subtracting the diameter of the complex from average junction-to-junction distance. Our calculation shows that the polymer linker has similar length in o-gel (~6.27 nm) and c-gel (~6.10 nm), both of which are between the length of a 4.6 kDa PEG chain in θ solvent (5.35 nm) and good solvent (7.31 nm). The results indicate that although the total number of junction points decreases drastically after UV irradiation due to the formation of larger spheres, the average length of polymer linkers remains mostly unchanged. We believe that the increase in junction-to-junction distance is partially compensated by an increase in the diameter of complex, partially balanced by a decrease in the degree of junction fluctuation, as discussed in the main text.

Computation of network branch functionality from G'

A measurement of $G' \sim |G|$ (i.e., $G' \gg G''$) allows us in principle to compute $\bar{f}$ in our polyMOCs and thereby validate the conclusions derived from our simulations. As mentioned in the main text, while recent studies have shown that the phantom network theory of elasticity is more suitable to describe polymer networks with low branch functionality, polymer networks with ultra-high branch functionality may transition to affine network behavior due to the restricted fluctuations around the junctions, which are densely wrapped with polymer chains (i.e., 48 polymer chains per junction). Therefore, we apply both affine and phantom network theories of elasticity to analyze the measured G' and compare the results to simulations to examine our postulation.

Affine network theory of elasticity:

Affine network theory of elasticity relates $|G|$ and ρ in the following form:

$$|G| = \frac{\rho RT}{M_{\text{chain}}}$$

Where ρ is the mass density of elastically active polymer chains, R is the universal gas constant, T is the temperature (in this case 298.15 K), M_{chain} is the number-average molecular weight (M_n) of the polymer chains separating the junctions.

Due to the presence of cyclic defects and dangling chains, ρ is not known *a priori*. However, the relationship between ρ and ρ_{ideal} could be derived by considering how affine network theory of elasticity predicts the impact of cyclic defects on polymer network elasticity. In affine network theory of elasticity, only primary loops are considered as 100% elastically inactive, while higher order cyclic defects (including secondary loops) are considered as 100% elastically active⁴. Therefore, even in the presence of higher-order loops, a first-order approximation (i.e., accounting only for primary loops) is still accurate to describe the network elasticity. In such first-order approximation, ρ scales linearly with the true f of the network – in other words a deviation of f from f_{ideal} by x % is expected to yield the same x % deviation of ρ from ρ_{ideal} . Thus, we have:

$$\rho = \frac{f}{f_{\text{ideal}}} \rho_{\text{ideal}} \quad \text{and} \quad |G| = \frac{f \rho_{\text{ideal}} RT}{f_{\text{ideal}} M_{\text{chain}}}$$

At the concentration we used to prepare polyMOCs, $\frac{\rho_{\text{ideal}}}{M_{\text{chain}}}$ is equal to the molar concentration of PL, which is 25.1 mM. $f_{\text{ideal}} = 6$ for o-gel and $f_{\text{ideal}} = 48$ for c-gel.

Phantom network theory of elasticity:

Phantom network theory of elasticity relates $|G|$ and f in the following form:

$$|G| = \frac{\rho RT}{M_{\text{chain}}} \left(\frac{f-2}{f} \right)$$

Similarly, in a first-order approximation, we would have

$$|G| = \frac{\rho_{\text{ideal}} RT}{f_{\text{ideal}} M_{\text{chain}}} (f-2) \quad (1)$$

However, in the phantom network theory of elasticity, while primary loops are considered as 100% elastically inactive, higher order cyclic defects (including secondary loops) are considered as only fractionally elastically active. Since we are interested in secondary loops, by applying a second-order approximation (i.e., accounting for primary loops and secondary loops) and taking into account the contribution of secondary loops to network elasticity⁴, we have

$$|G| = \frac{\rho_{\text{ideal}} RT}{M_{\text{chain}}} \frac{f_{\text{ideal}} - 2}{f_{\text{ideal}}} (1 - Ax_{1,f} - Bx_{2,f}) \quad (2)$$

Where $x_{1,f}$ and $x_{2,f}$ are primary loop fraction and secondary loop fraction, respectively, A and B are coefficients that describe their negative contributions to network elasticity.

By comparing Eq. (1) and Eq. (2) (i.e., as if we still use the first-order approximation to treat the system), we have

$$f_{\text{ideal}} (1 - Ax_{1,f} - Bx_{2,f}) = f + 2(Ax_{1,f} + Bx_{2,f}) \quad (3)$$

Eq. (3) shows that even accounting for primary loops and secondary loops, the f we compute from a first-order approximation will only differ from the “real” f by $2(Ax_{1,f} + Bx_{2,f})$, whose value in most cases is no more than 2. Therefore, we still use

the first-order approximation to compute f via phantom network theory of elasticity for simplicity.

Spectroscopic data

All ^1H -NMR spectra (500 MHz) were taken in CDCl_3 , except for the ^1H -NMR spectrum of **poly(ethylene glycol) (average Mn 4600) bis(tosylate)**, which was taken in $\text{DMSO-}d_6$. All ^{13}C -NMR spectra (126 MHz) were taken in CDCl_3 .

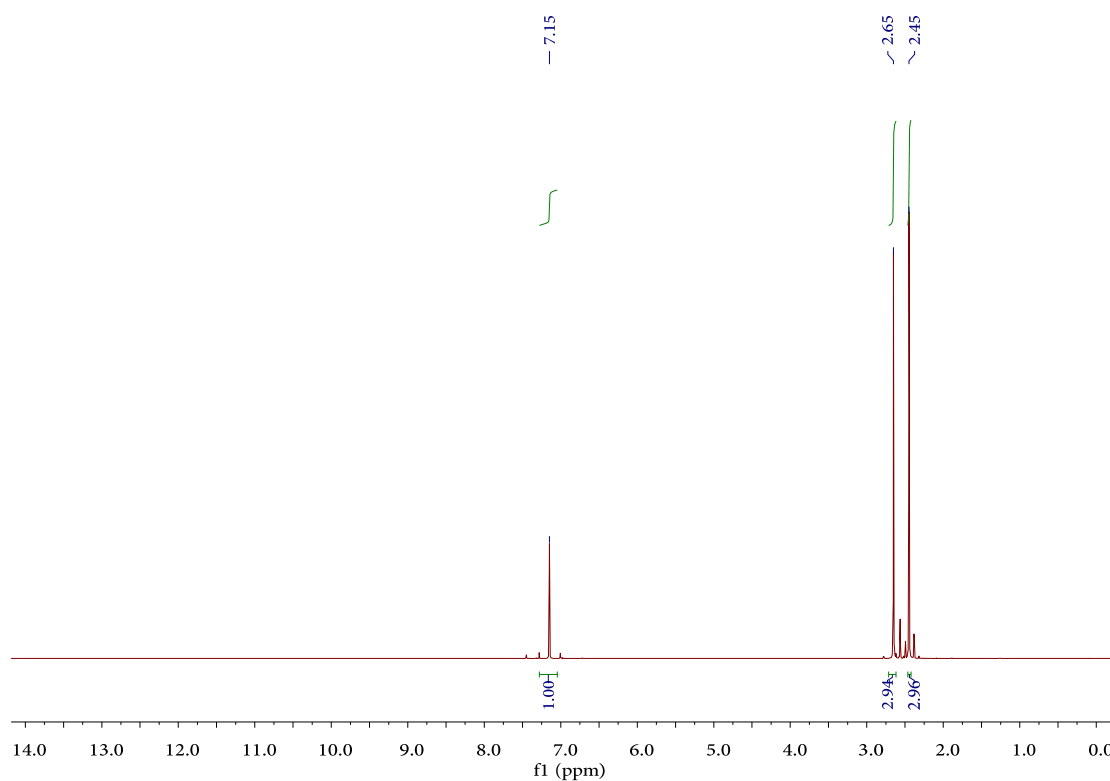


Figure S5. ^1H -NMR spectrum of 1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one

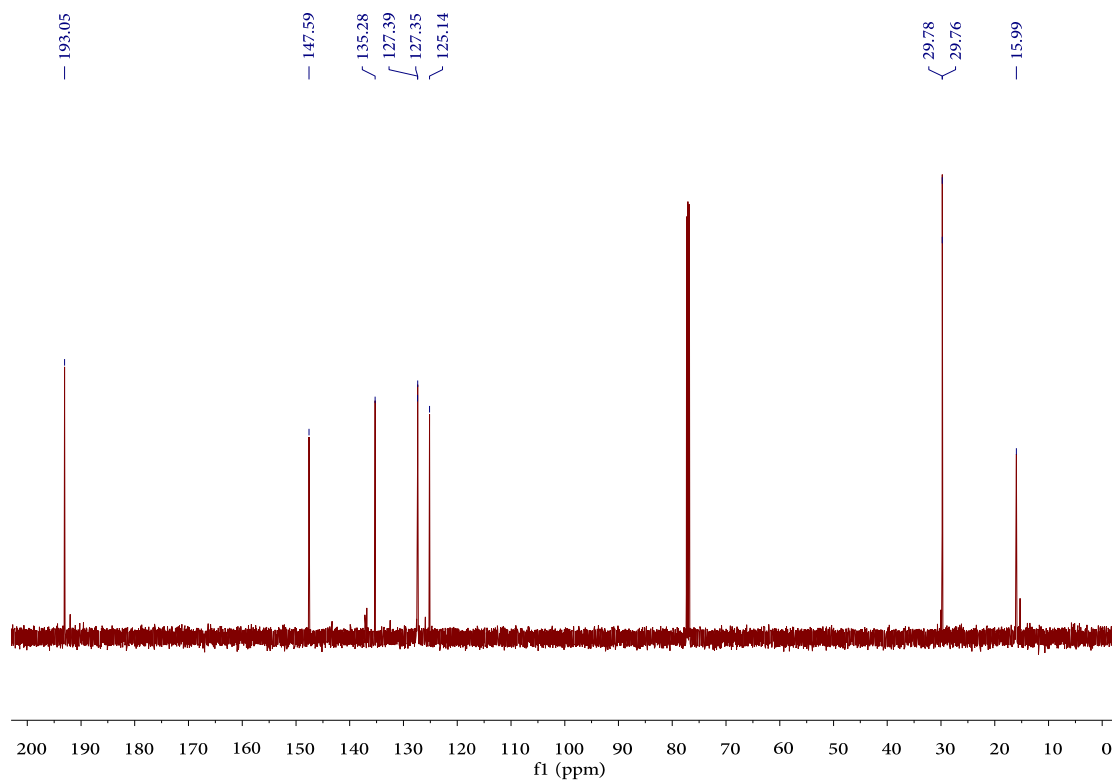


Figure S6. ¹³C-NMR spectrum of 1-(5-chloro-2-methylthiophen-3-yl)ethan-1-one

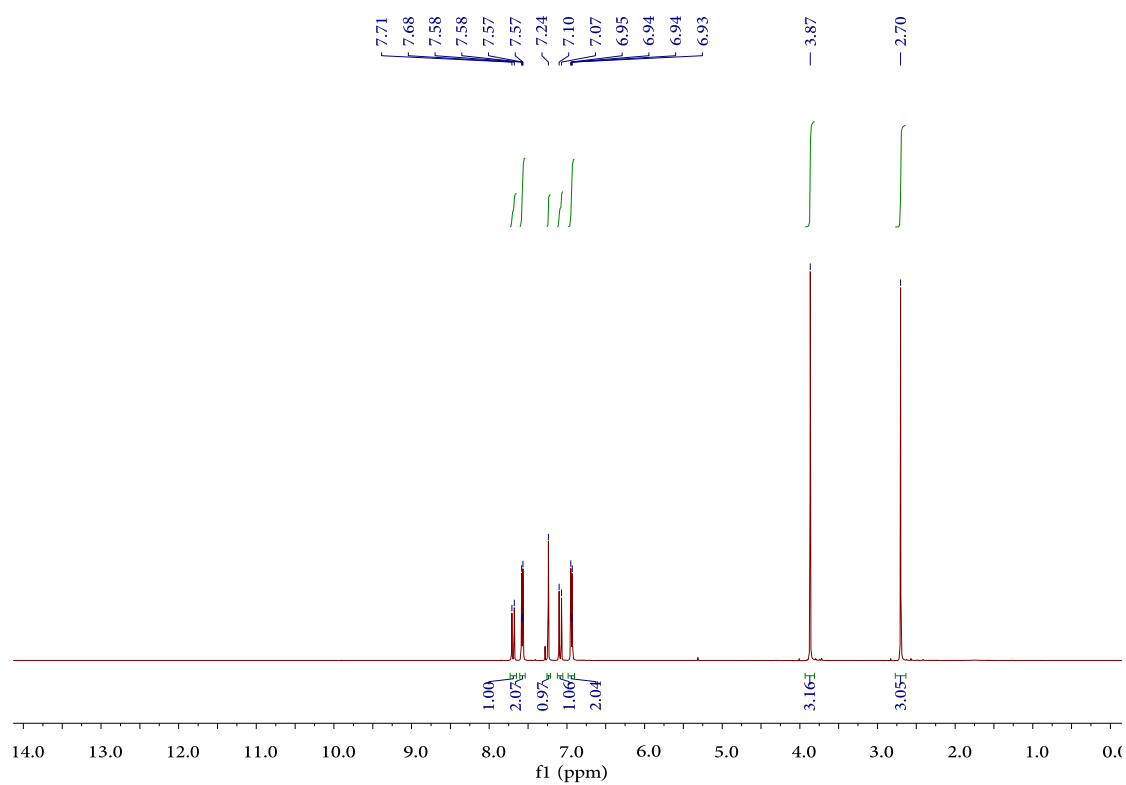


Figure S7. ¹H-NMR spectrum of 1-(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one

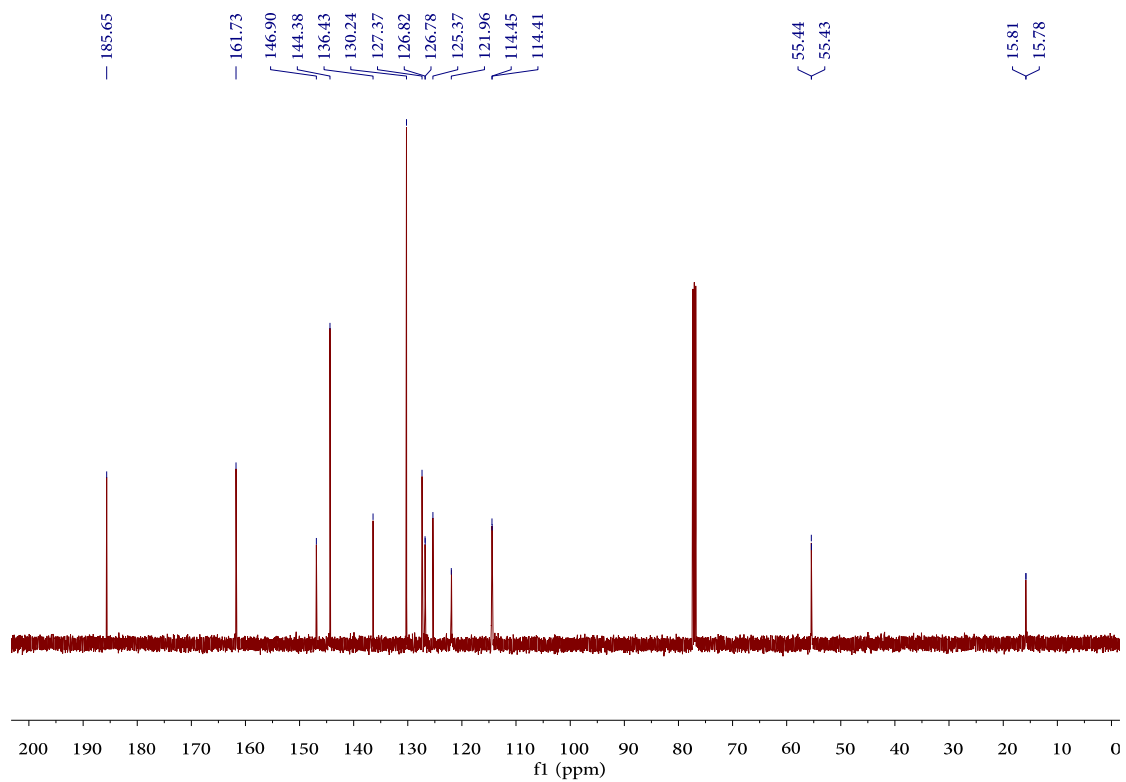


Figure S8. ¹³C-NMR spectrum of 1-(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one

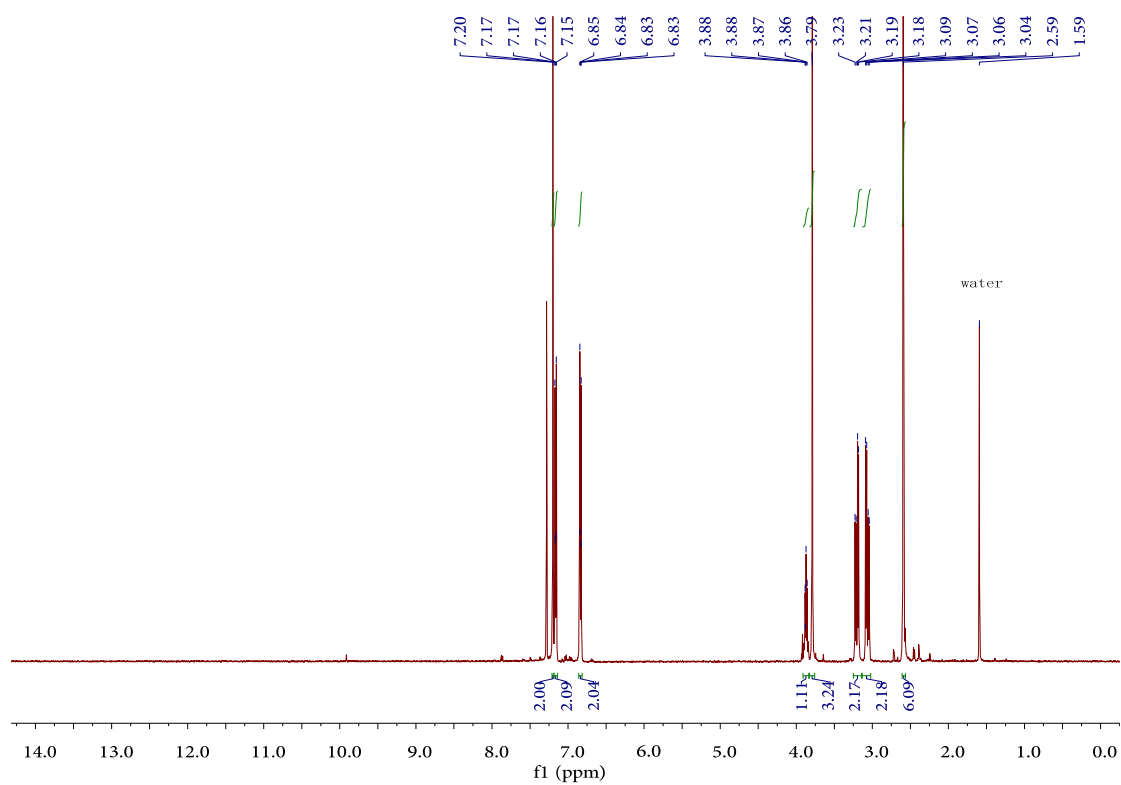


Figure S9. ^1H -NMR spectrum of 1,5-bis(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)pentane-1,5-dione

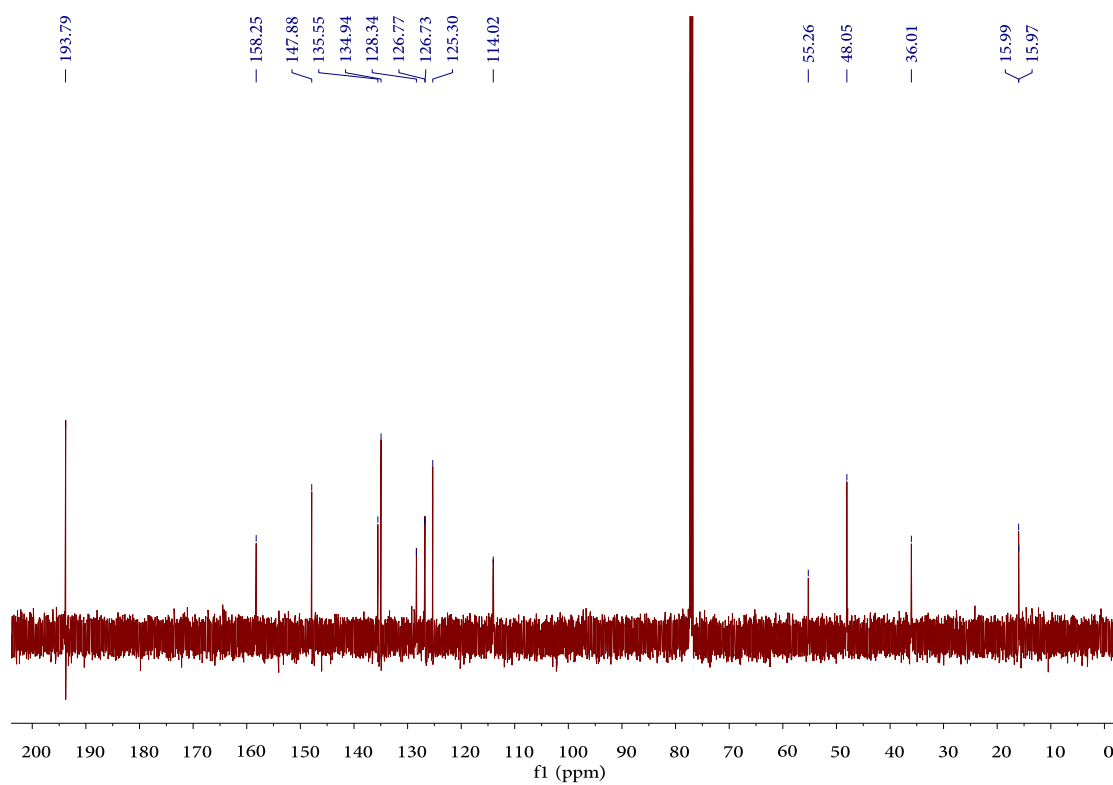


Figure S10. ^{13}C -NMR spectrum of 1,5-bis(5-chloro-2-methylthiophen-3-yl)-3-(4-methoxyphenyl)pentane-1,5-dione

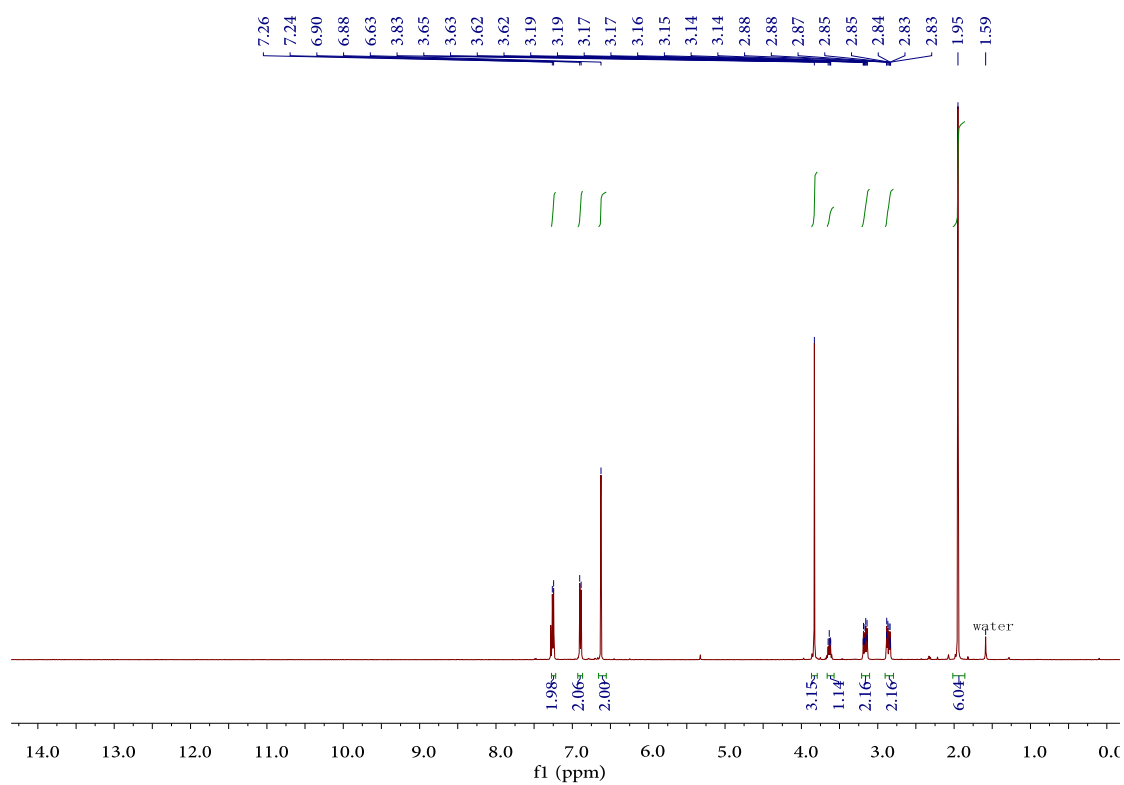


Figure S11. ¹H-NMR spectrum of 3,3'-(4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene)

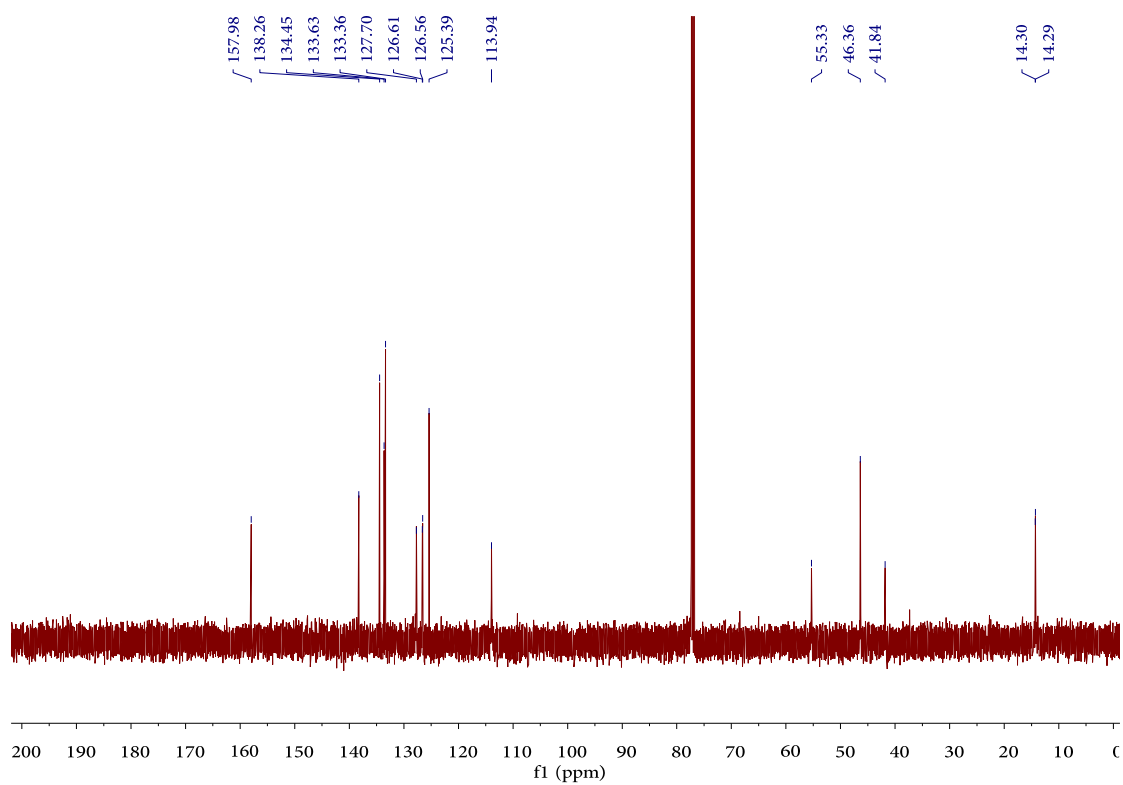


Figure S12. ¹³C-NMR spectrum of 3,3'-(4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene)

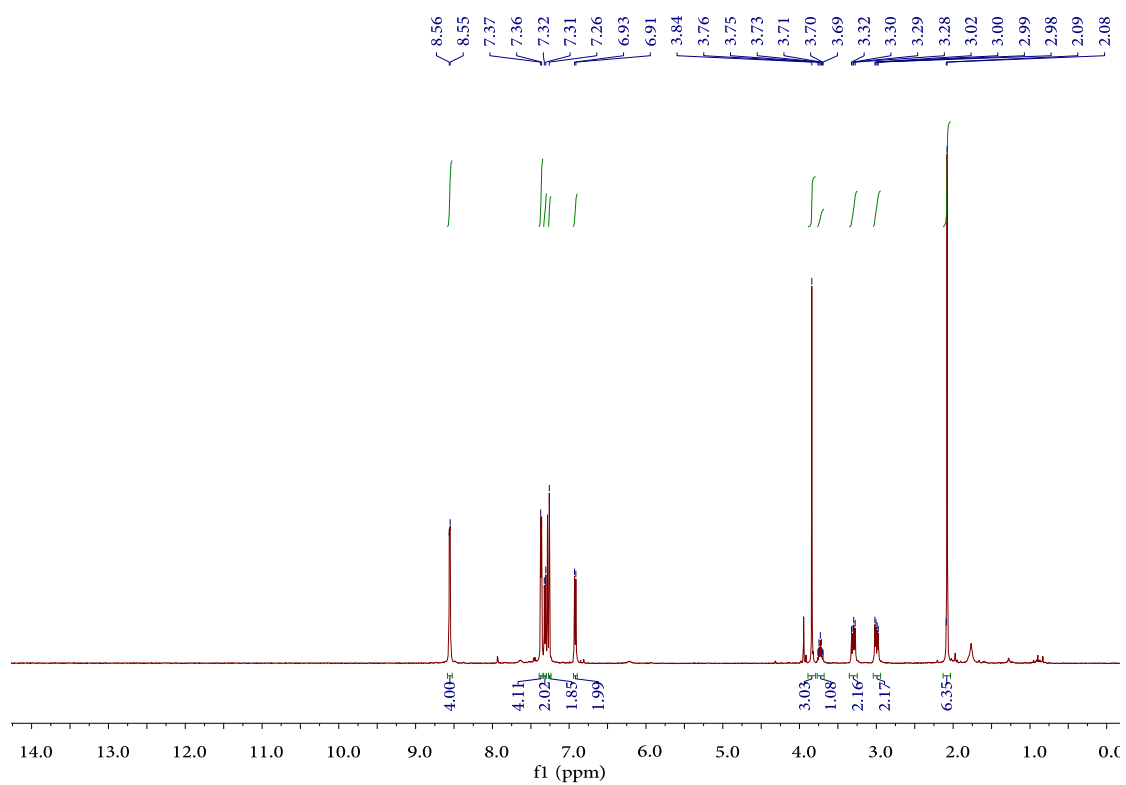


Figure S13. ^1H -NMR spectrum of 4,4'-((4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dipyridine

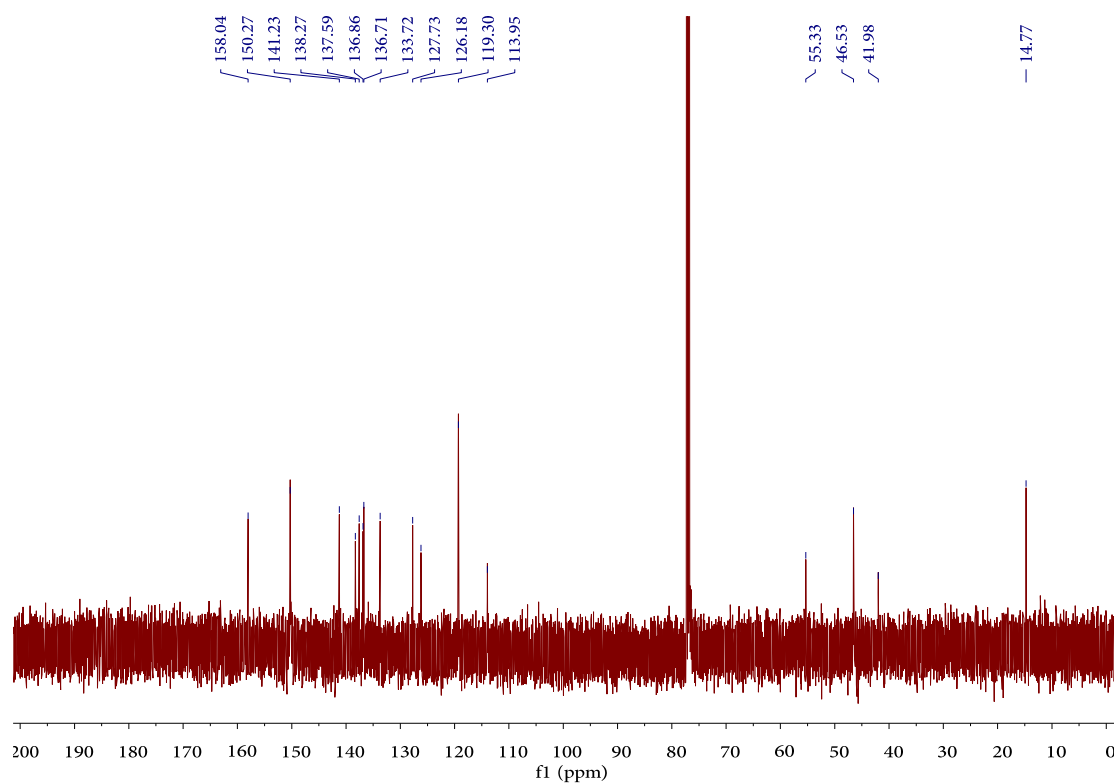


Figure S14. ¹³C-NMR spectrum of 4,4'-((4-(4-methoxyphenyl)cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dipyridine

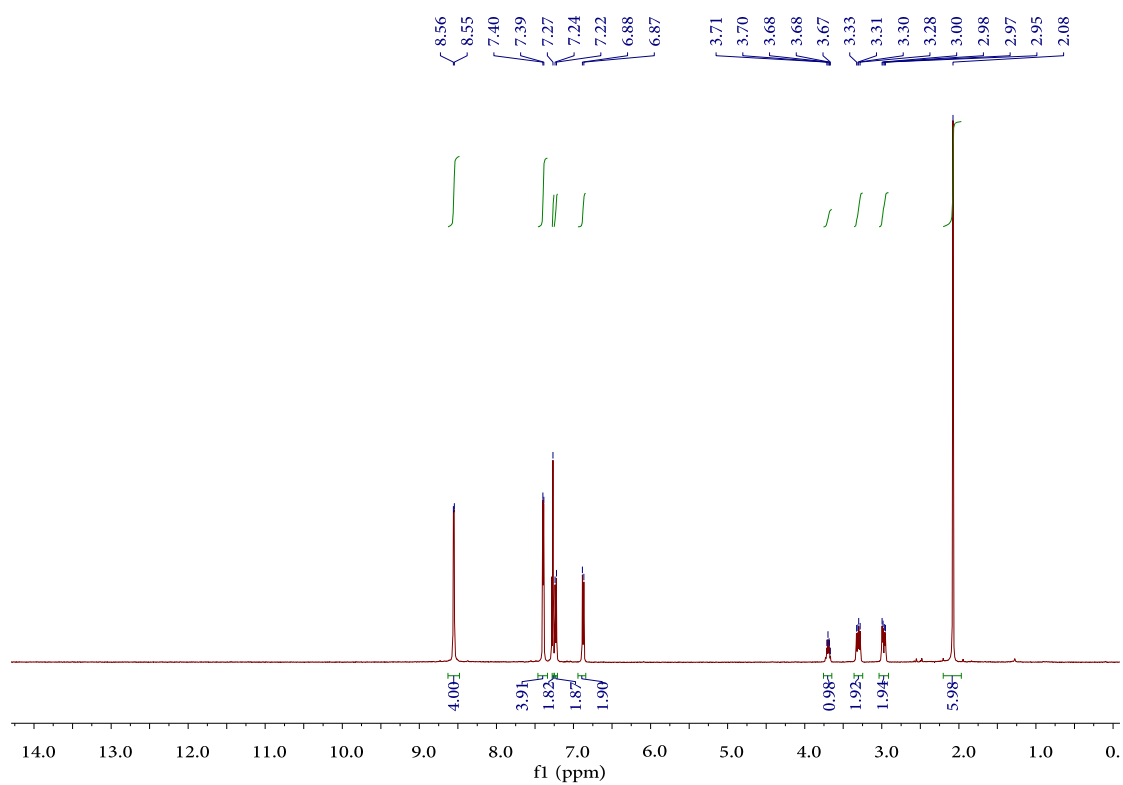


Figure S15. ¹H-NMR spectrum of 4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol

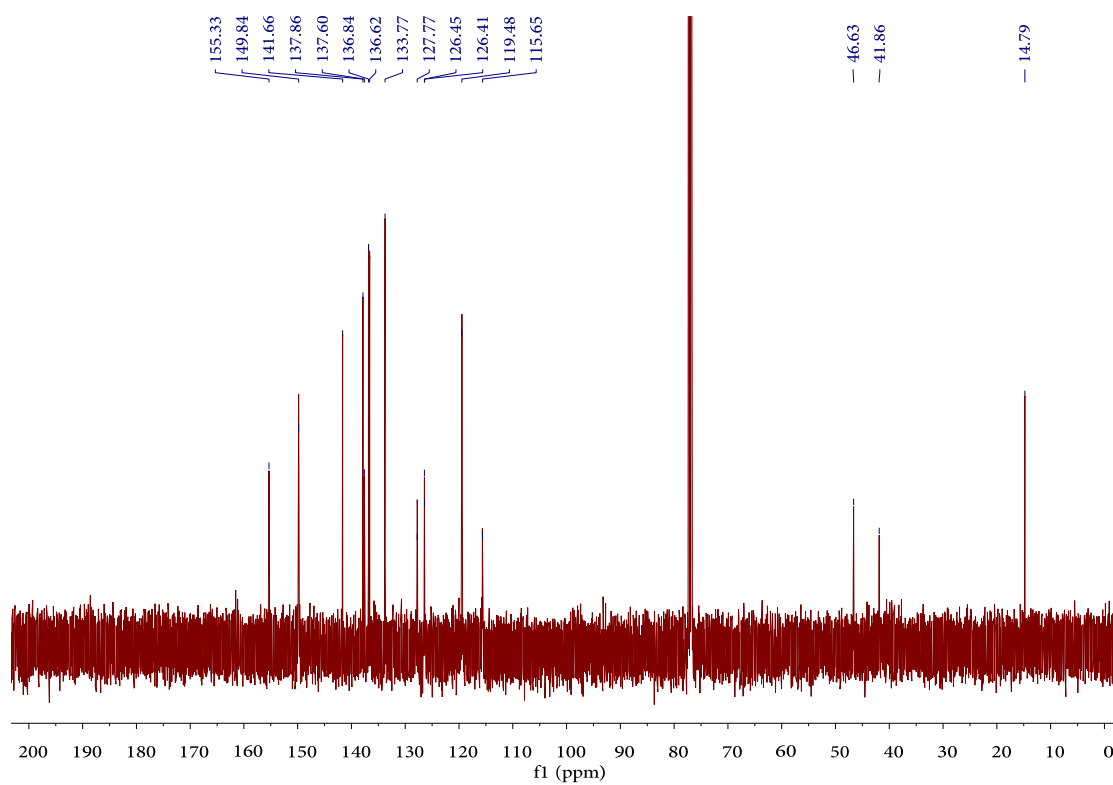


Figure S16. ¹³C-NMR spectrum of 4-(3,4-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-3-en-1-yl)phenol

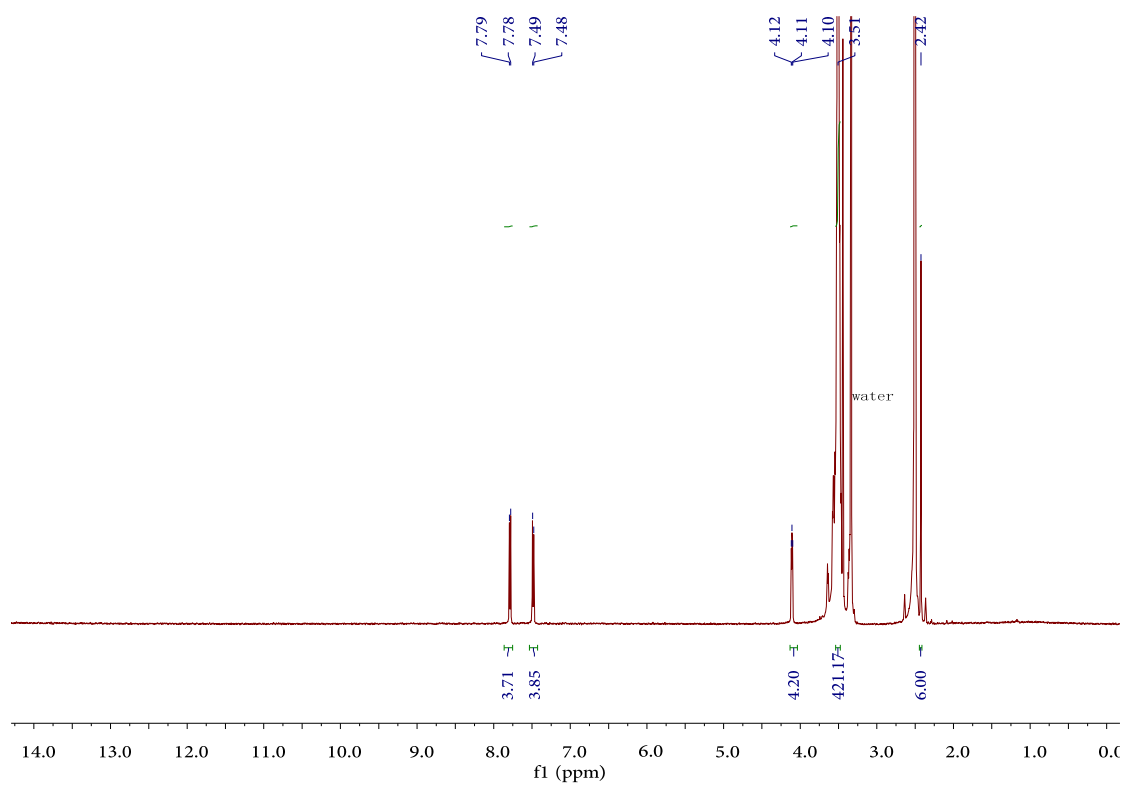


Figure S17. ^1H -NMR spectrum of Poly(ethylene glycol) (average M_n 4600) bis(tosylate)

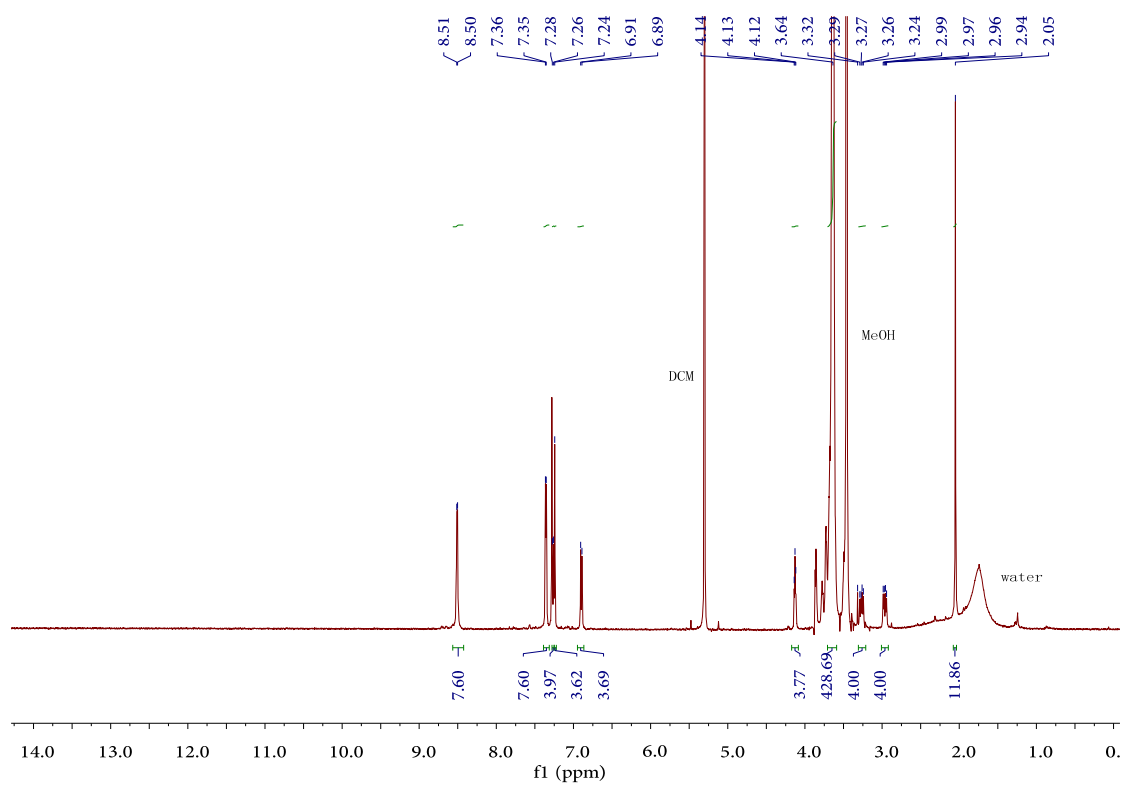


Figure S18. ¹H-NMR spectrum of Polymer ligand (PL)

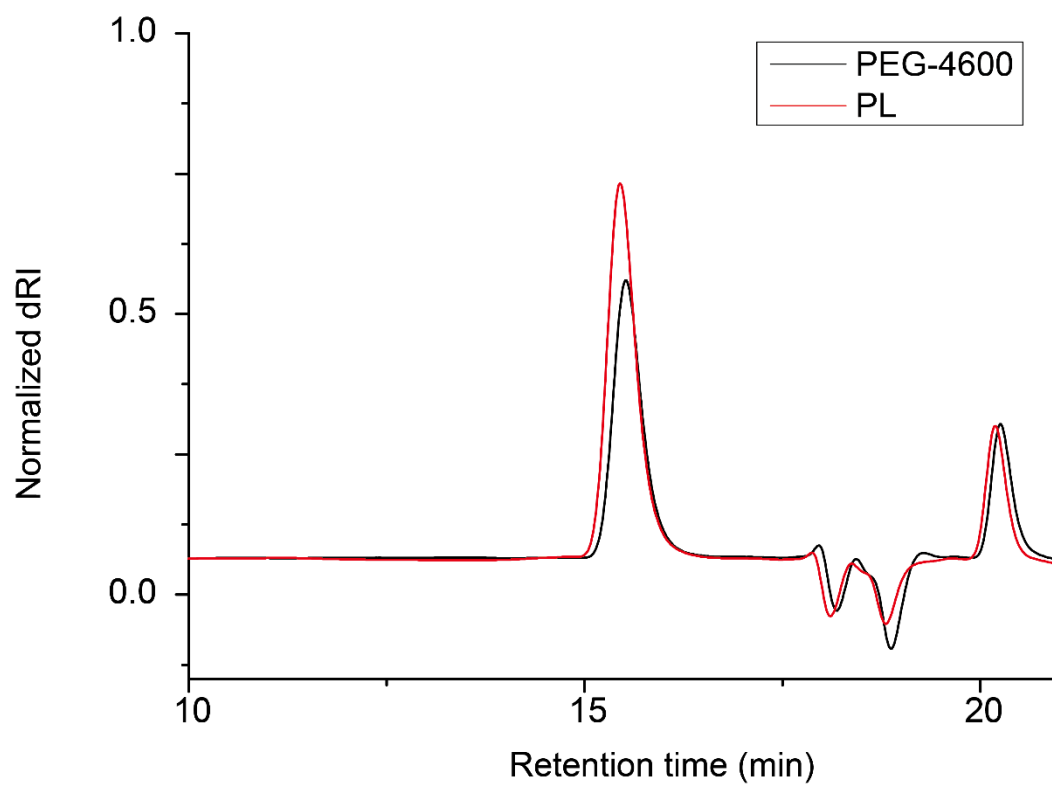


Figure S19. GPC traces of PEG-4600 and PL. RI = refractive index detector response.

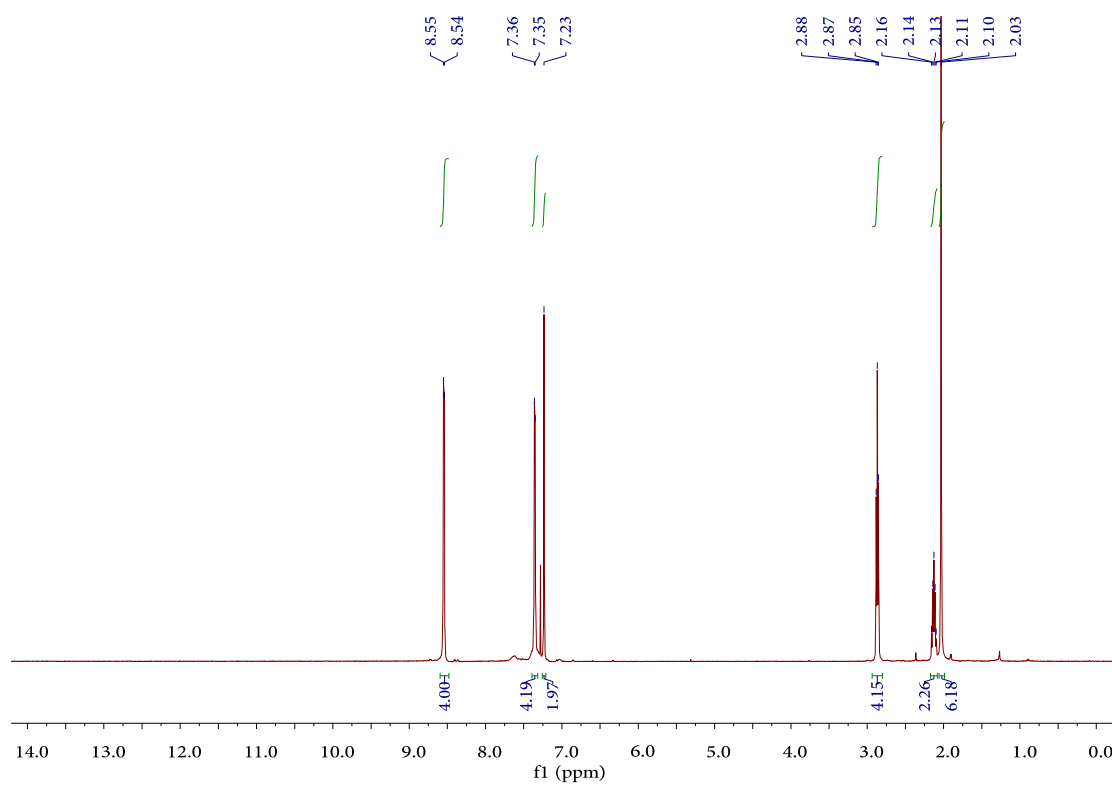


Figure S20. ¹H-NMR spectrum of 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene

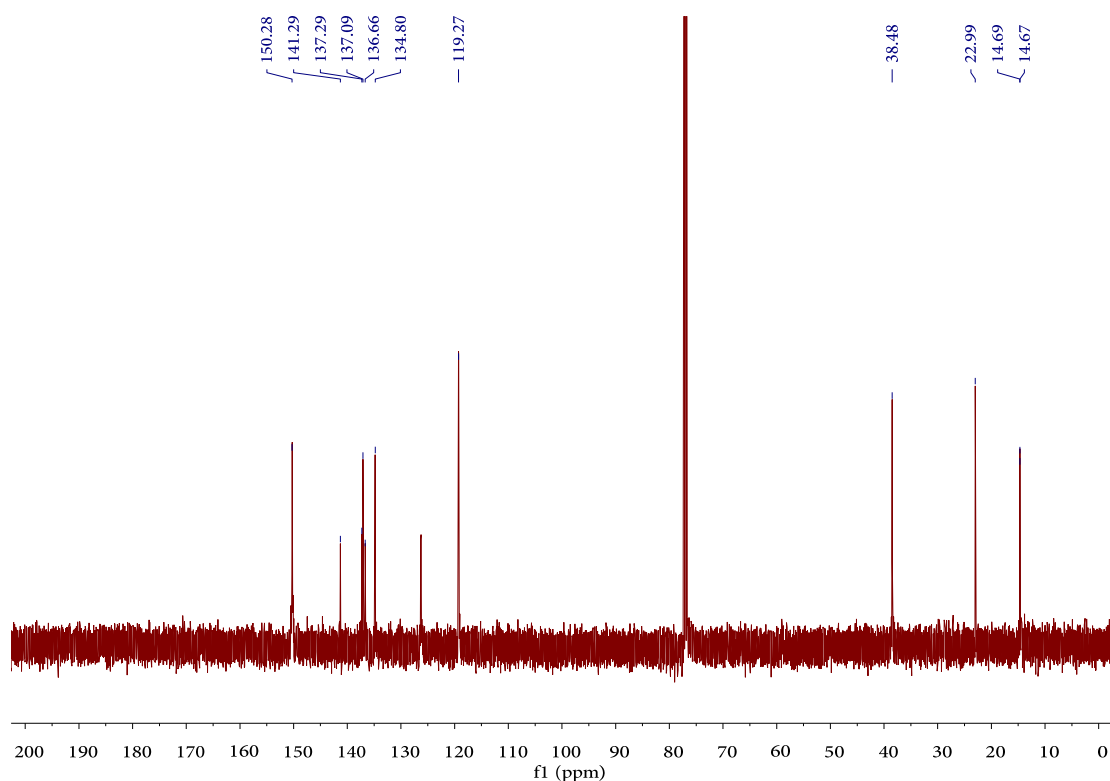


Figure 21. ^{13}C -NMR spectrum of 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene

References

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- 4 Zhong, M., Wang, R., Kawamoto, K., Olsen, B. D. & Johnson, J. A. Quantifying the impact of molecular defects on polymer network elasticity. *Science* **353**, 1264-1268 (2016).