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Supporting information

Synthesis and Properties of Dithienylethene-Functionalized Switchable Antibacterial Agents

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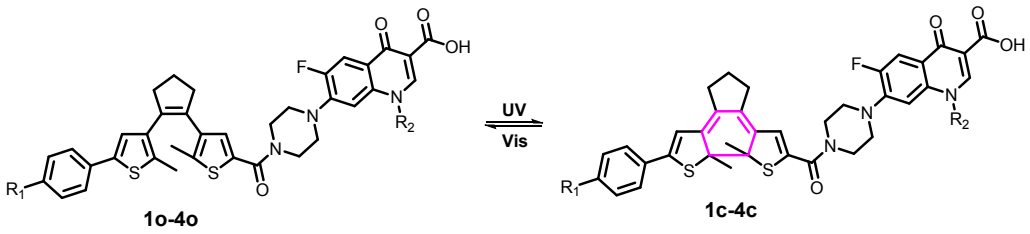


Scheme S1 Photoisomerization of switchable antibacterial agents **1-4**.

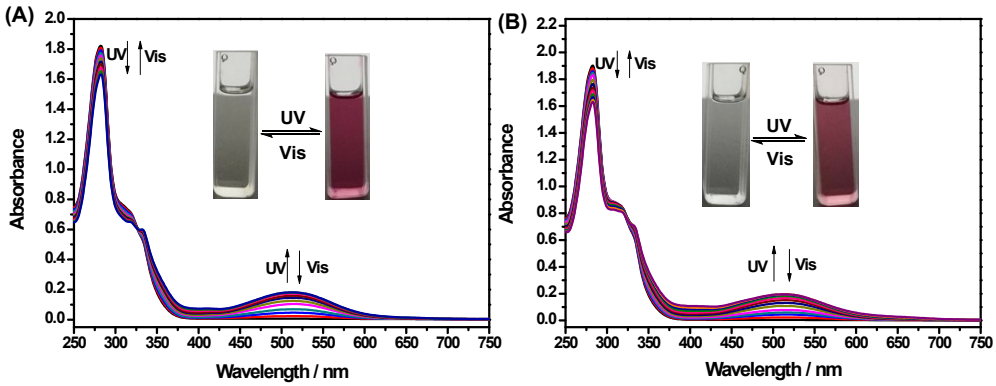


Fig. S1 Absorption spectral changes of dithienylethenes **1b** and **3b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding color changes of dithienylethene **1b** and **3b** in DMSO upon photoirradiation. (A) absorption spectral changes for **1b** [0 s, 5 s, 10 s, 15 s, 25 s, 35 s, 45 s, 55 s, 70 s, 85 s, 100 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, 80 s, 100 s, 130 s, 160 s, 190 s (PSS-open)]; (B) absorption spectral changes for **3b** [0 s, 5 s, 10 s, 15 s, 25 s, 35 s, 45 s, 55 s, 60 s, 75 s, 90 s, 105 s, 120 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, 80 s, 100 s, 130 s, 160 s, 190 s, 230 s, 260 s (PSS-open)].

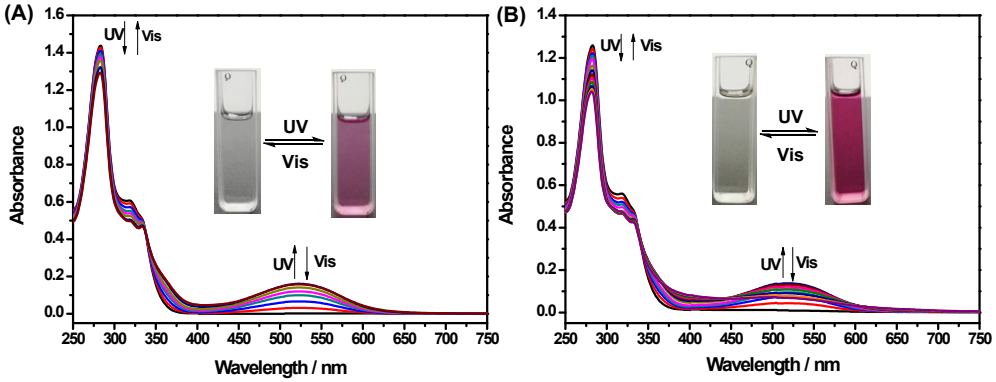


Fig. S2 Absorption spectral changes of dithienylethenes **2a** and **2b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding color changes of dithienylethene **2a** and **2b** in DMSO upon photoirradiation. (A) absorption spectral changes for **2a** [0 s, 5 s, 10 s, 15 s, 20 s, 30 s, 45 s, 60 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, 80 s, 110 s (PSS-open)]; (B) absorption spectral changes for **2b** [0 s, 5 s, 10 s, 15 s, 20 s, 30 s, 40 s, 50 s, 60 s, 75 s, 95 s, 115 s, 135 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, 80 s, 100 s, 130 s, 160 s, 200 s, 240 s, 280 s (PSS-open)].

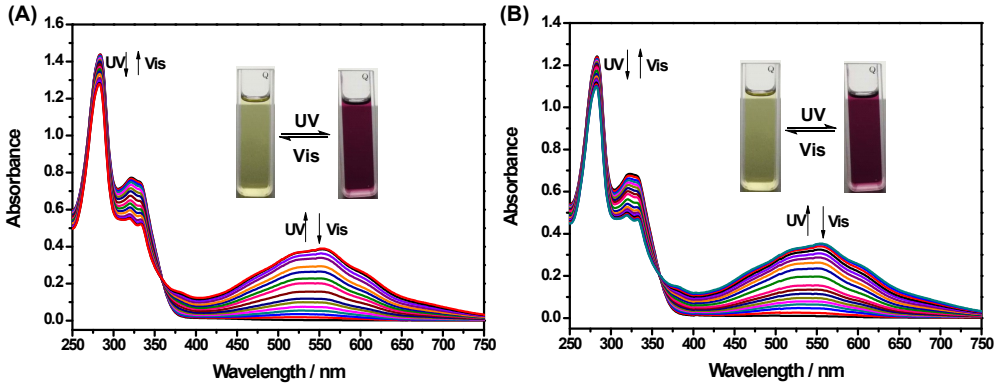


Fig. S3 Absorption spectral changes of dithienylethenes **4a** and **4b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding color changes of dithienylethene **4a** and **4b** in DMSO upon photoirradiation. (A) absorption spectral changes for **4a** [0 s, 3 s, 6 s, 9 s, 12 s, 15 s, 20 s, 25 s, 30 s, 40 s, 50 s, 60 s, 70 s, 80s, 90 s, 100 s, 115 s, 125 s, 135 s (PSS-closed); 0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s, 40 s, 60 s, 80 s, 100 s, 200 s, 220 s, 240 s, 260 s, 280 s, 330 s (PSS-open)]; (B) absorption spectral changes for **4b** [0 s, 3 s, 6 s, 9 s, 12 s, 15 s, 20 s, 25 s, 30 s, 40 s, 50 s, 60 s, 70 s, 80s, 90 s, 100 s, 110 s, 120 s (PSS-closed); 0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s, 35 s, 40 s, 50 s, 60 s, 80 s, 110 s, 140 s, 170 s, 200 s, 230 s, 270 s (PSS-open)].

Table S1 Absorption characteristics and photochromic quantum yields of **1-4** in DMSO (2.0×10^{-5} mol/L)

Compounds	λ_{max}^{Abs} / nm[a] ($\varepsilon\times10^4$) (Open)	λ_{max}^{Abs} / nm[b] ($\varepsilon\times10^4$) (PSS)	Φ[c] $\varphi_{o\text{-}c}$ (λ / nm)	Φ[c] $\varphi_{c\text{-}o}$ (λ / nm)
1a	283 (1.08)	510 (0.11)	0.21 (510)	0.0014 (283)
1b	281 (0.92)	510 (0.10)	0.18 (510)	0.0011 (281)
2a	283 (0.72)	522 (0.09)	0.24 (522)	0.0040 (283)
2b	283 (0.63)	520 (0.07)	0.20 (520)	0.0034 (283)
3a	282 (0.66)	511 (0.07)	0.25 (511)	0.0076 (282)
3b	283 (0.95)	510 (0.10)	0.16 (542)	0.0055 (296)
4a	283 (0.73)	542 (0.20)	0.33 (542)	0.0042 (283)
4b	282 (0.62)	543 (0.18)	0.31 (543)	0.0038 (282)

a Absorption maxima of open-ring isomers.

b Absorption maxima of closed-ring isomers.

c Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.

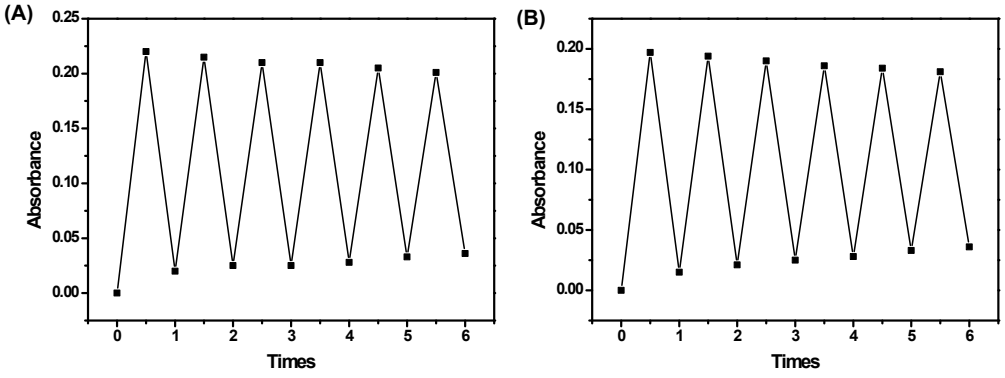


Fig. S4 Fatigue resistance of dithienylethenes **1a** (A) at 510 nm and **1b** (B) at 510 nm on alternate excitation at 254 nm and > 402 nm Vis light irradiation over six cycles in DMSO (2.0×10^{-5} mol/L) at 298 K.

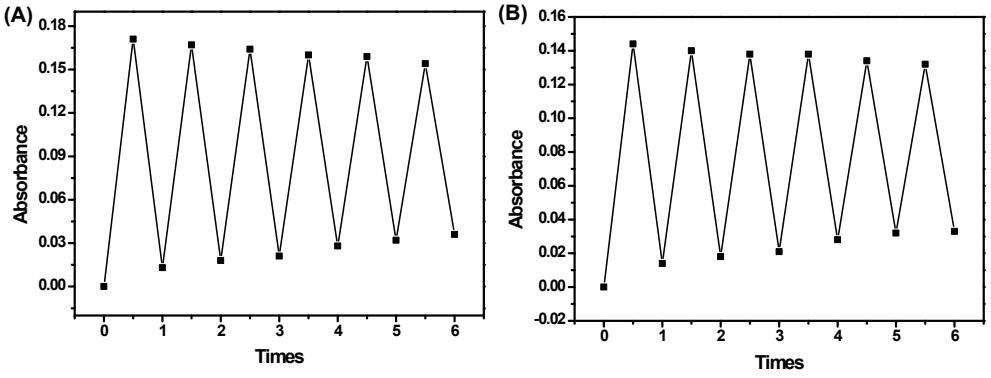


Fig. S5 Fatigue resistance of dithienylethenes **2a** (A) at 522 nm and **2b** (B) at 520 nm on alternate excitation at 254 nm and > 402 nm Vis light irradiation over six cycles in DMSO (2.0×10^{-5} mol/L) at 298 K.

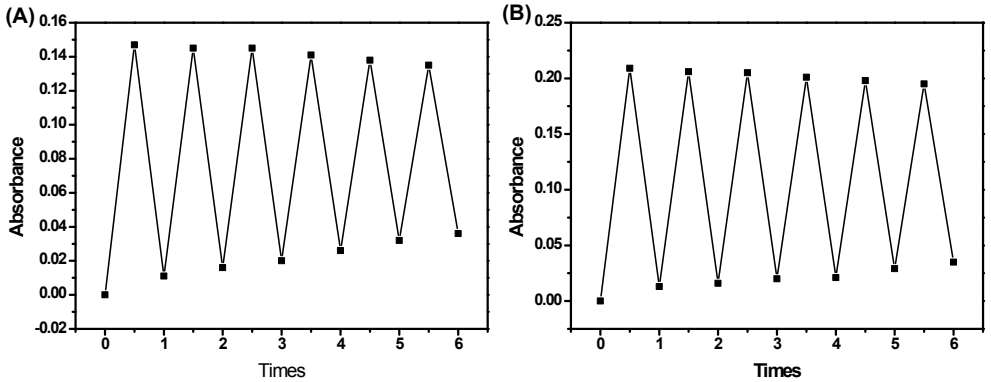


Fig. S6 Fatigue resistance of dithienylethenes **3a** (A) at 511 nm and **3b** (B) at 510 nm on alternate excitation at 254 nm and > 402 nm Vis light irradiation over six cycles in DMSO (2.0×10^{-5} mol/L) at 298 K.

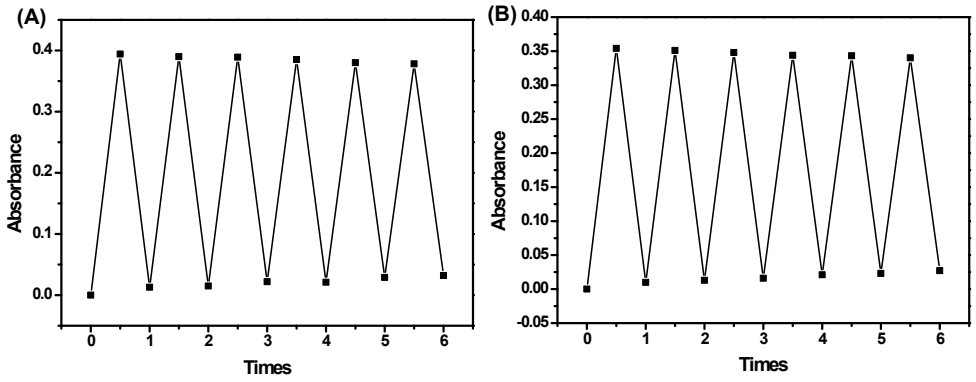


Fig. S7 Fatigue resistance of dithienylethenes **4a** (A) at 542 nm and **4b** (B) at 543 nm on alternate excitation at 254 nm and > 402 nm Vis light irradiation over six cycles in DMSO (2.0×10^{-5} mol/L) at 298 K.

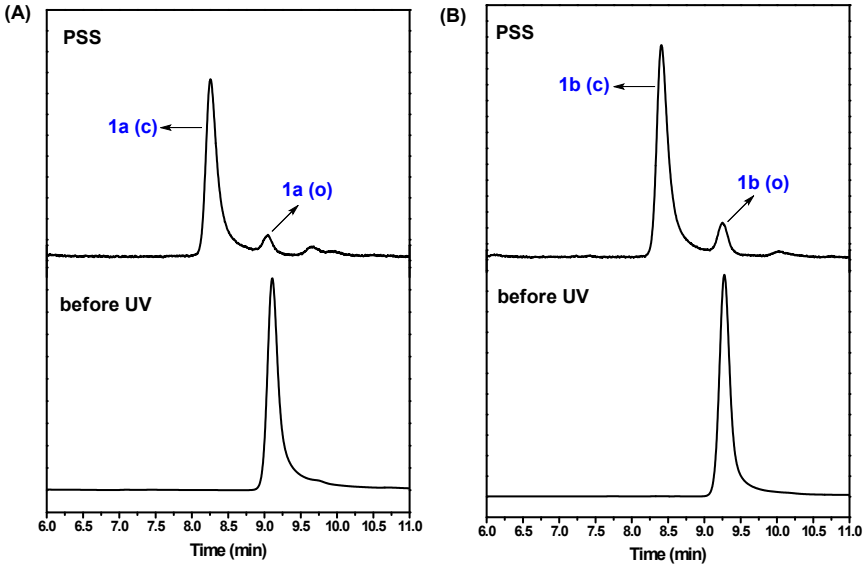


Fig. S8 HPLC traces of **1** before UV irradiation and in the PSS state detected at the isosbestic point of 326 nm (CH_3CN / H_2O = 80 / 20, v / v) at a flow rate of 1.0 mL min^{-1}, (A) HPLC for **1a**; (B) HPLC for **1b**.

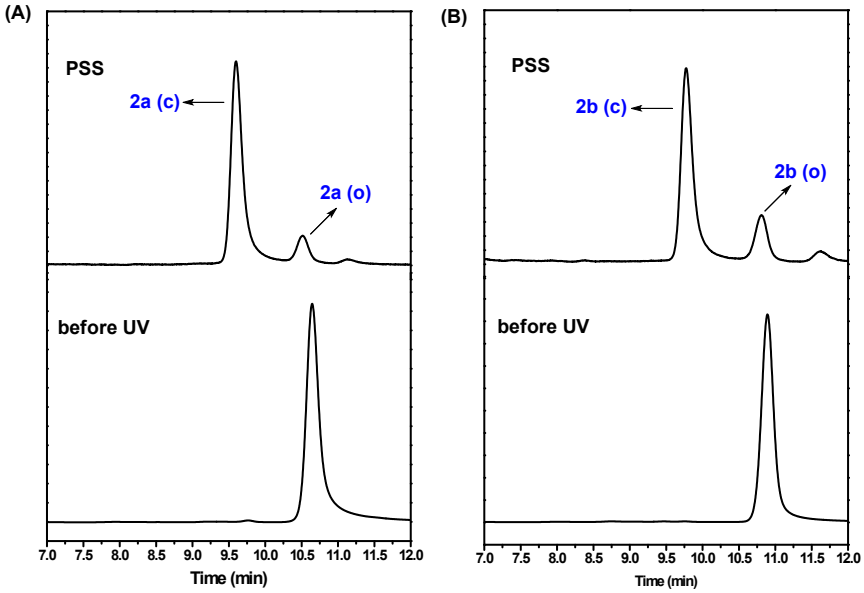


Fig. S9 HPLC traces of **2** before UV irradiation and in the PSS state detected at the isosbestic point of 338 nm (CH_3CN / H_2O = 80 / 20, v / v) at a flow rate of 1.0 mL min^{-1}, (A) HPLC for **2a**; (B) HPLC for **2b**.

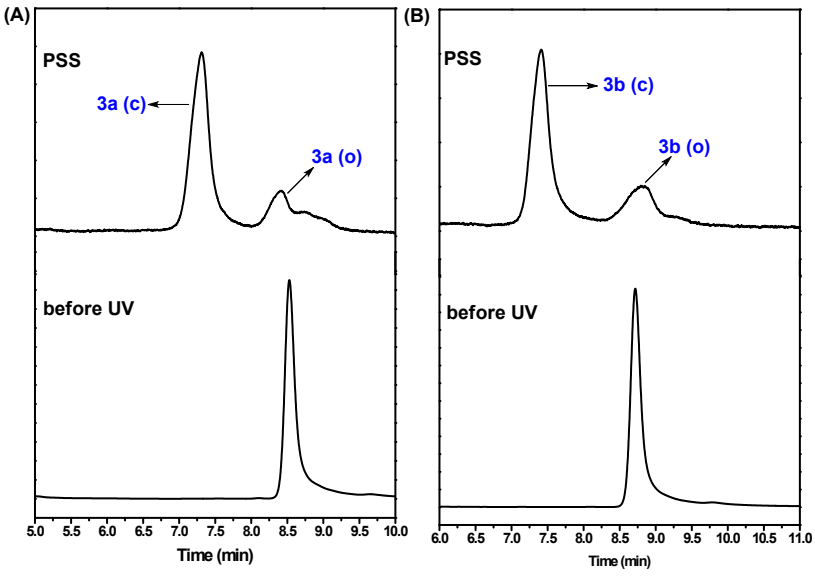


Fig. S10 HPLC traces of **3** before UV irradiation and in the PSS state detected at the isosbestic point of 324 nm (CH_3CN / H_2O = 80 / 20, v / v) at a flow rate of 1.0 mL min^{-1}, (A) HPLC for **3a**; (B) HPLC for **3b**.

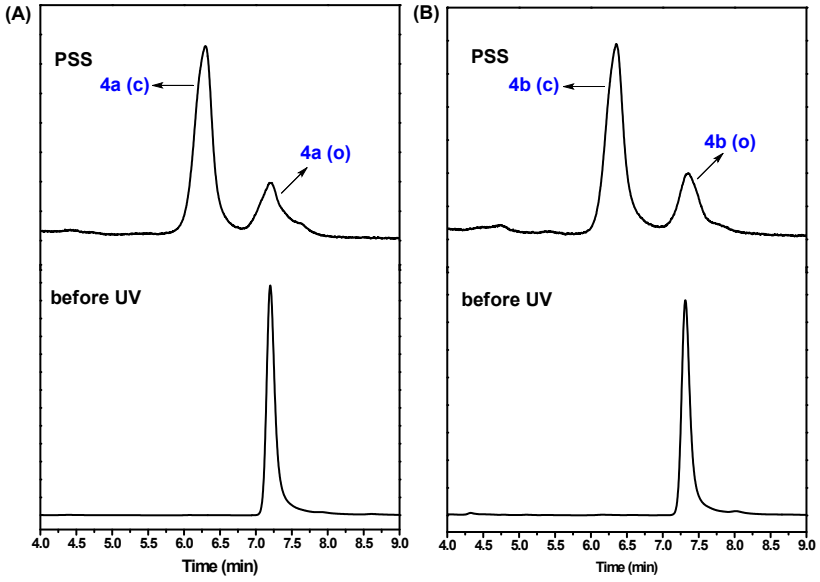


Fig. S11 HPLC traces of **4** before UV irradiation and in the PSS state detected at the isosbestic point of 359 nm (CH_3CN / H_2O = 80 / 20, v / v) at a flow rate of 1.0 mL min^{-1}, (A) HPLC for **4a**; (B) HPLC for **4b**.

Table S2 The conversion ratio of switchable antibacterial agents **1-4** at the photostationary state (PSS).

Compounds	Conversion ratio (%)	Compounds	Conversion ratio (%)
1a	93	**1b**	88
2a	89	**2b**	81
3a	89	**3b**	80
4a	83	**4b**	79

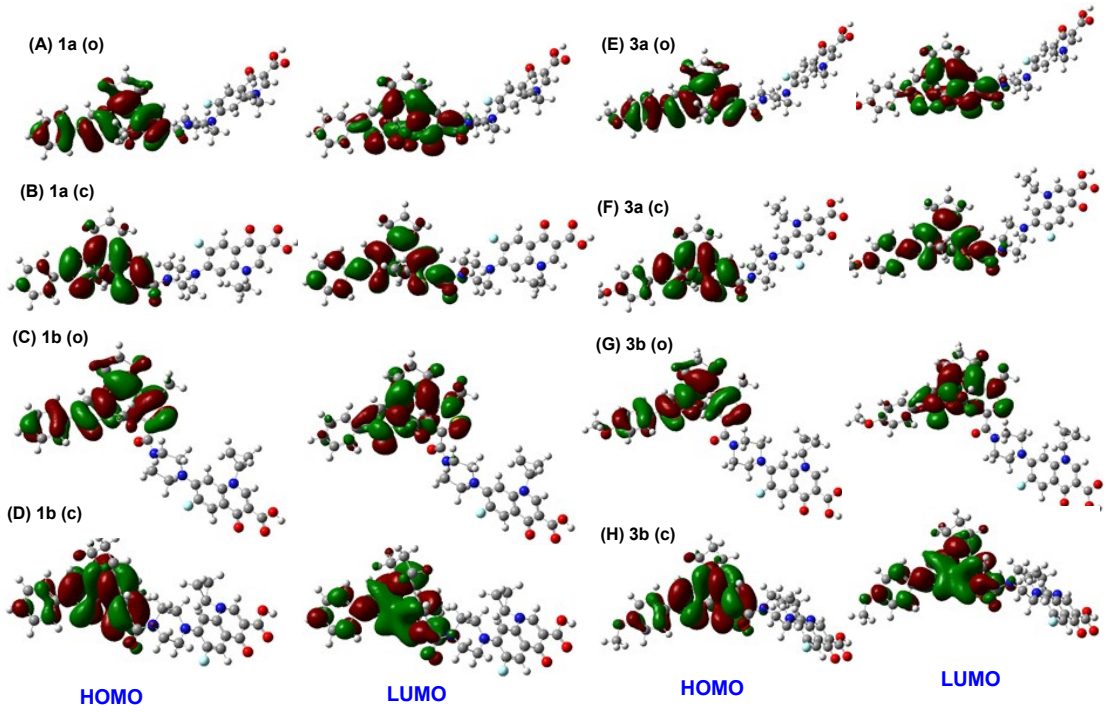


Fig. S12 Frontier molecular orbital profiles of **1** and **3** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

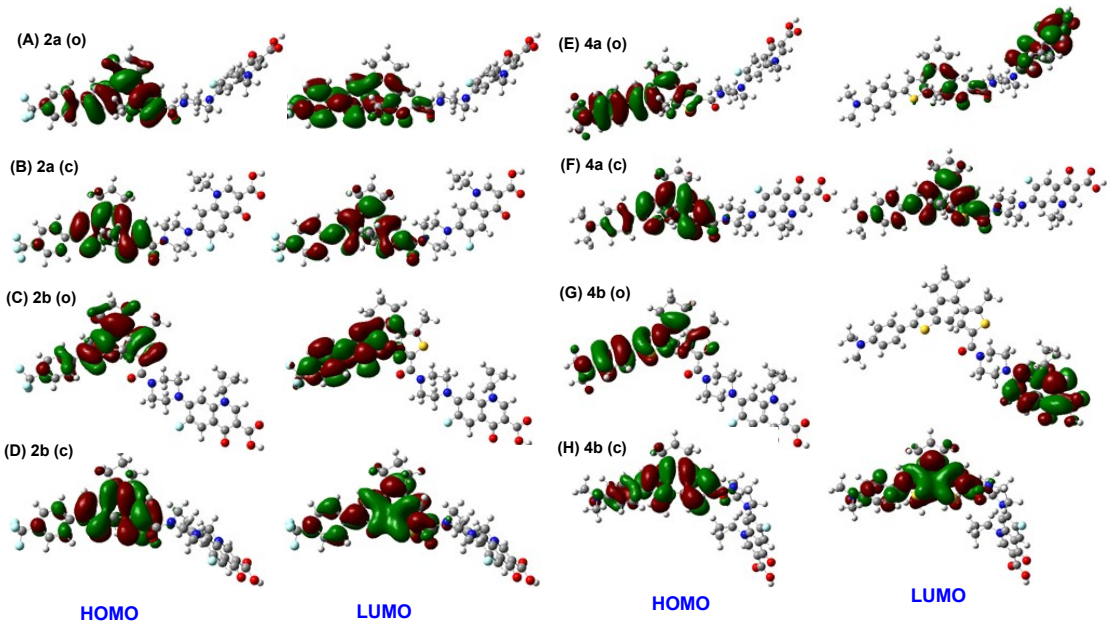


Fig. S13 Frontier molecular orbital profiles of **2** and **4** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

Table S3 Calculated parameters for dithienylathenes **1-4**.

Cpds	HOMO (ev)	LUMO (ev)	Eg (ev)	Cpds	HOMO (ev)	LUMO (ev)	Eg (ev)
1a (o)	-5.24	-1.16	4.08	**1a (c)**	-4.08	-2.40	1.68
1b (o)	-5.16	-1.12	4.04	**1b (c)**	-4.18	-2.49	1.69
2a (o)	-5.42	-1.33	4.09	**2a (c)**	-4.33	-2.63	1.70
2b (o)	-5.32	-1.23	4.09	**2b (c)**	-4.38	-2.74	1.64
3a (o)	-5.13	-1.15	3.98	**3a (c)**	-4.15	-2.44	1.71
3b (o)	-5.12	-1.09	4.03	**3b (c)**	-4.11	-2.42	1.69
4a (o)	-4.62	-1.04	3.58	**4a (c)**	-3.74	-2.03	1.71
4b (o)	-4.50	-1.01	3.49	**4b (c)**	-3.81	-2.13	1.68

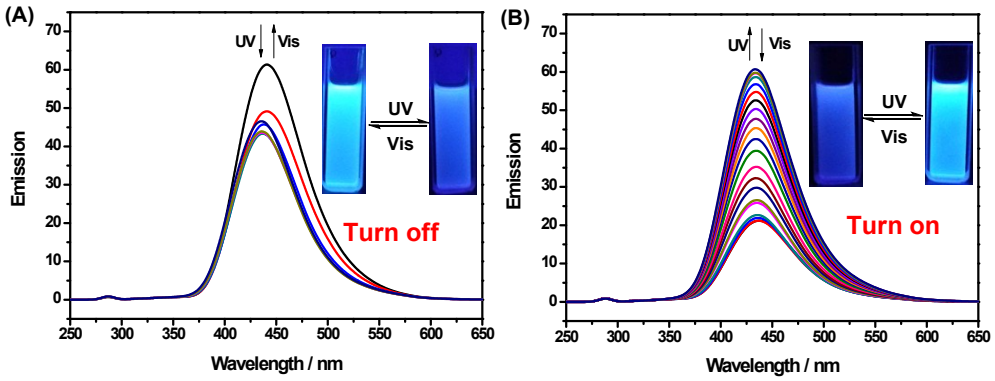


Fig. S14 Emission spectral changes of of dithienylethenes **1b** and **3b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding fluorescence intensity changes of dithienylethene **1b** and **3b** in DMSO upon photoirradiation. (A) emission spectral changes for **1b** [0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s (PSS-closed); 0 s, 10 s, 20 s, 30 s,40 s, 50 s, 60 s (PSS-open)]; (B) emission spectral changes for **3b** (0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s, 35 s, 45 s, 55 s, 65 s, 80 s, 95 s, 110 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 70 s, 90 s, 110 s, 130 s, 150 s, 170 s, 200 s, 230 s (PSS-open)].

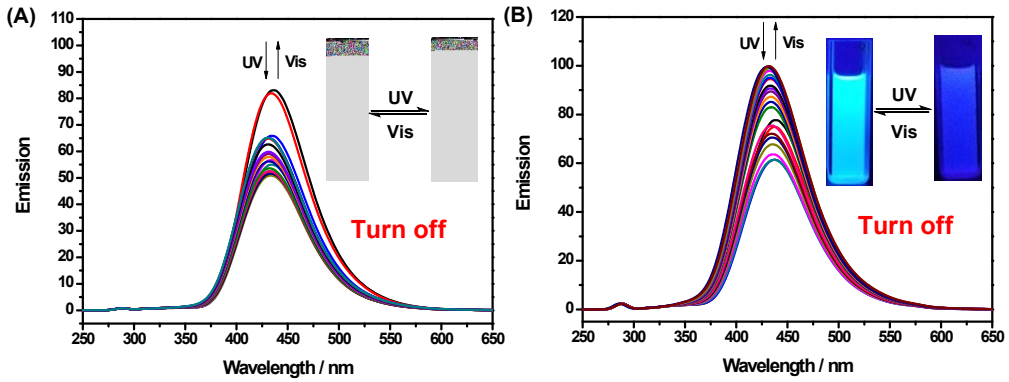


Fig. S15 Emission spectral changes of of dithienylethenes **2a** and **2b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding fluorescence intensity changes of dithienylethene **2a** and **2b** in DMSO upon photoirradiation. (A) emission spectral changes for **2a** [0 s, 5 s, 10 s, 15 s, 25 s, 30 s, 45 s, 55 s, 60 s, 65 s, 70 s, 75 s, 80 s, 85 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, 80 s, 100 s, 120 s, 150 s, 180 s, 200 s (PSS-open)]; (B) emission spectral changes for **2b** [0 s, 5 s, 10 s, 15 s, 25 s, 30 s, 45 s, 55 s, 60 s, 65 s, 70 s, 75 s, 80 s, 90 s, 95 s, 100 s, 110 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, 80 s, 100 s, 120 s, 140 s, 170 s, 200 s, 230 s, 260 s, 300 s (PSS-open)]

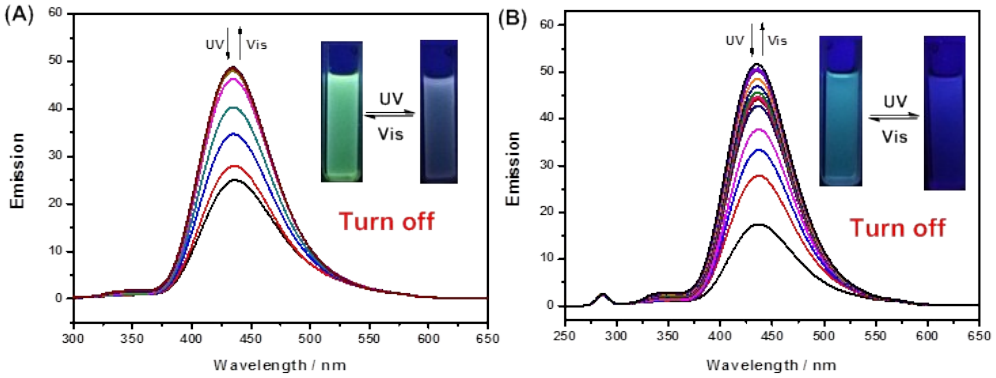


Fig. S16 Emission spectral changes of of dithienylethenes **4a** and **4b** with 254 nm UV and > 402 nm visible light irradiation in DMSO (2.0×10^{-5} mol/L) at 298 K. (Inset) Corresponding fluorescence intensity changes of dithienylethene **4a** and **4b** in DMSO upon photoirradiation. (A) emission spectral changes for **4a** [0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s, 35 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, 80 s, 100 s (PSS-open)]; (B) emission spectral changes for **4b** [0 s, 5 s, 10 s, 15 s, 20 s, 25 s, 30 s, 35 s, 40 s, 45 s, 55 s, 65 s, 75 s, 85 s, 95 s (PSS-closed); 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, 80 s, 100 s, 120 s, 140 s, 160 s, 180 s, 200 s, 230 s (PSS-open)].

Table S4 The fluorescence data of dithienylethenes **1-4** in DMSO at 298 K (2.0×10^{-5} mol/L)

Compounds	λ_{em} [a] (nm)	Φ_f (open) [b]	Φ_f (closed) [c]
1a	440	0.35	0.14
1b	440	0.29	0.12
2a	436	0.41	0.20
2b	431	0.48	0.22
3a	428	0.06	0.40
3b	432	0.11	0.33
4a	434	0.23	0.12
4b	435	0.25	0.08

[a] Fluorescence emission maxima; [b] Fluorescence quantum yield of open isomers determined by a standard method with quinoline sulfate in 0.1 M aqueous H_2SO_4 ($\Phi_f = 0.55$, $\lambda_{ex} = 313$ nm) as reference; [c] Fluorescence quantum yield of closed isomers determined by a standard method with quinoline sulfate in 0.1 M aqueous H_2SO_4 ($\Phi_f = 0.55$, $\lambda_{ex} = 313$ nm) as reference.

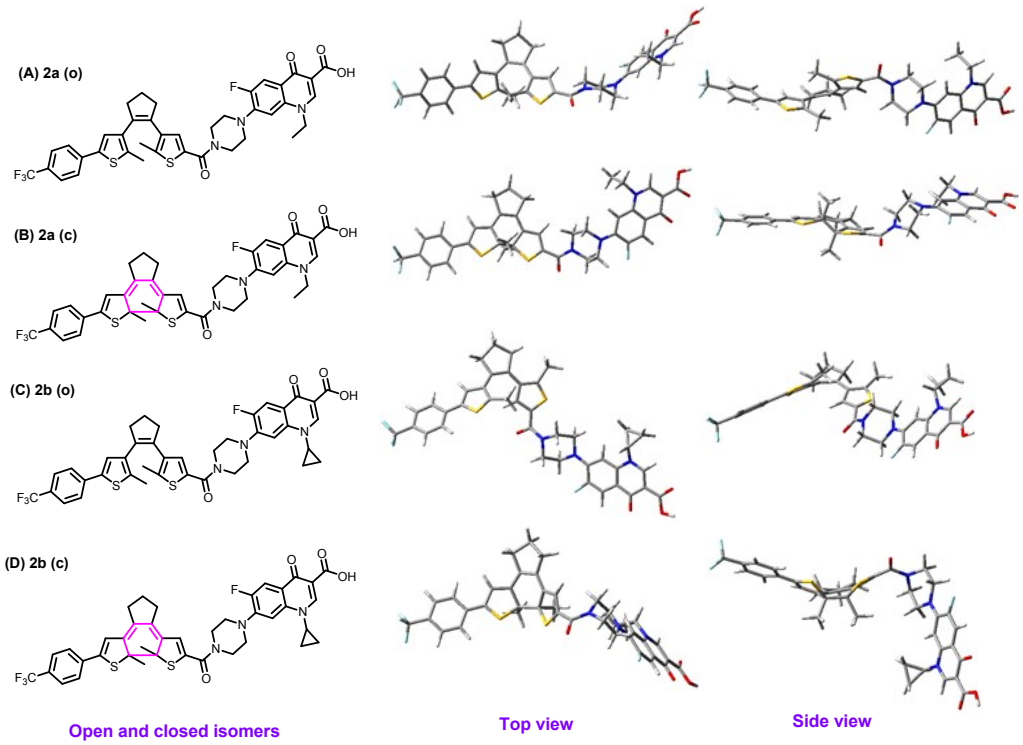


Fig. S17 The energy-minimized structure of open and closed isomers of **2a** and **2b** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

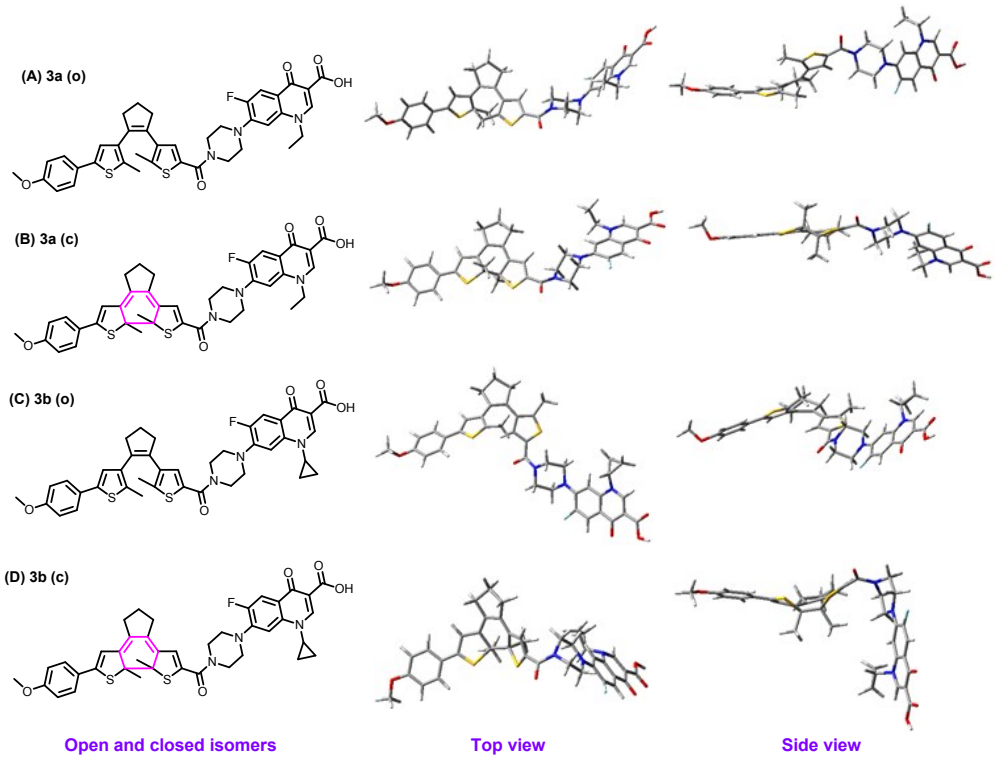


Fig. S18 The energy-minimized structure of open and closed isomers of **3a** and **3b** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

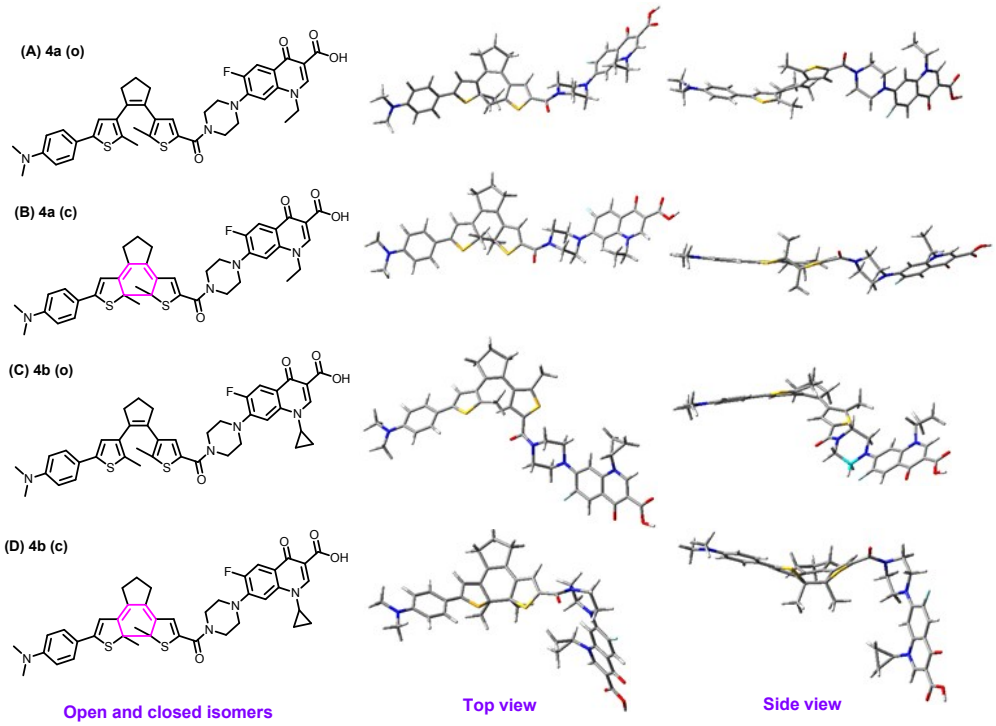


Fig. S19 The energy-minimized structure of open and closed isomers of **4a** and **4b** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

Appendix: NMR and Mass spectra

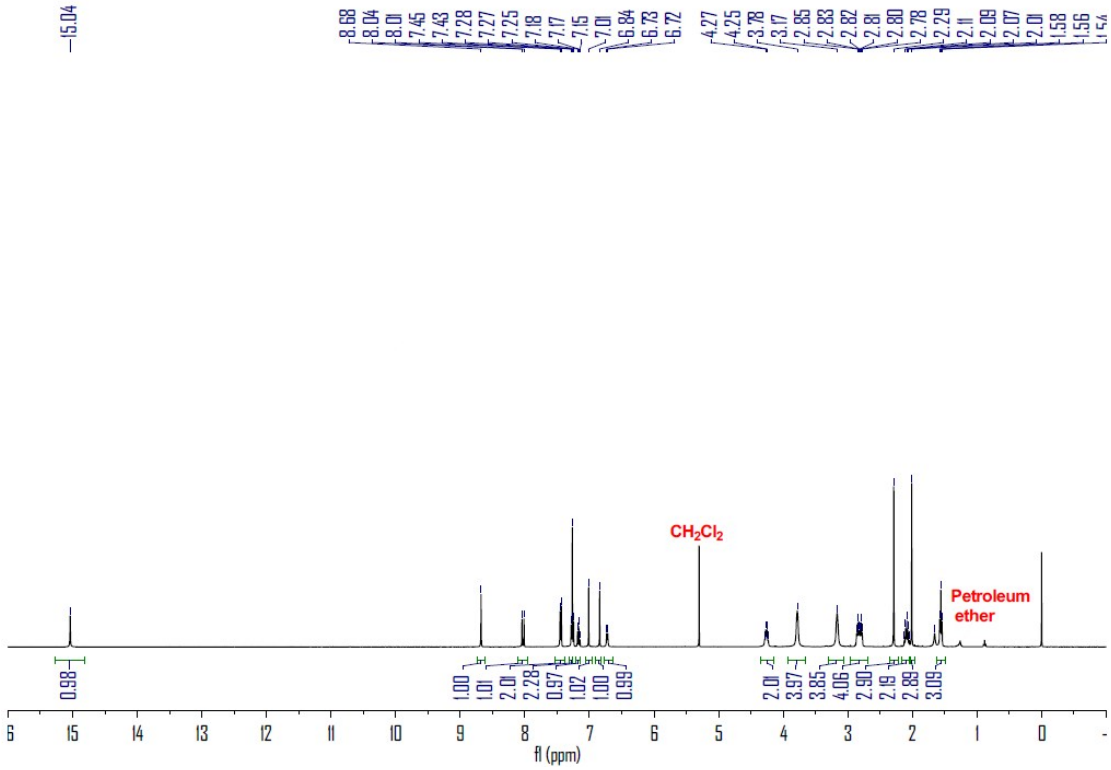


Fig. S20 400 MHz ^{1}H NMR spectrum of dithienylethene **1a** in $CDCl_3$ at room temperature.

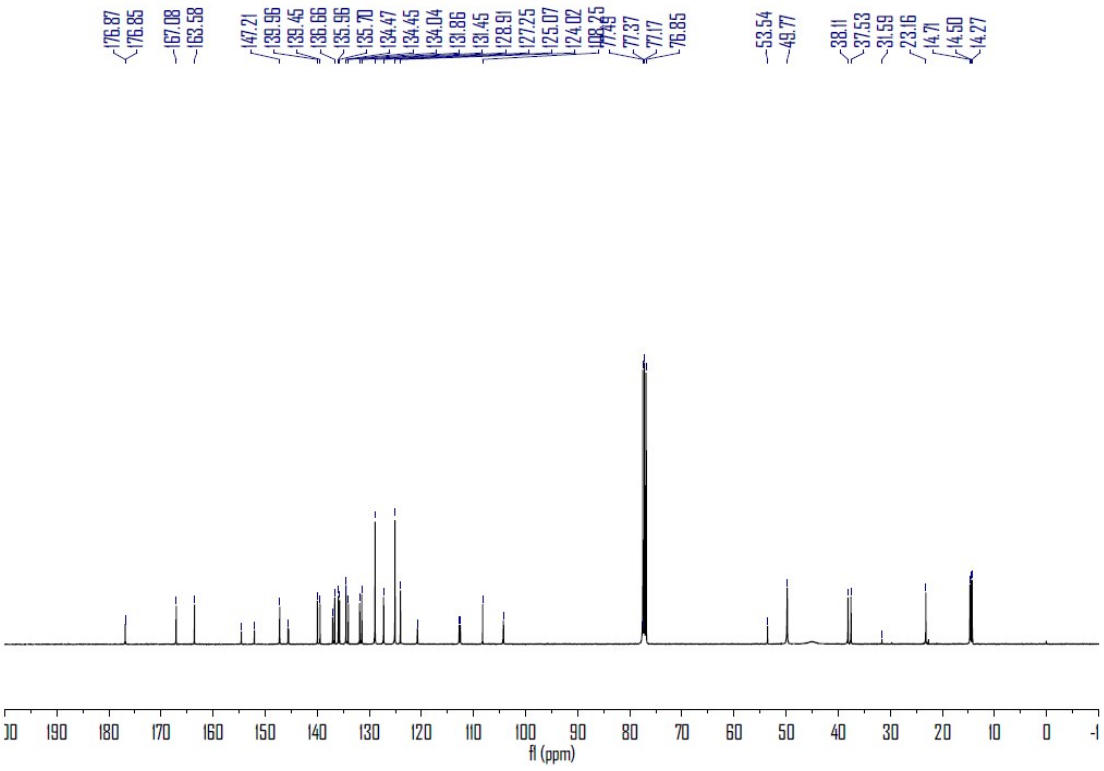


Fig. S21 100 MHz ^{1}H NMR spectrum of dithienylethene **1a** in $CDCl_3$ at room temperature.

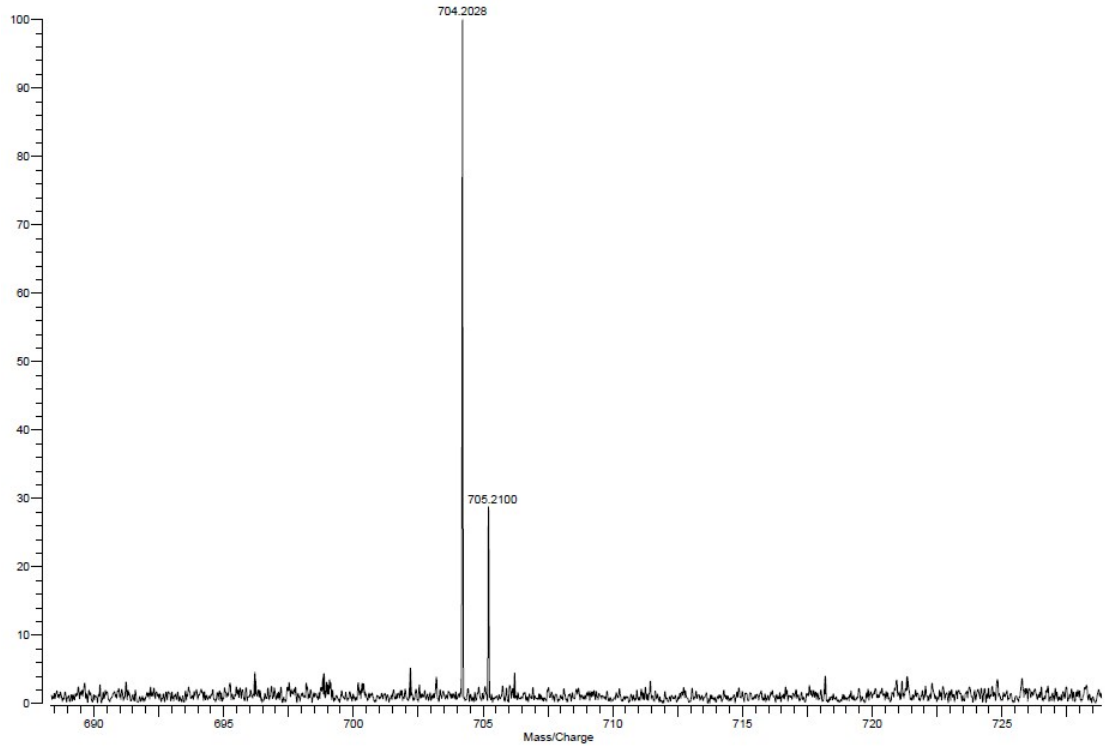


Fig. S22 HRMS of dithienylethene **1a**.

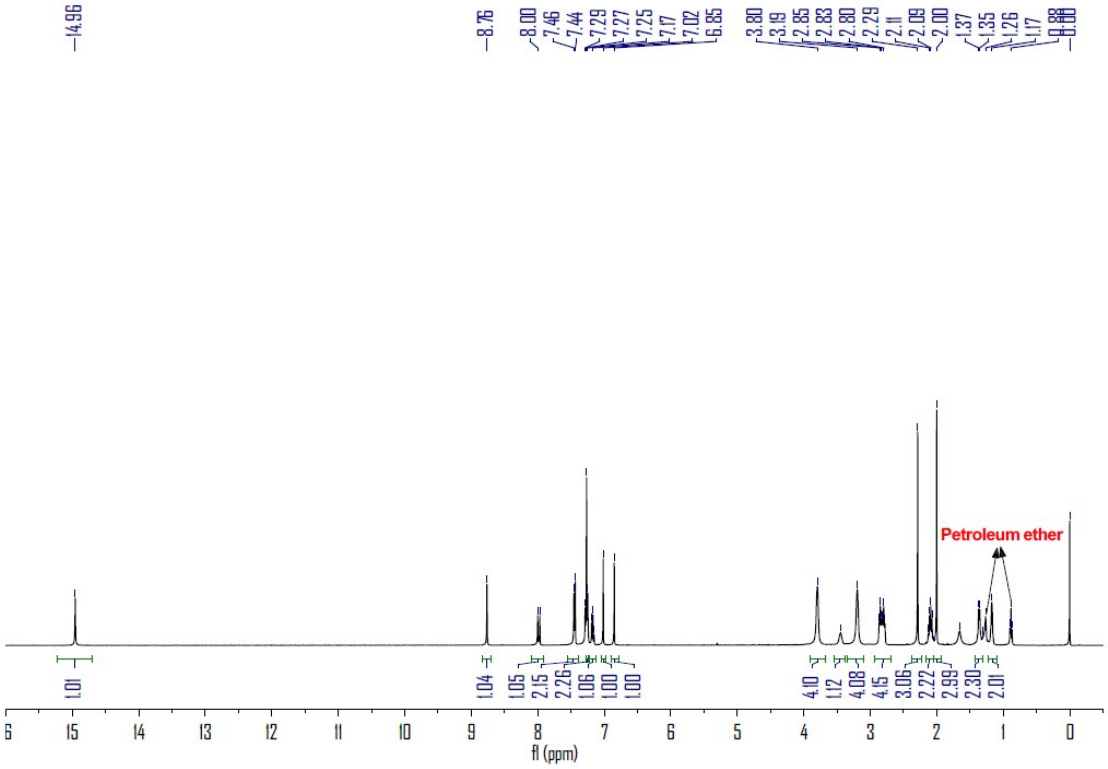


Fig. S23 400 MHz ^{1}H NMR spectrum of dithienylethene **1b** in $CDCl_3$ at room temperature.

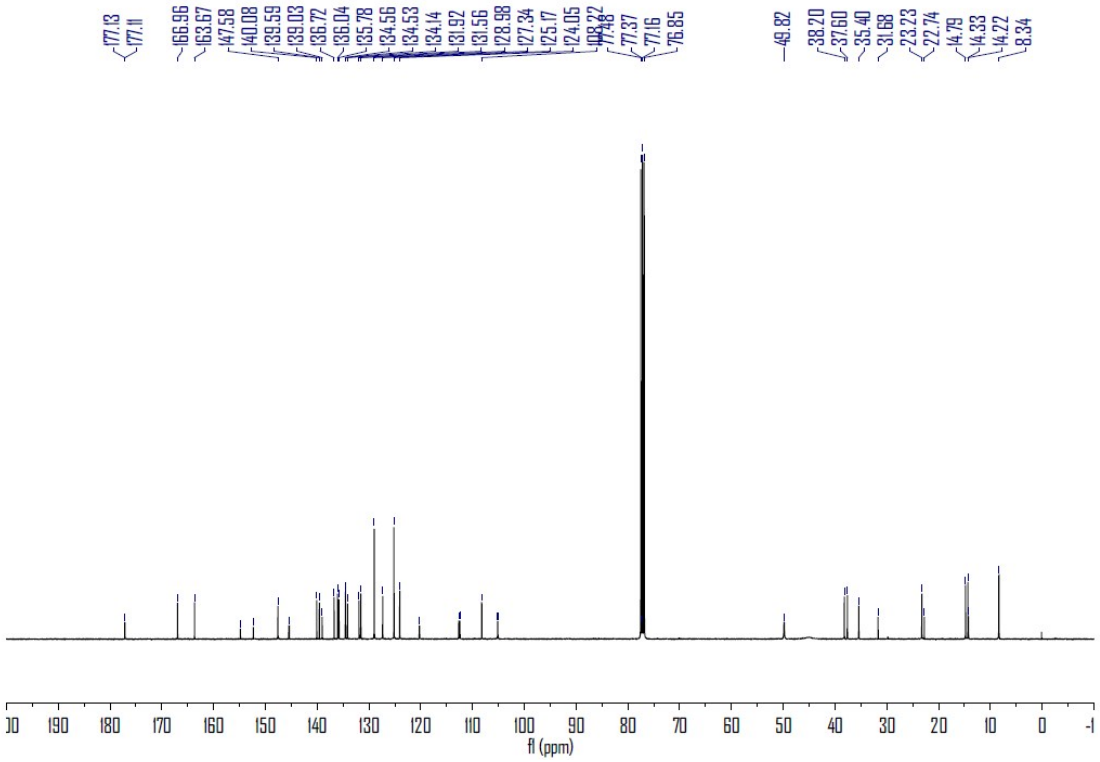


Fig. S24 100 MHz ^{1}H NMR spectrum of dithienylethene **1b** in $CDCl_3$ at room temperature.

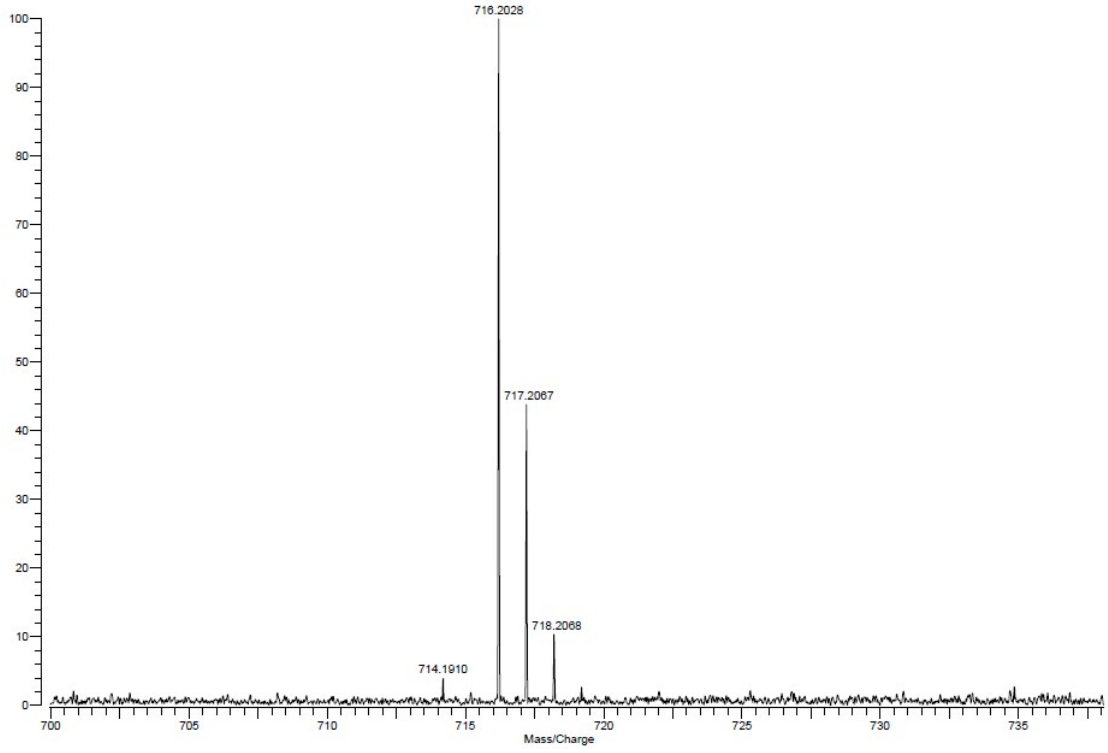


Fig. S25 HRMS of dithienylethene **1b**.

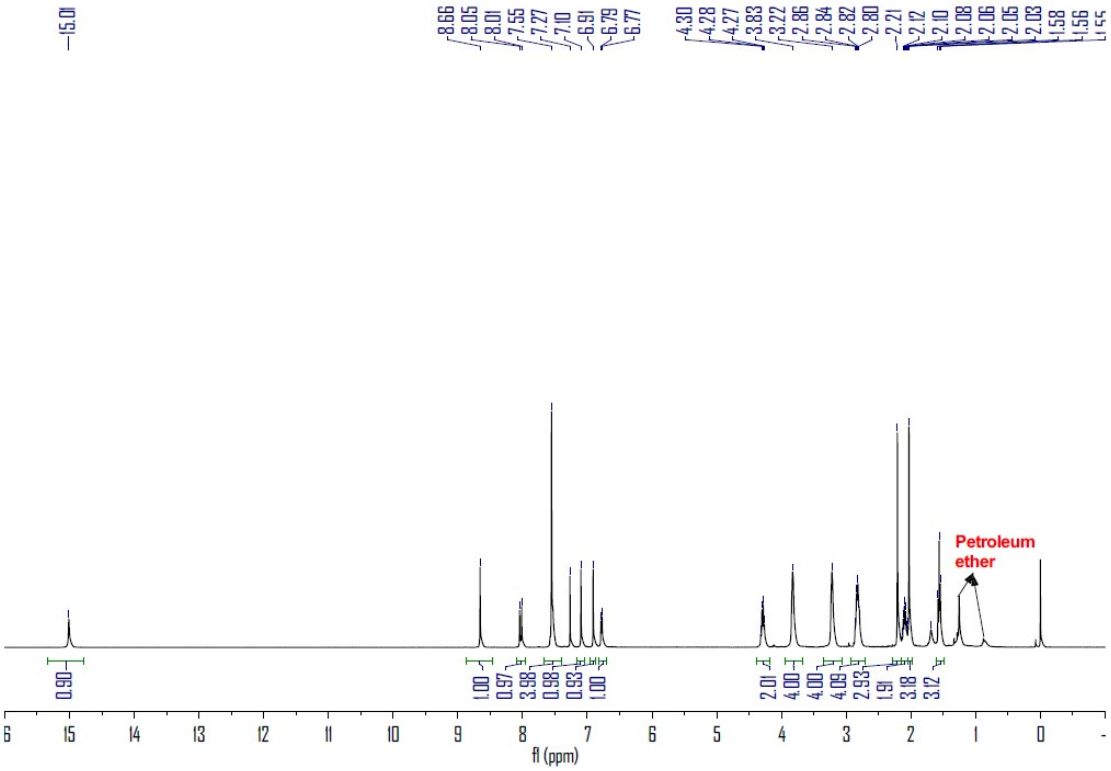


Fig. S26 400 MHz ^{1}H NMR spectrum of dithienylethene **2a** in $CDCl_3$ at room temperature.

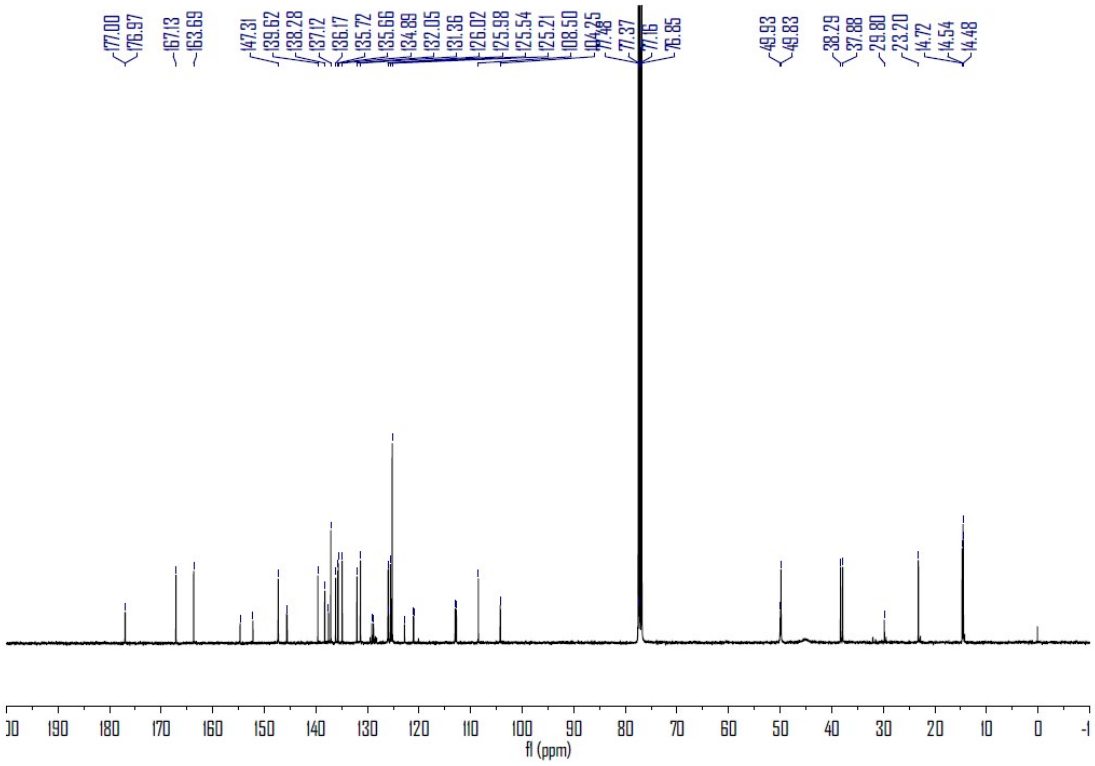


Fig. S27 100 MHz ^{1}H NMR spectrum of dithienylethene **2a** in $CDCl_3$ at room temperature.

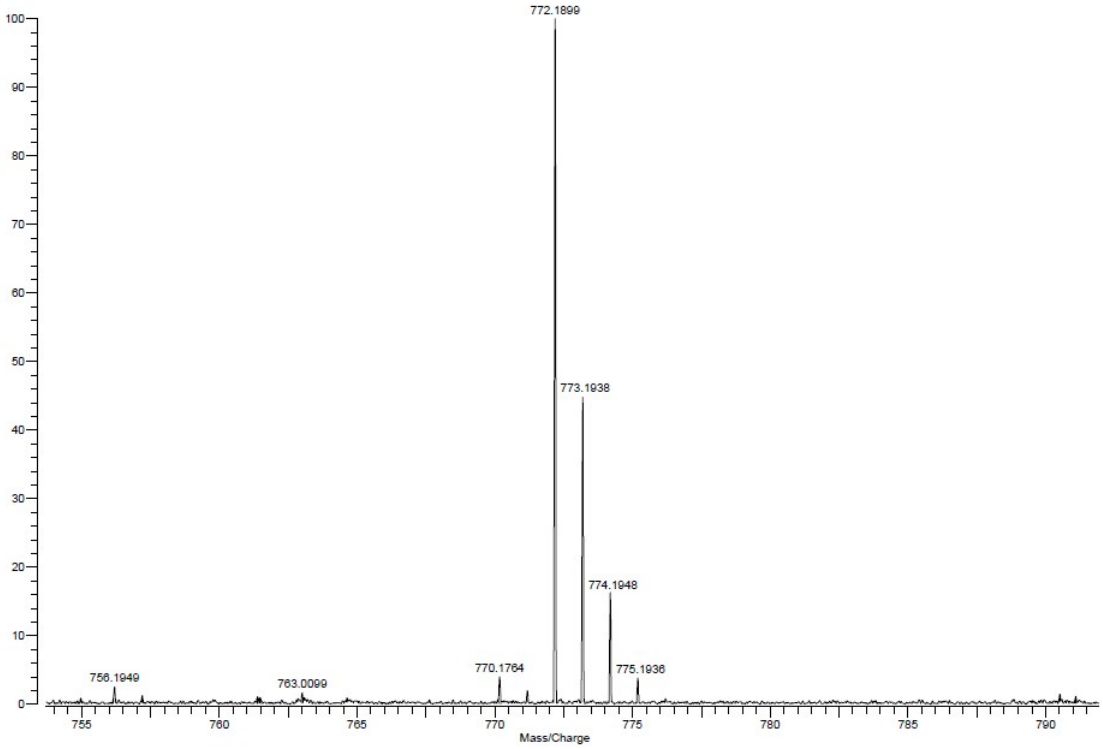


Fig. S28 HRMS of dithienylethene **2a**.

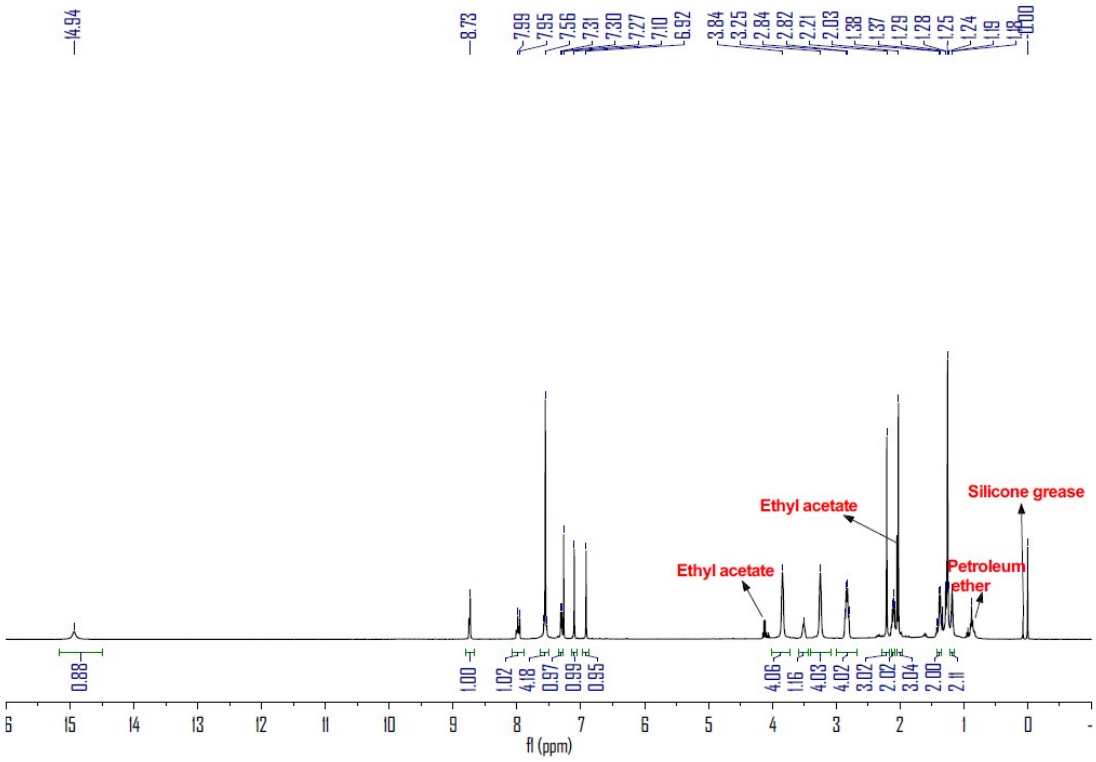


Fig. S29 400 MHz ^{1}H NMR spectrum of dithienylethene **2b** in $CDCl_3$ at room temperature.

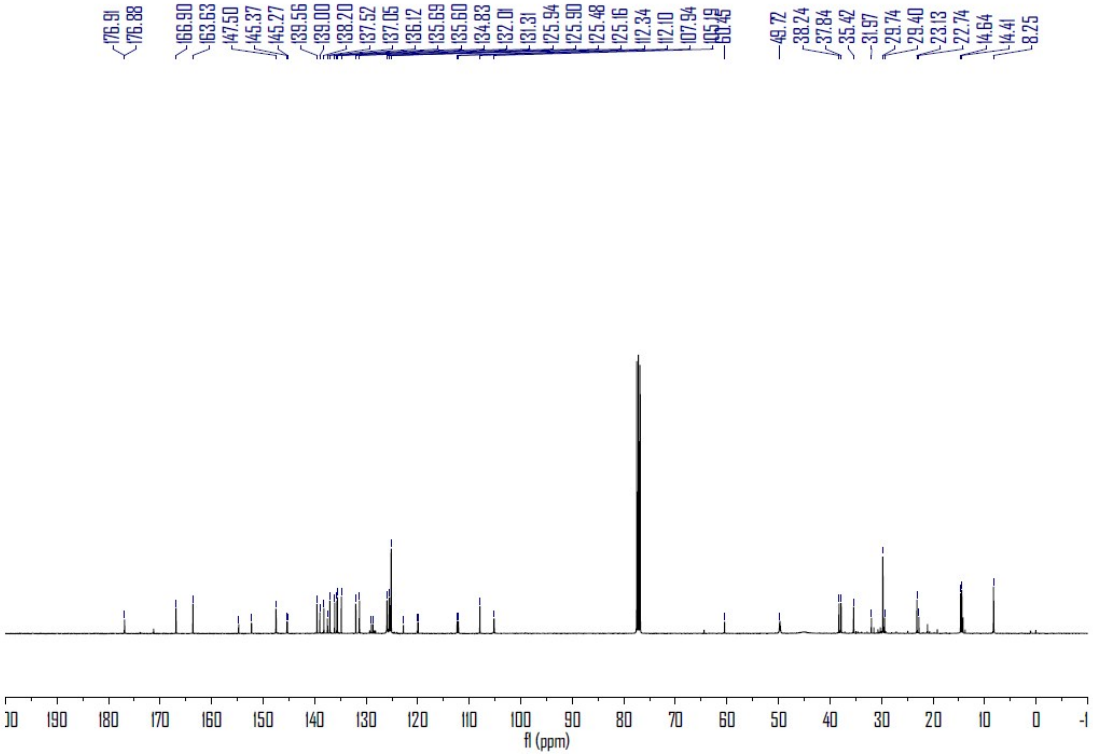


Fig. S30 100 MHz ^{1}H NMR spectrum of dithienylethene **2b** in $CDCl_3$ at room temperature.

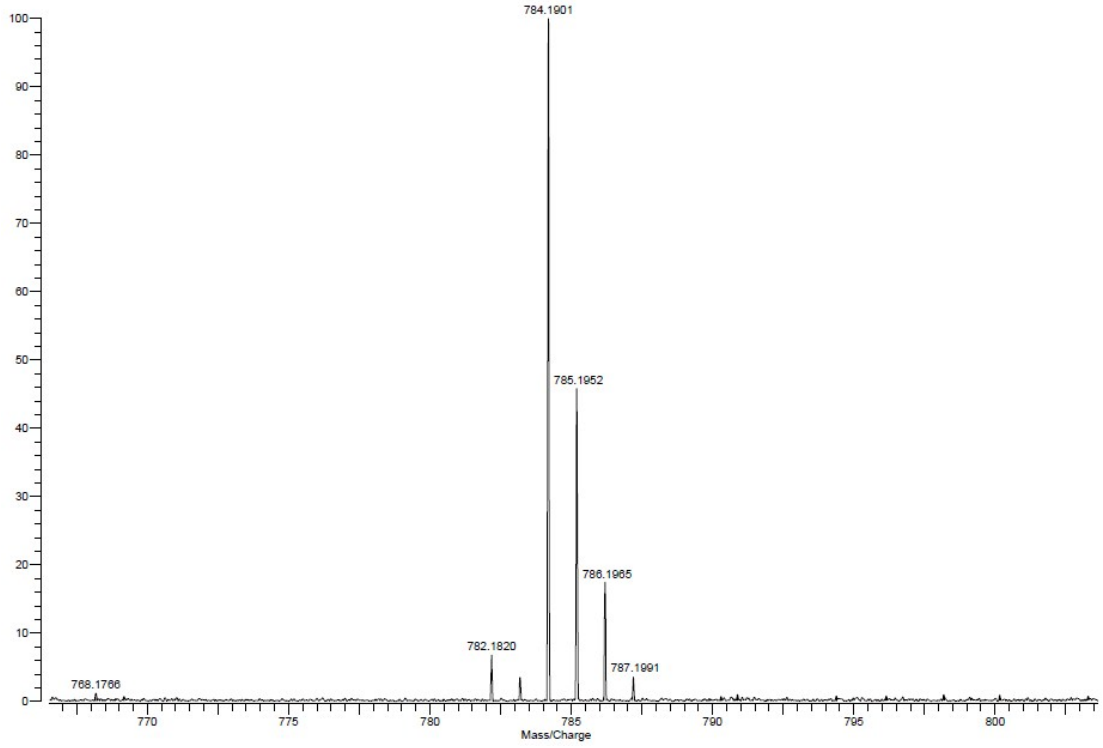


Fig. S31 HRMS of dithienylethene **2b**.

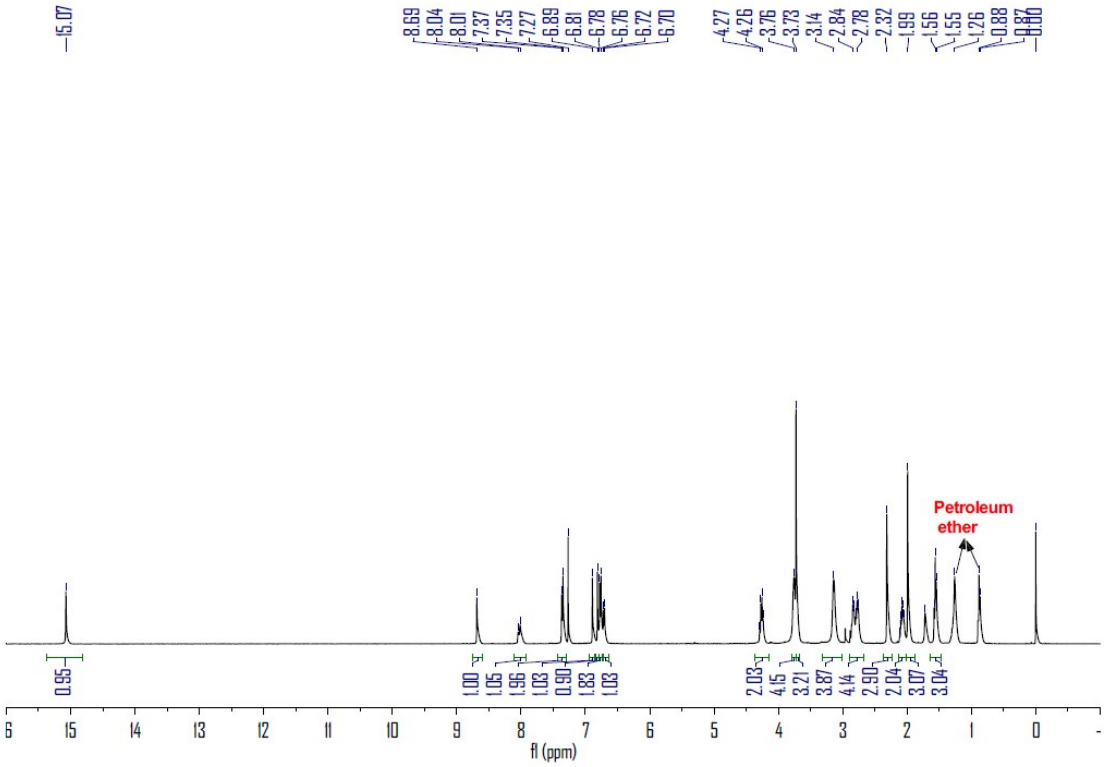


Fig. S32 400 MHz ^{1}H NMR spectrum of dithienylethene **3a** in $CDCl_3$ at room temperature.

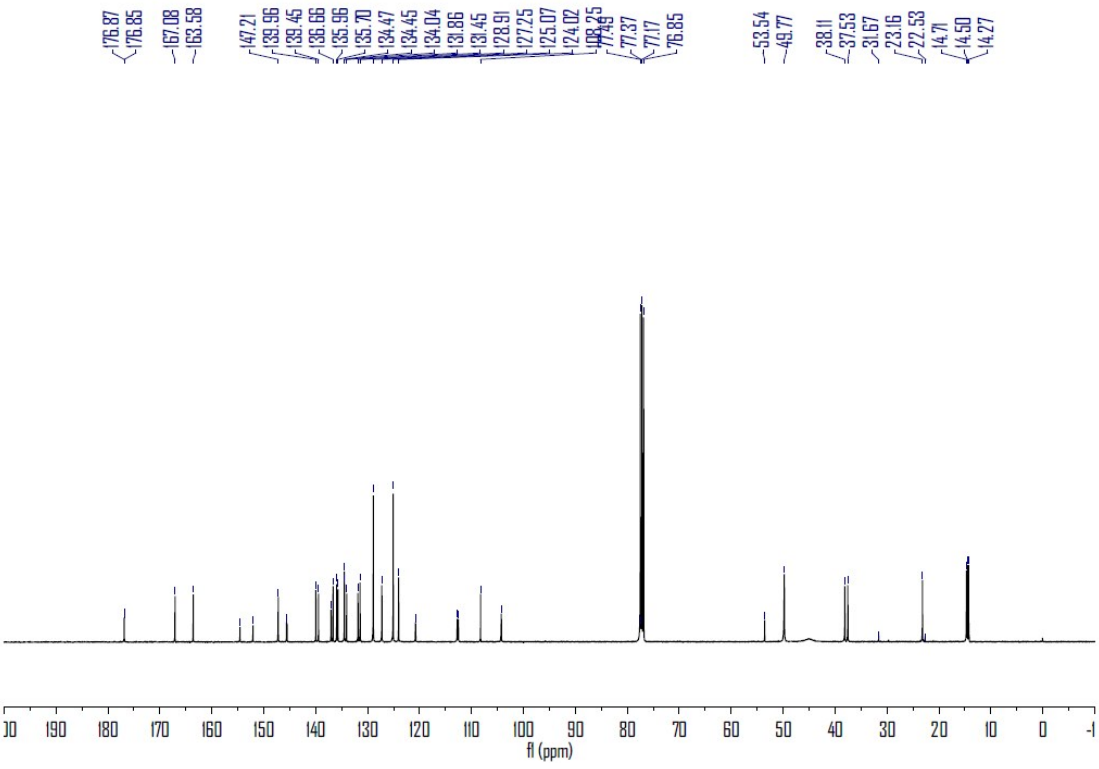


Fig. S33 100 MHz ^{1}H NMR spectrum of dithienylethene **3a** in $CDCl_3$ at room temperature.

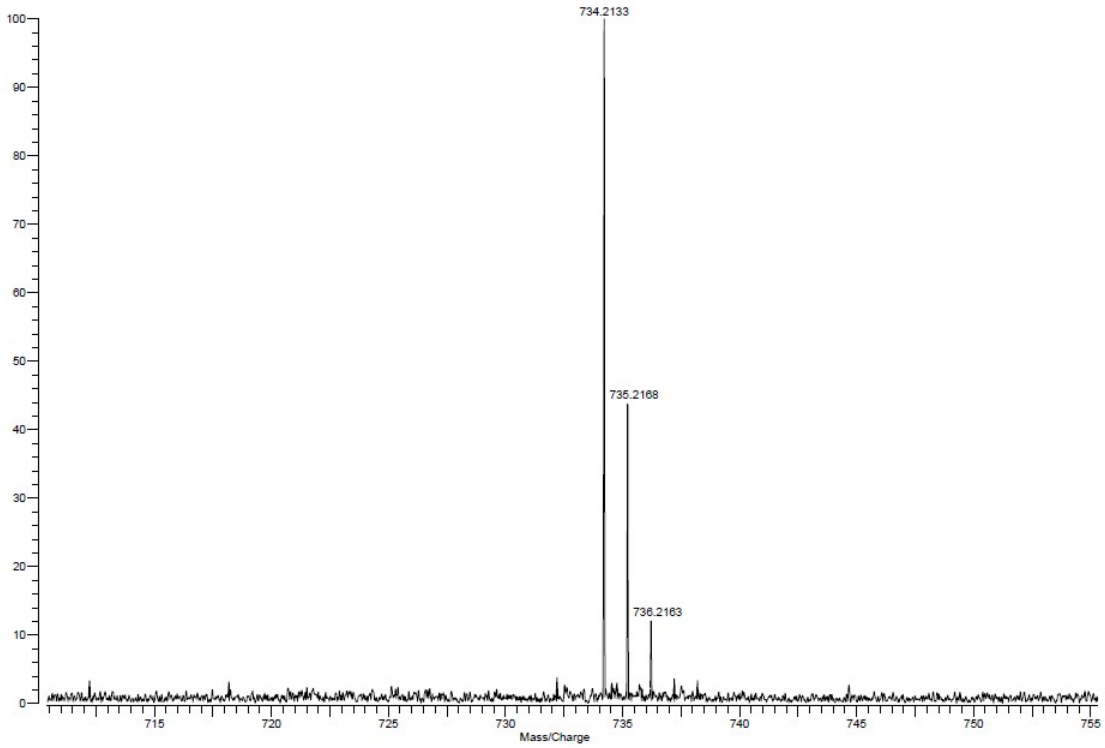


Fig. S34 HRMS of dithienylethene **3a**.

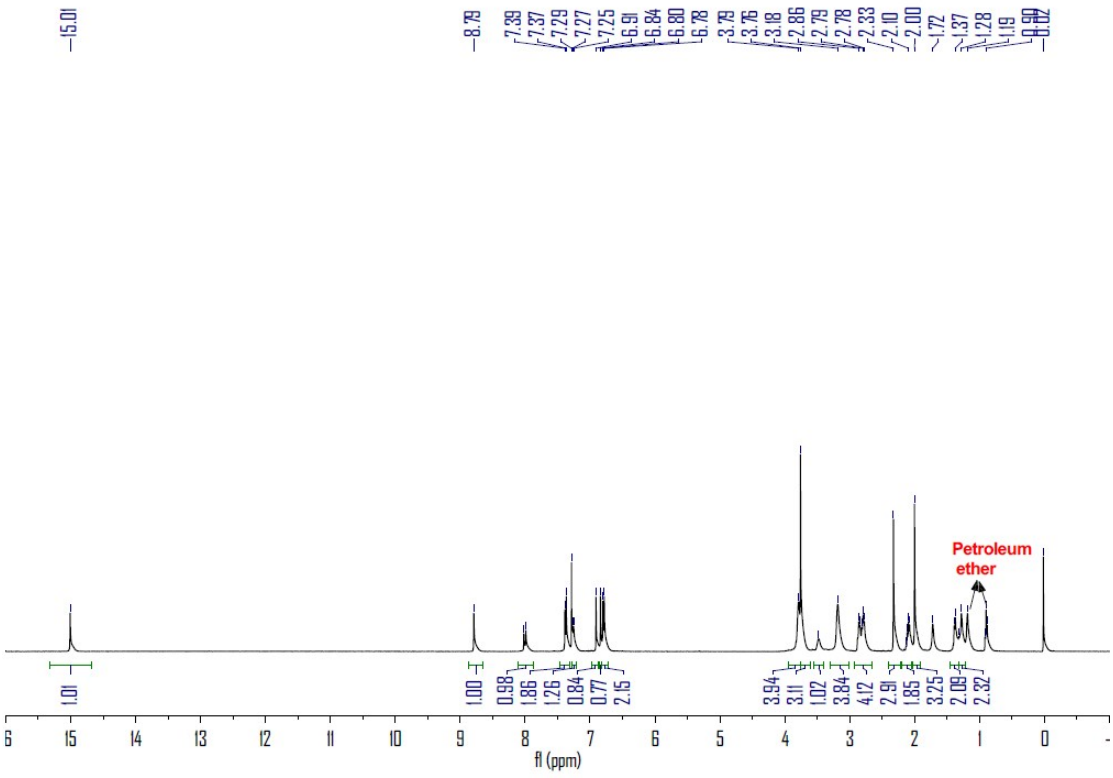


Fig. S35 400 MHz ^{1}H NMR spectrum of dithienylethene **3b** in $CDCl_3$ at room temperature.

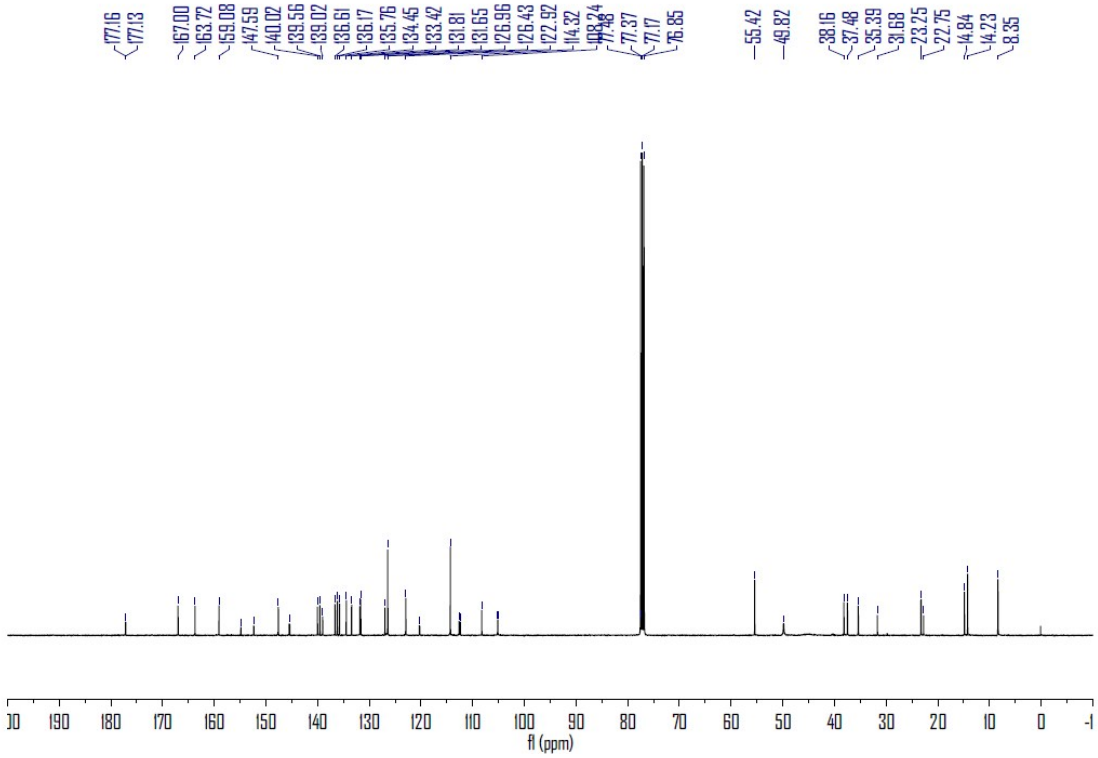


Fig. S36 100 MHz ^{1}H NMR spectrum of dithienylethene **3b** in $CDCl_3$ at room temperature.

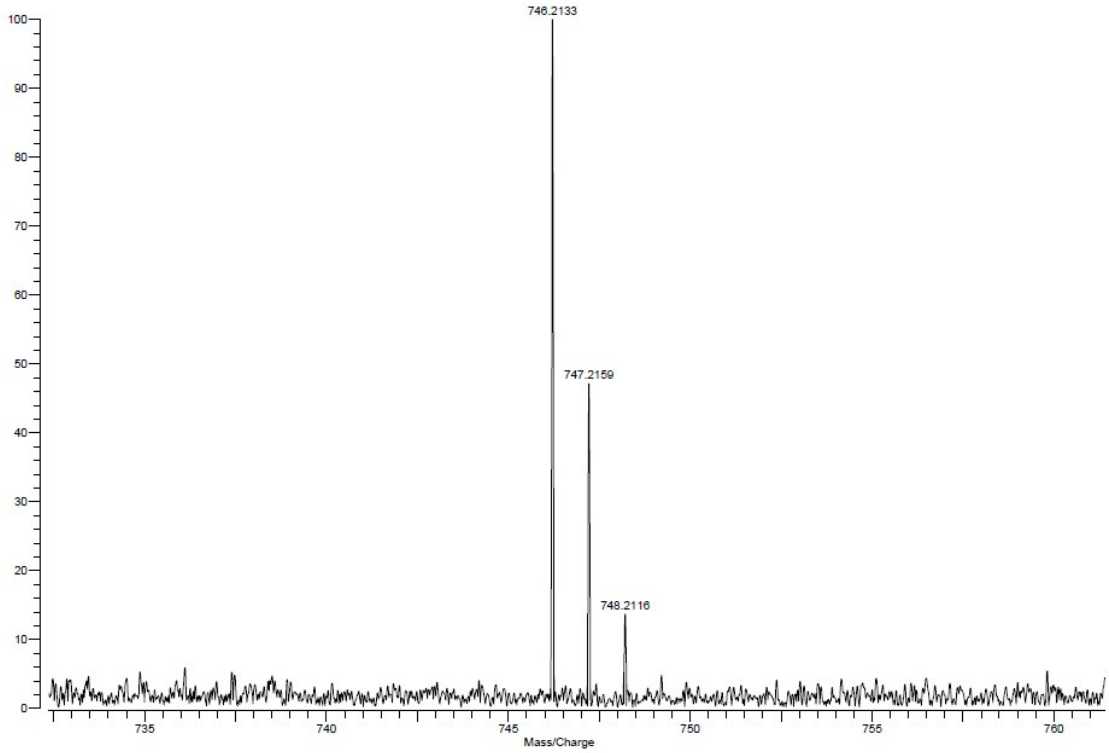


Fig. S37 HRMS of dithienylethene **3b**.

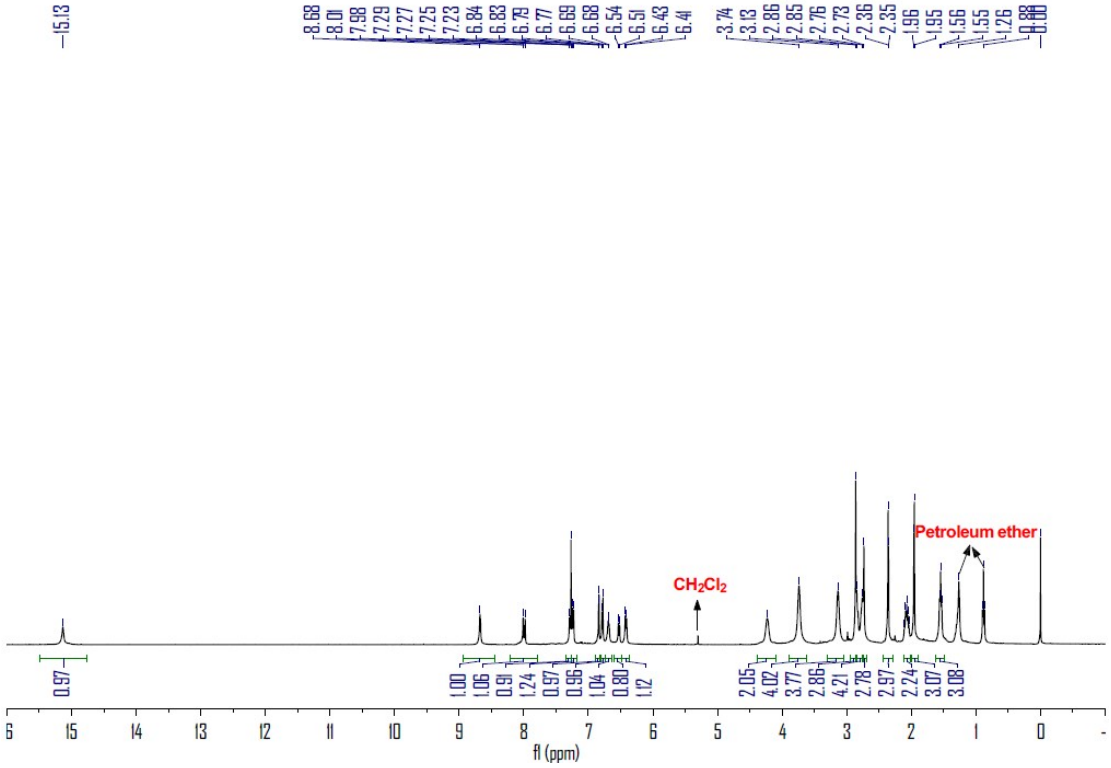


Fig. S38 400 MHz ^{1}H NMR spectrum of dithienylethene **4a** in $CDCl_3$ at room temperature.

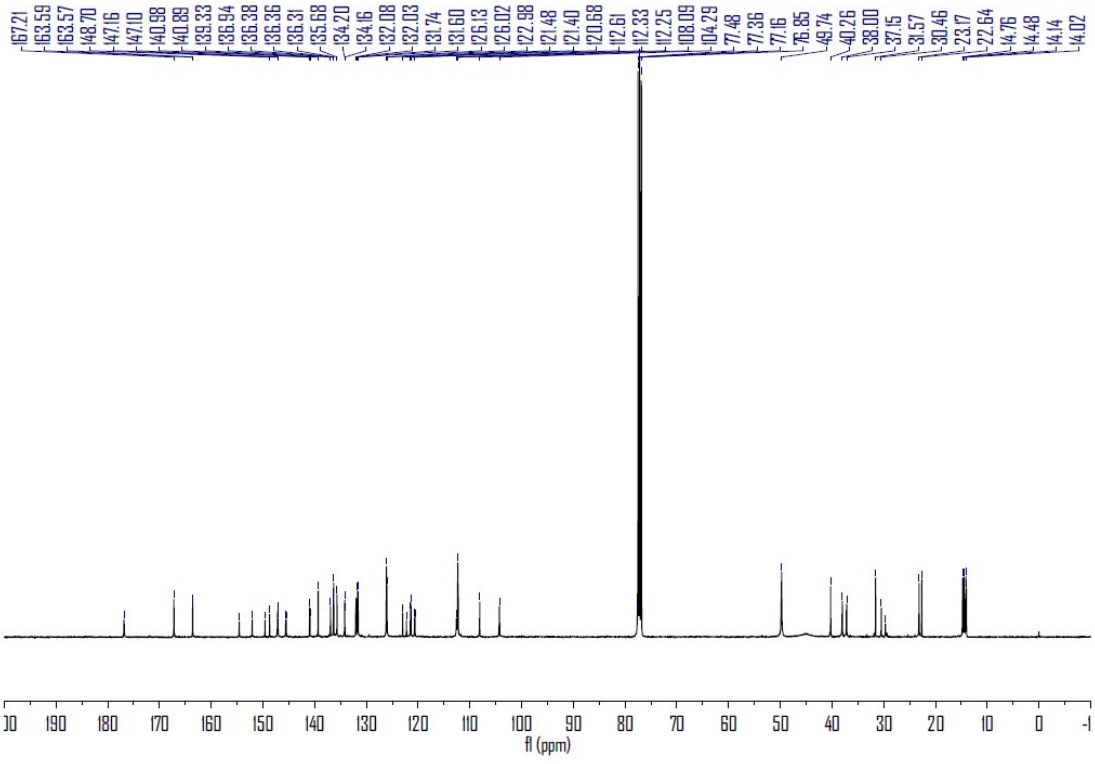


Fig. S39 100 MHz ^{1}H NMR spectrum of dithienylethene **4a** in $CDCl_3$ at room temperature.

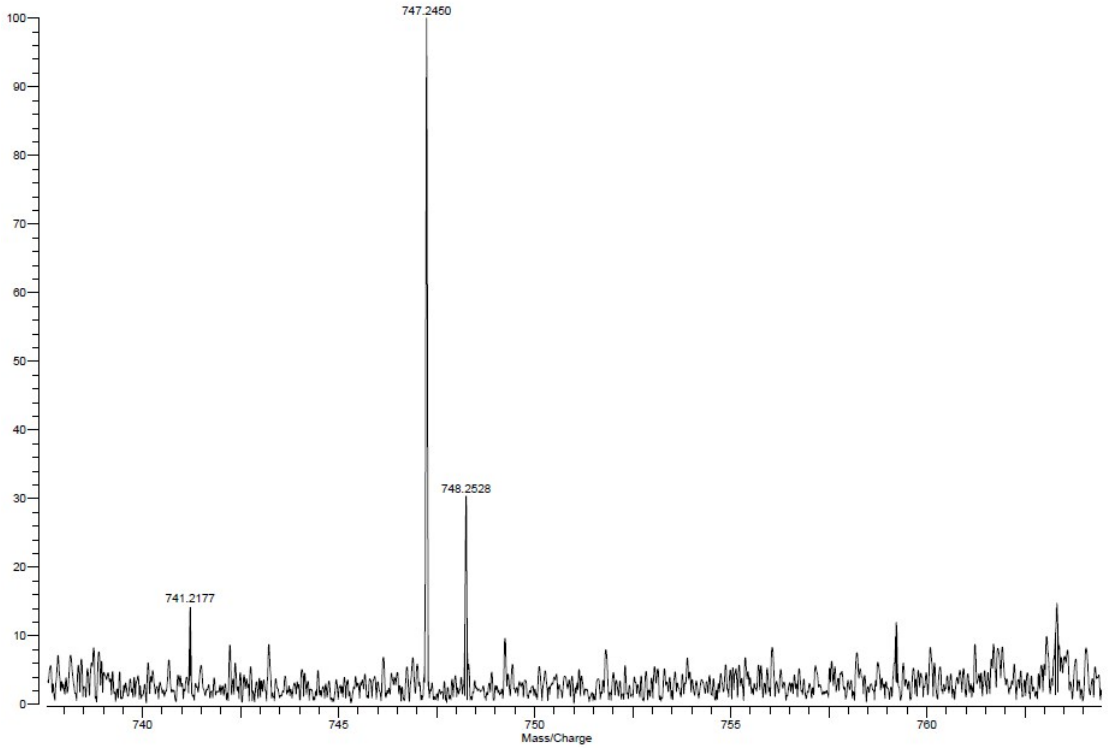


Fig. S40 HRMS of dithienylethene **4a**.

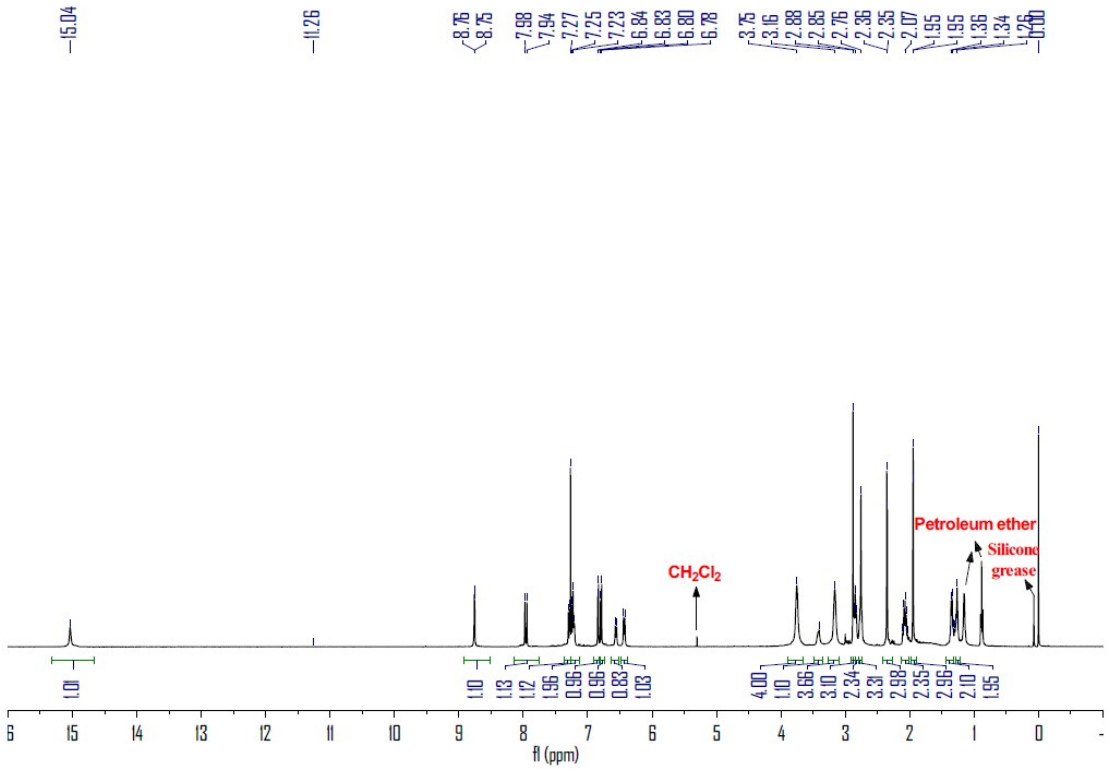


Fig. S41 400 MHz ^{1}H NMR spectrum of dithienylethene **4b** in $CDCl_3$ at room temperature.

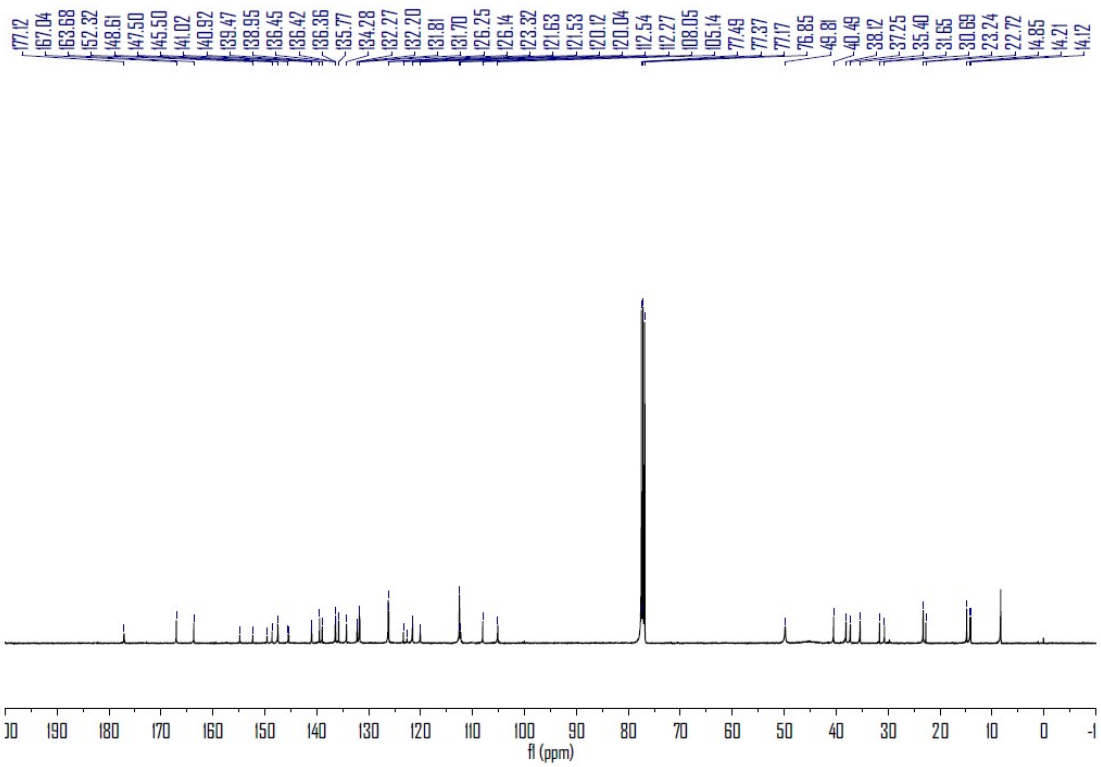


Fig. S42 100 MHz ^{1}H NMR spectrum of dithienylethene **4b** in $CDCl_3$ at room temperature.

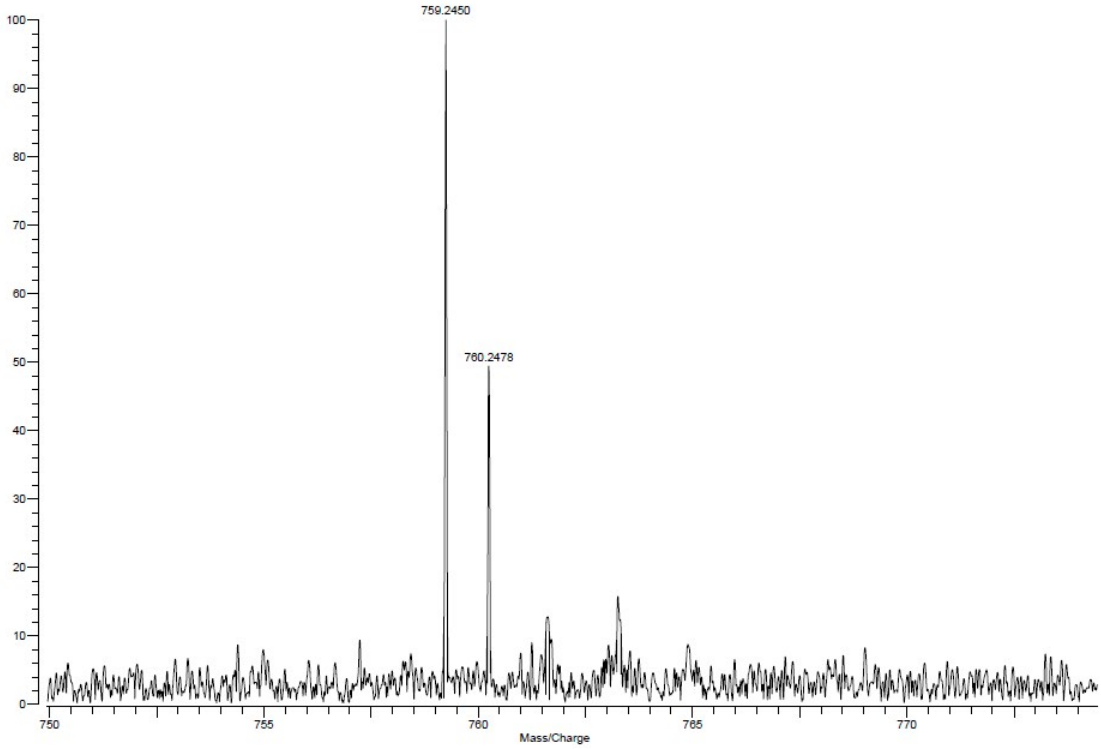
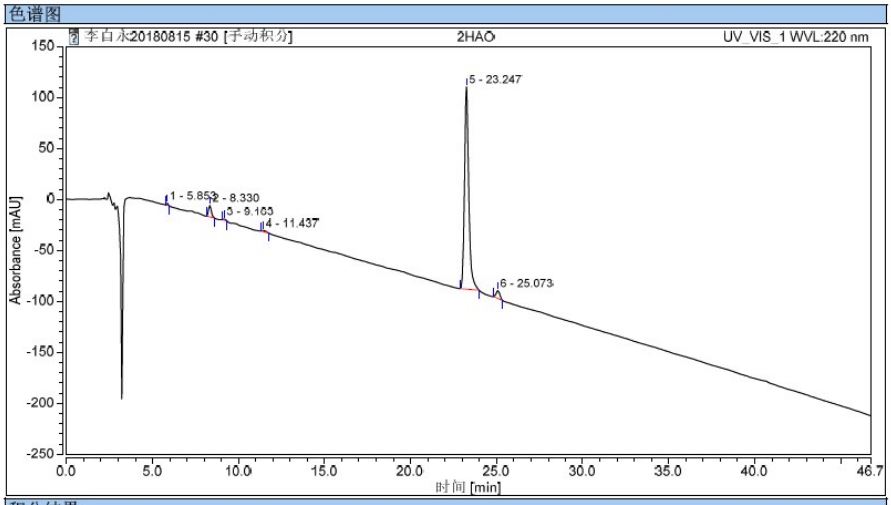


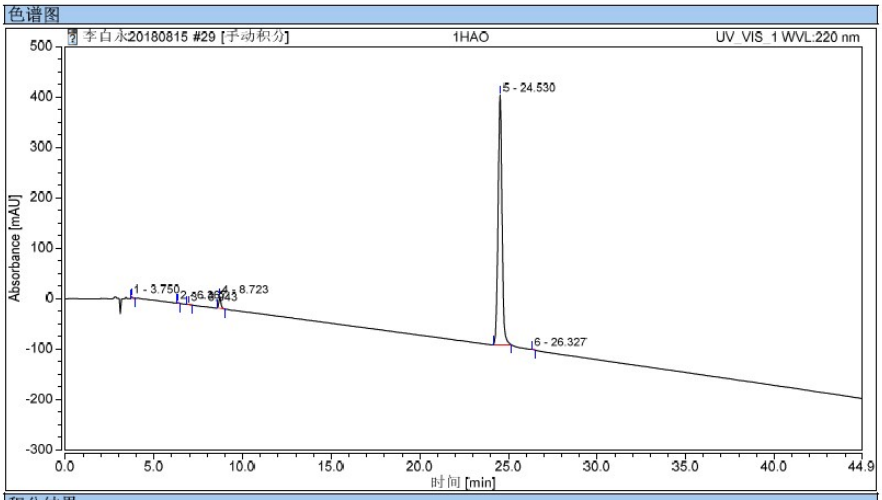
Fig. S43 HRMS of dithienylethene **4b**.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.853	0.167	1.857	0.27	0.84	n.a.
2		8.330	2.141	11.257	3.45	5.09	n.a.
3		9.163	0.205	1.068	0.33	0.48	n.a.
4		11.437	0.308	1.071	0.50	0.48	n.a.
5		23.247	57.296	198.329	92.38	89.67	n.a.
6		25.073	1.907	7.596	3.07	3.43	n.a.
总和:			**62.023**	**221.178**	**100.00**	**100.00**	

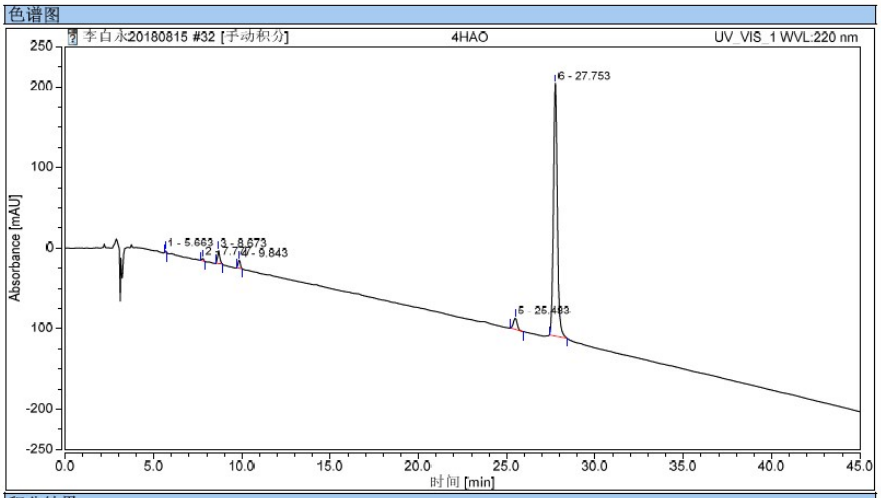
Fig. S44 HPLC of dithienylethene **1a**.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		3.750	0.266	3.223	0.21	0.62	n.a.
2		6.367	0.138	1.380	0.11	0.26	n.a.
3		6.943	0.093	0.728	0.07	0.14	n.a.
4		8.723	2.914	22.221	2.25	4.25	n.a.
5		24.530	125.964	495.392	97.33	94.70	n.a.
6		26.327	0.050	0.188	0.04	0.04	n.a.
总和:			**129.425**	**523.133**	**100.00**	**100.00**	

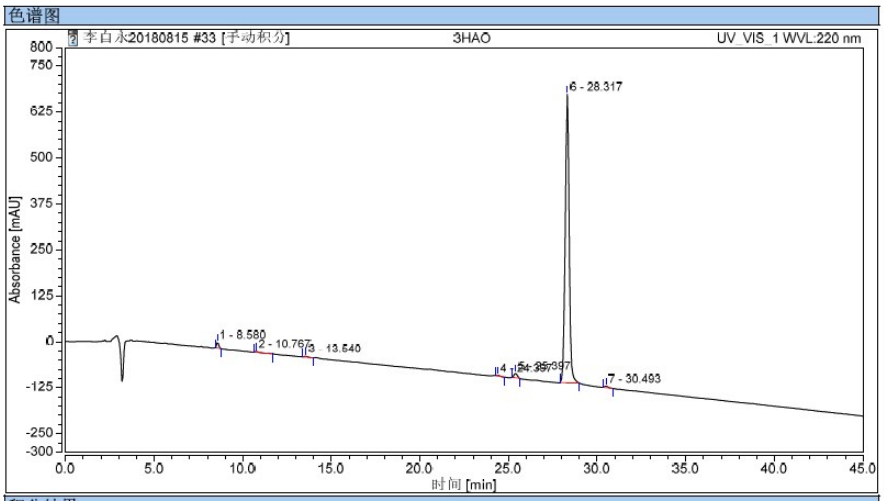
Fig. S45 HPLC of dithienylethene **1b**.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.663	0.268	3.200	0.30	0.89	n.a.
2		7.777	0.348	3.105	0.39	0.86	n.a.
3		8.673	2.281	16.386	2.59	4.55	n.a.
4		9.843	1.356	9.965	1.54	2.77	n.a.
5		25.483	3.362	14.079	3.81	3.91	n.a.
6		27.753	80.576	313.642	91.37	87.03	n.a.
总和:			88.190	360.378	100.00	100.00	

Fig. S46 HPLC of dithienylethene **2a**.

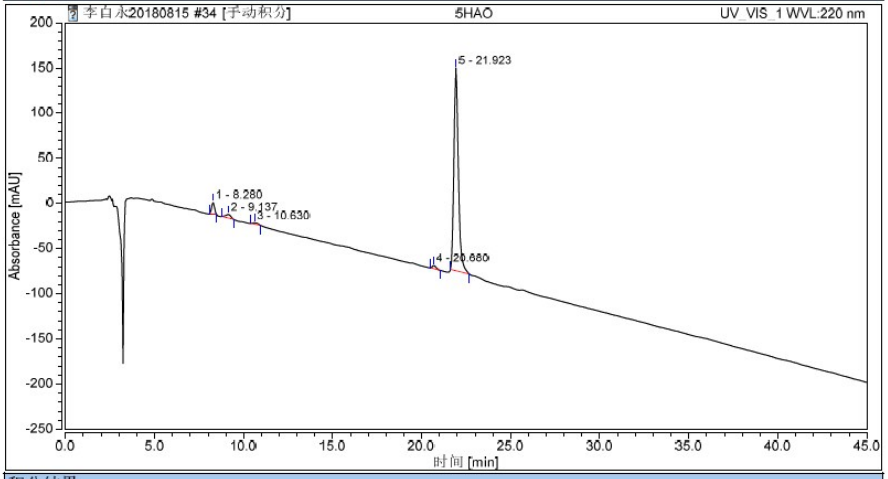


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.580	2.142	15.826	1.01	1.92	n.a.
2		10.767	0.386	2.011	0.18	0.24	n.a.
3		13.540	0.523	2.386	0.25	0.29	n.a.
4		24.397	0.375	1.890	0.18	0.23	n.a.
5		25.397	2.404	11.461	1.13	1.39	n.a.
6		28.317	205.108	785.148	96.83	95.48	n.a.
7		30.493	0.894	3.621	0.42	0.44	n.a.
总和:			211.832	822.344	100.00	100.00	

Fig. S47 HPLC of dithienylethene **2b**.

色谱图

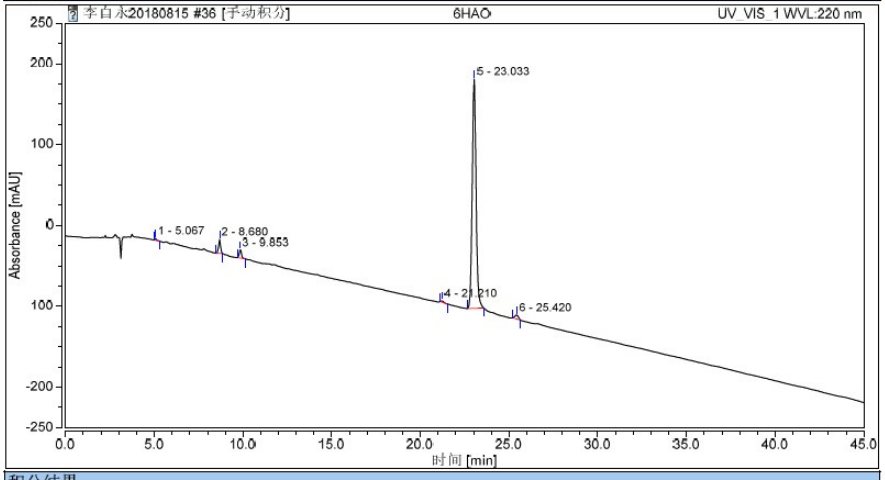


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.280	2.361	13.073	3.36	5.30	n.a.
2		9.137	1.271	3.822	1.81	1.55	n.a.
3		10.630	0.516	1.501	0.73	0.61	n.a.
4		20.680	0.881	3.463	1.25	1.40	n.a.
5		21.923	65.238	224.707	92.84	91.14	n.a.
总和:			70.266	246.565	100.00	100.00	

Fig. S48 HPLC of dithienylethene **3a**.

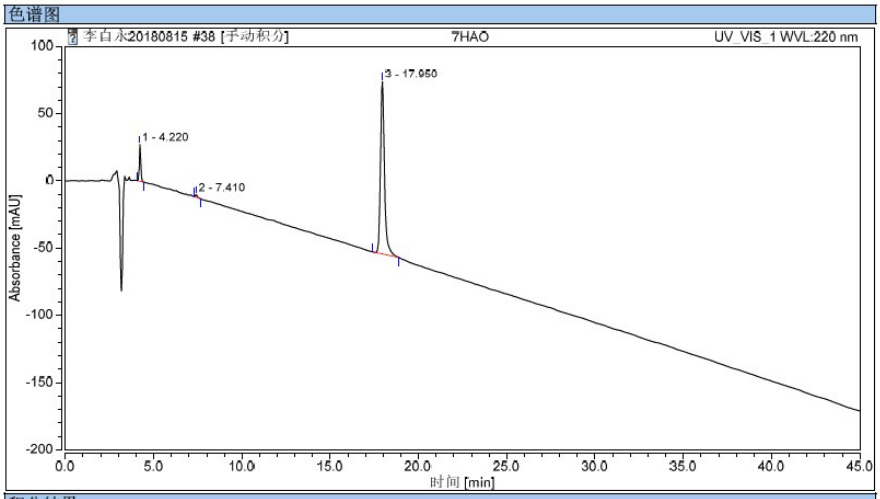
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.067	0.239	2.501	0.32	0.78	n.a.
2		8.680	2.210	17.624	2.93	5.50	n.a.
3		9.853	1.413	10.143	1.87	3.17	n.a.
4		21.210	0.278	1.577	0.37	0.49	n.a.
5		23.033	70.179	283.425	93.03	88.51	n.a.
6		25.420	1.120	4.932	1.48	1.54	n.a.
总和:			75.439	320.202	100.00	100.00	

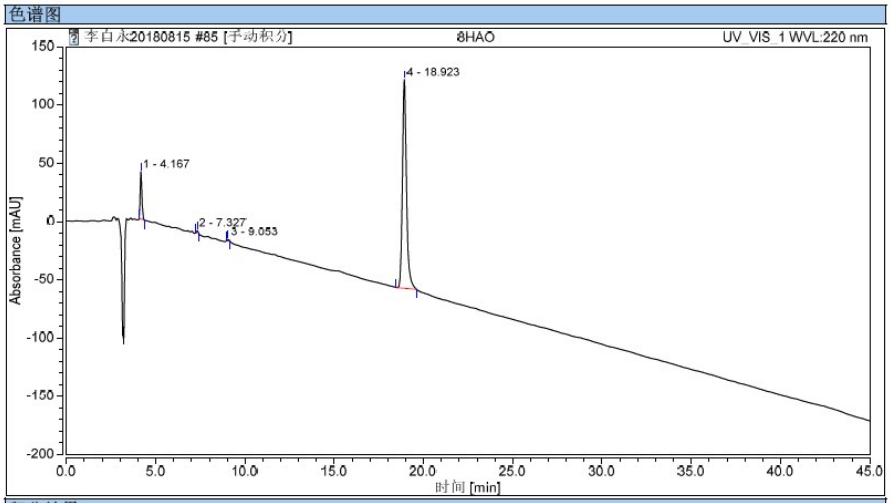
Fig. S49 HPLC of dithienylethene **3b**.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.220	2.376	27.282	6.64	17.33	n.a.
2		7.410	0.250	1.911	0.70	1.21	n.a.
3		17.950	33.162	128.244	92.66	81.46	n.a.
总和:			**35.787**	**157.437**	**100.00**	**100.00**	

Fig. S50 HPLC of dithienylethene **4a**.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.167	4.316	40.385	8.30	18.12	n.a.
2		7.327	0.186	2.191	0.36	0.98	n.a.
3		9.053	0.107	1.063	0.21	0.48	n.a.
4		18.923	47.368	179.266	91.13	80.42	n.a.
总和:			**51.976**	**222.905**	**100.00**	**100.00**	

Fig. S51 HPLC of dithienylethene **4b**.