**Electronic Supplementary Information (ESI)**

# Acid-base responsive multifunctional poly(formyl sulfide)s through a facile catalyst-free click polymerization of aldehyde-activated internal diynes and dithiols

Baixue Li,[a] Xue Wang,[a] Die Huang,[b] Mingzhao Li,[b] Anjun Qin,*[b] Yusheng Qin,*[a] and Ben Zhong Tang[c]

[a] College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, China

[b] State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China

[c] School of Science and Engineering, Shenzhen Institute of Aggregate Science and Technology, The Chinese University of Hong Kong, Shenzhen (CUHK-Shenzhen), Shenzhen 518172, China

# Contents

**Materials and instruments.**

**Materials:** 4,4′-Thiobisbenzenethiol (**2a**), 1,4-benzenedithiol (**2b**) and 1,3-benzenedithiol (**2c**) were purchased from TCI or Energy. Tetrakis (acetonitrile)copper(I) hexafluorophosphate [$Cu(MeCN)_4PF_6$], tetramethylpiperidine 1-oxyl (TEMPO) were purchased from TCI, and copper(I) iodide (CuI) was purchased from Energy. Cinnamaldehyde, 4-methylbenzenethiol were purchased from Bidepharm. All the commercial chemicals were purchased and used directly without further purification. THF, $CHCl_3$ and toluene were distilled under argon at normal pressure from sodium benzophenone ketyl immediately prior to use. DCM and DMF were extra-dry grade. Other commercial chemicals were purchased and used as received.

**Instruments:** Fourier transform infrared (FT-IR) spectra were collected on a Shimadzu IRAffinity-1S spectrometer (KBr disks). The $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker AVANCE NEO spectrometer in $CDCl_3$ using tetramethylsilane (TMS, $\delta = 0$) as internal reference. The weight- and number-average molecular weights ($M_w$ and $M_n$) and polydispersity index (PDI, $M_w/M_n$) of the polymers were estimated by gel permeation chromatography (GPC) on a Waters 2414 binary system equipped with a refractive index detector, using monodisperse polystyrene as calibration and THF as the eluent at a flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) measurements were carried out on a Netzsch TG 209 under dry nitrogen at a heating rate of 20 °C/min. UV-visible absorption spectra were recorded on a Persee TU-1901 spectrophotometer. Photoluminescence (PL) spectra were measured on a Hitachi F-4700 spectrofluorometer. Refractive indices of the resultant polymers were measured

on J. A. Woollam V-VASE variable angle ellipsometry system. The thin films of polymers were fabricated on silicon wafers by spin-coating procedure from their solutions in dichloroethane (15 mg/mL$^{-1}$, 100 µL). The Cauchy dispersion law was applied to analyze the polymer layer. High resolution mass spectrometry (HRMS) measurements were performed on a Bruker Agilent1290/maXis impact mass spectrometer.

**Synthesis and characterization**

**Monomers:** Monomers diynes **1a** and **1b** were prepared according to the published procedures.[1,2] The detailed synthetic routes are shown in Scheme S1.

Characterization data of **1a**: FT-IR (KBr disk), $v$ (cm$^{-1}$): 2956, 2930, 2857, 2183, 1659, 1607, 1465, 1384, 1280, 1013, 993, 967, 870, 824, 712, 624, 539. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 9.46, 7.75, 7.61, 1.99, 1.09, 0.68, 0.55. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 176.73, 151.92, 143.05, 133.04, 128.17, 120.95, 118.86, 95.97, 89.45, 55.60, 40.02, 26.01, 22.96, 13.82.

Characterization data of **1b**: FT-IR (KBr disk), $v$ (cm$^{-1}$): 2928, 2849, 2172, 1650, 1604, 1010, 984, 848, 814, 720, 488. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 9.46, 7.76, 7.70, 7.63, 1.51. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 176.79, 154.63, 141.20. 133.19, 127.93, 121.29, 119.19, 95.73, 89.34, 47.27, 26.80.
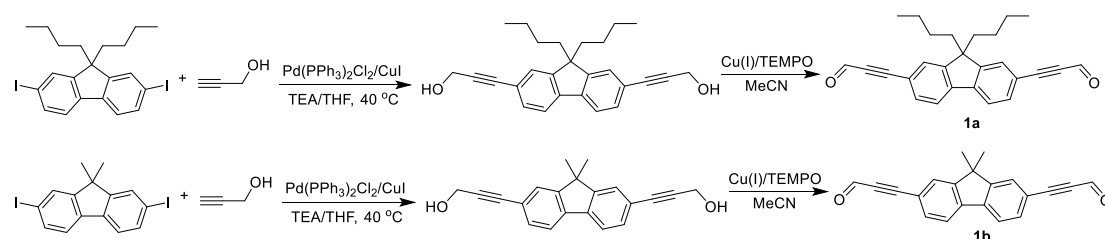


**Scheme S1** Synthesis of monomer **1a** and **1b**.

**Molecule model reaction:** Into a 25 mL Schlenk tube were added 3-phenylpropiolaldehyde (130.1 mg, 1 mmol) and 4-methylbenzenethiol (124.2 mg, 1 mmol), followed by 2 mL of extra-dry DMF under argon. The mixture was stirred at 60 °C for 10 h. The solution was condensed and the crude product was purified by silica-gel column chromatography using a hexane/ethyl acetate mixture (v/v = 100/1) as the eluent. The model product **3** was obtained in 65% yield. The detailed synthetic route is shown in Scheme S2.

Characterization data of model compound **3**: FT-IR (KBr disk), $v$ (cm$^{-1}$): 2962, 2922, 2846, 1663, 1562, 1490, 1453, 1381, 1306, 1261, 1162, 1121, 1018, 897, 808, 737, 699, 506. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.32, 9.26, 7.51, 7.45, 7.28, 7.10, 6.94, 6.52, 5.63, 2.40, 2.21. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.65, 190.13, 169.76, 140.96, 135.48, 134,87, 131.04, 130.52, 129.56, 128.78, 125.38, 123.29, 21.48.
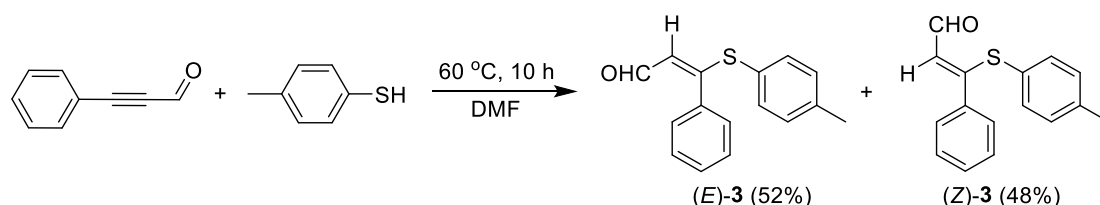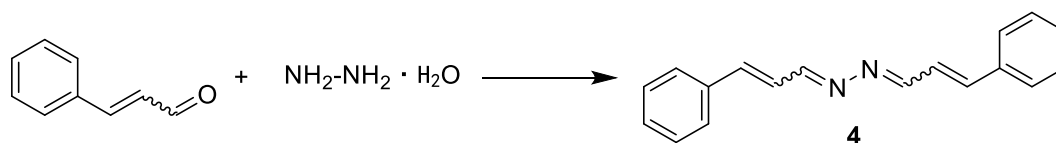


**Scheme S2** Synthesis of model compound **3**.

**Hydrazine responsive model reaction:** Into a 25 mL Schlenk tube were added cinnamaldehyde (132.1 mg, 1 mmol) and hydrazine hydrate (88.6 mg, 1.4 mmol), followed by 2 mL of THF under air atmosphere. The mixture was stirred at room temperature for overnight. The solution was condensed and the crude product was purified by silica-gel column chromatography using a hexane/ethyl acetate mixture (v/v

= 30/1) as the eluent. The model product **4** was obtained in 50% yield. The detailed

synthetic route is shown in Scheme S3.

Characterization data of model compound **4**: FT-IR (KBr disk), $v$ (cm$^{-1}$): 2922, 1628,

1585, 1446, 1285, 1070, 974, 744, 690. 508. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS,

ppm): 8.38, 8.36, 7.53, 7.52, 7.41, 7.39, 7.37, 7.36, 7.34, 7.09, 7.08. HRMS: m/z

261.1389 ([M + H]$^+$, calcd 260.1313).



**Scheme S3** Synthesis of model compound **4**.

**Fluorescence changing of the various pattens**

The THF solutions of imino-P**1a2a**, P**2** and MTBZ-Br with the concentration of 1.0

mg/mL were loaded on filter papers with the assistance of different masks. Then the

HCl and NH$_3$ vapors were then fumed on the pattens, respectively. The detailed

synthetic routes of P**2** and MTBZ-Br are shown in Scheme S4 and S5.
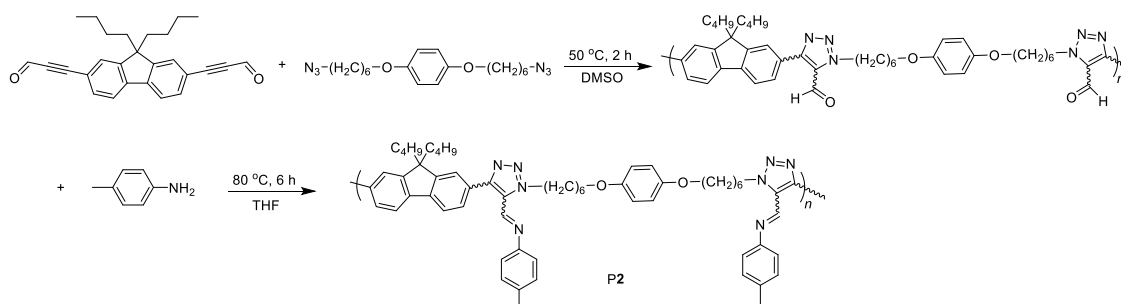


**Scheme S4** Synthesis of P**2**.

P**2** was prepared according to the published procedure[3]. A light-yellow powder, $M_w$:

21250; PDI: 1.65. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.17, 8.64, 8.52, 7.88-

6.72, 4.96, 4.38, 3.85, 2.37-0.61.
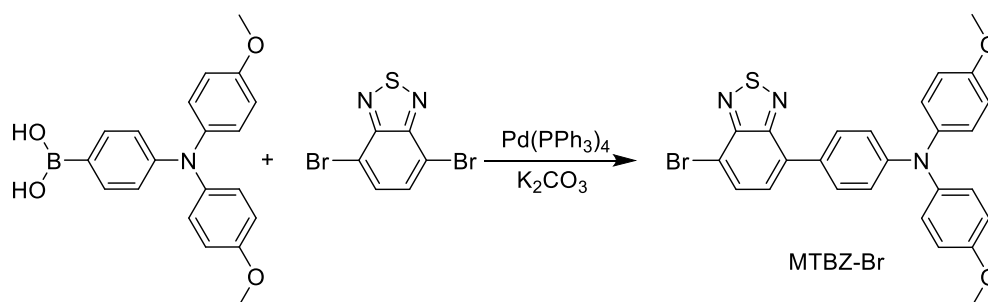
**Scheme S5** Synthesis of MTBZ-Br.

MTBZ-Br was prepared according to the published procedure[4]. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 7.88-7.85, 7.75-7.74, 7.51-7.49, 7.14-7.13, 7.04-7.02, 6.87-6.86, 3.81.

**Polymerization:** Unless otherwise stated, all the polymerizations of aldehyde-activated internal diynes **1** and dithiols **2** were conducted under argon using standard Schlenk techniques. Typical experimental procedure for the polycycloaddition is given below. Monomer **1a** (38.1 mg, 0.1 mmol) and **2a** (25.0 mg, 0.1 mmol) were added into a 10 mL Schlenk tube. After evacuated and refilled with argon for three times, extra-dry DMF (0.5 mL) was injected to dissolve the monomers. The mixture was stirred at 60 °C for 4 h. The resultant solution was diluted with 2 mL CHCl$_3$ and dropwise added to 100 mL $n$-hexane through a cotton filter under stirring. The precipitates were filtered and washed with $n$-hexane for several times and dried under vacuum at 40 °C to a constant weight.

Characterization data of **P1a2a**. A light-yellow powder was obtained in 86% yield. $M_w$: 40260; PDI: 2.74. FT-IR (KBr disk), $v$ (cm$^{-1}$): 2960, 2925, 2860, 1665, 1571, 1472, 1384, 1306, 1123, 1011, 1009, 816, 739, 495. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.31, 9.32, 7.71, 7.51, 7.33, 7.18, 7.08, 7.01, 6.85, 6.63, 5.80, 5.71, 1.90, 1.80,

0.97, 0.60, 0.37, 0.15. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.38, 189.69, 168.55, 158.02, 151.75, 142.53, 136.78, 136.00, 134.26, 133.22, 132.17, 131.47, 130.43, 129.04, 128.34, 124.34, 123.30, 120.42, 55.33, 39.85, 25.92, 23.13, 13.91.

Characterization data of **P1a2b**. A pale-yellow powder was obtained in 80% yield. $M_w$: 42390; PDI: 2.64. FT-IR (KBr disk), $v$ (cm$^{-1}$): 2956, 2928, 2855, 1665, 1569, 1464, 1385, 1308, 1263, 1215, 1123, 1011, 818, 736, 701, 498. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.36, 9.33, 7.76, 7.58, 7.49, 6.93, 6.73, 6.58, 5.85. 5.58, 1.99, 1.05, 0.65, 0.38. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.58, 189.70, 151.82, 142.72, 136.33, 135.45, 132.65, 131.43, 129.07, 128.20, 127.23, 124.43, 123.21, 120.58, 59.78, 55.58, 39.83, 38.17, 31.96, 31.26, 29.77, 29.42, 26.01, 22.95, 13.93.

Characterization data of **P1b2a**. A faint yellow powder was obtained in 84% yield. $M_w$: 22140; PDI: 1.84. FT-IR (KBr disk), $v$ (cm$^{-1}$): 2962, 2922, 2849, 1662, 1569, 1473, 1416, 1384, 1312, 1264, 1160, 1123, 1010, 816, 738, 700, 498. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.35, 10.29, 9.33, 7.81, 7.75, 7.59, 7.53, 7.51, 7.38, 7.21, 7.18, 7.00, 6.83, 6.66, 5.79, 5.66, 1.53, 1.39, 1.35, 1.20, 1.18. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.15, 168.62, 154.62, 140.39 136.99, 136.10, 134.40, 133.27, 132.30, 131.16, 130.35, 129.22, 128.25, 124.37, 123.64, 120.73, 47.19, 38.37, 31.98, 31.25, 26.96.

Characterization data of **P1b2b**. A primrose yellow powder was obtained in 85% yield. $M_w$: 22100; PDI: 1.79. FT-IR (KBr disk), $v$ (cm$^{-1}$): 2962, 2925, 2849, 1662, 1558, 1460, 1416, 1385, 1312, 1264, 1163, 1123, 1012, 819, 737, 700, 503. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.35, 10.18, 9.35, 9.25, 8.03, 7.76, 7.61, 7.48, 7.33, 6.97, 6.73,

6.58, 5.80, 5.53, 1.53, 1.49, 1.42, 1.36, 1.32. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.47, 189.81, 154.75, 140.67, 136.56, 135.73, 134.05, 131.95, 129.39, 128.24, 124.12, 123.30, 120.83, 47.16, 26.75.

Characterization data of **P1b2c**. A light-yellow powder was obtained in 88% yield. $M_w$: 10850; PDI: 1.93. FT-IR (KBr disk), $v$ (cm$^{-1}$): 2959, 2925, 2852, 2178, 1662, 1606, 1554, 1460, 1416, 1380, 1122, 993, 819, 773, 735, 685, 454. $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 10.36, 10.20, 9.30, 9.20, 7.67, 7.50, 7.05, 6.89, 6.67, 6.60, 5.75, 5.44, 1.61, 1.48, 1.40, 1.31, 1.18. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 190.31, 158.12, 154.50, 140.59, 137.71, 136.63, 135.23, 134.08, 131.53, 130.38, 129.64, 128.41, 124.21, 123.30, 120.99, 46.99, 26.91.

**Optimization of polymerization conditions**

To obtain soluble poly(formyl sulfide)s with high molecular weights and high yields, the polyhydrothiolation conditions were systematically optimized using aldehyde-activated internal diyne **1a** and dithiol **2a** as model monomers.

**Table S1** Effect of solvent on the polymerization of **1a** and **2a**[a]

| Entry | Solvent | Yield (%) | $M_w$[b] | PDI[b] |
|-------|---------|-----------|----------|--------|
| 1 | THF | 58 | 880 | 1.06 |
| 2 | DCM | 60 | 1 510 | 1.25 |
| 3 | CHCl$_3$ | 61 | 3 330 | 1.27 |
| 4 | toluene | 70 | 1 240 | 1.15 |
| 5 | DMF | 75 | 29 540 | 2.09 |

[a] Carried out at 40 °C for 4 h under argon at a monomer concentration of 0.2 M, [**1a**] = [**2a**]. [b] Estimated by GPC using THF as an eluant on the basis of a polystyrene (PS) calibration; $M_w$ = weight-average molecular weight; PDI = $M_w/M_n$; $M_n$ = number-average molecular weight.

**Table S2** Effect of reaction temperature on the polymerization of **1a** and **2a**[a]

| Entry | $T$ (°C) | Yield (%) | $M_w$[b] | PDI[b] |
|-------|----------|-----------|----------|--------|
| 1 | 30 | 63 | 10 070 | 1.64 |
| 2[c] | 40 | 75 | 29 540 | 2.09 |
| 3 | 50 | 83 | 33 300 | 2.13 |
| 4 | 60 | 80 | 41 560 | 2.59 |

[a] Carried out in DMF for 4 h under argon at a monomer concentration of 0.2 M, [**1a**] = [**2a**]. [b] Estimated by GPC using THF as an eluant on the basis of a PS calibration; $M_w$ = weight-average molecular weight; PDI = $M_w/M_n$; $M_n$ = number-average molecular weight. [c] Data taken from Table S1, entry 5.

**Table S3** Effect of monomer concentration on the polymerization of **1a** and **2a**[a]

| Entry | $C$ (M) | Yield (%) | $M_w$[b] | PDI[b] |
|-------|---------|-----------|----------|--------|
| 1 | 0.05 | 50 | 6 150 | 1.82 |
| 2 | 0.10 | 69 | 19 100 | 1.60 |
| 3[c] | 0.20 | 80 | 41 560 | 2.59 |
| 4 | 0.25 | 86 | 40 260 | 2.74 |
| 5[d] | 0.33 | gel | 44 700 | 2.91 |

[a] Carried out in DMF at 60 °C under argon for 4 h, [**1a**] = [**2a**]. [b] Estimated by GPC using THF as an eluent on the basis of a PS calibration; $M_w$ = weight-average molecular weight; PDI = $M_w/M_n$; $M_n$ = number-average molecular weight. [c] Data taken from Table S2, entry 4. [d] Molecular weight of the soluble part.

**Table S4** Time course of the polymerization of **1a** and **2a**[a]

| Entry | t (h) | Yield (%) | $M_w$[b] | PDI[b] |
|-------|-------|-----------|----------|--------|
| 1 | 2 | 73 | 32 320 | 2.23 |
| 2 | 3 | 73 | 41 980 | 2.12 |
| 3[c] | 4 | 86 | 40 260 | 2.74 |
| 4 | 5 | 77 | 32 230 | 2.03 |
| 5 | 6 | 76 | 37 340 | 2.54 |

[a] Carried out in DMF at 60 °C under argon at a monomer concentration of 0.25 M, [**1a**] = [**2a**]. [b] Estimated by GPC using THF as an eluent on the basis of a PS calibration; $M_w$ = weight-average molecular weight; PDI = $M_w/M_n$; $M_n$ = number-average molecular weight. [c] Data taken from Table S3, entry 4.

**Table S5** Polymerization of **1a** and **2a** in the presence of γ-terpinene[a]

| Entry | $[T]^{b}$ (mM) | Yield (%) | $M_{\text{w}}^{c}$ | PDI[c] |
|-------|------|-----------|--------|--------|
| 1 | 0 | 74 | 38 340 | 2.98 |
| 2 | 50 | 77 | 32 400 | 1.86 |
| 3 | 100 | 76 | 34 350 | 1.96 |

[a] Carried out in DMF at 60 °C for 2 h under argon at a monomer concentration of 0.2 M, [**1a**] = [**2a**]. [b] T=γ-terpinene. [c] Estimated by gel permeation chromatography using THF as an eluant on the basis of a polystyrene calibration; $M_{\text{w}}$ = weight-average molecular weight; PDI = $M_{\text{w}}/M_{\text{n}}$; $M_{\text{n}}$ = number-average molecular weight.
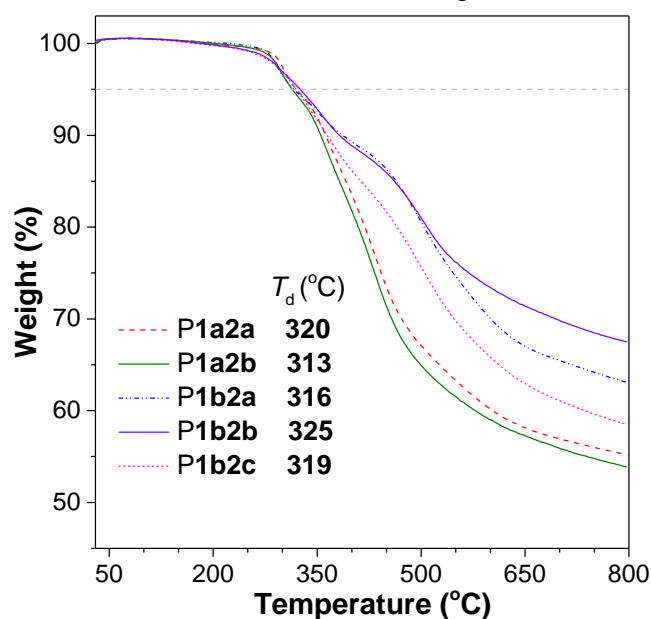


**Fig. S1** TGA curves of **P1a2a**-**P1b2c** at a heating rate of 20 °C/min under nitrogen. $T_{\text{d}}$ presents temperature of 5% weight loss.
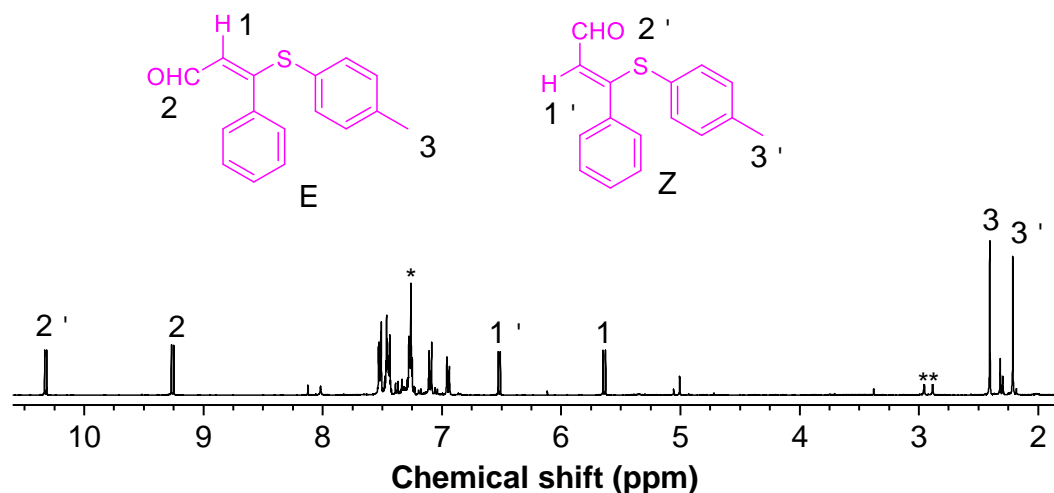


**Fig. S2** $^1$H NMR spectra of model compound in in CDCl$_3$. The solvent peaks are marked with asterisks.
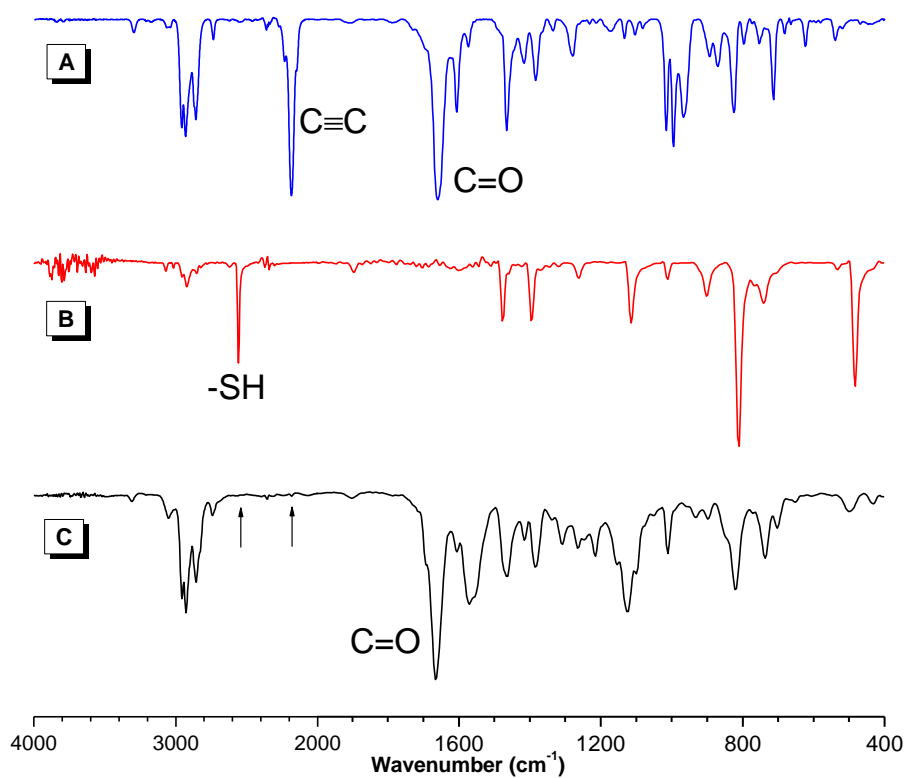
**Fig. S3** FT-IR spectra of **1a** (A), **2b** (B) and P**1a2b** (C).
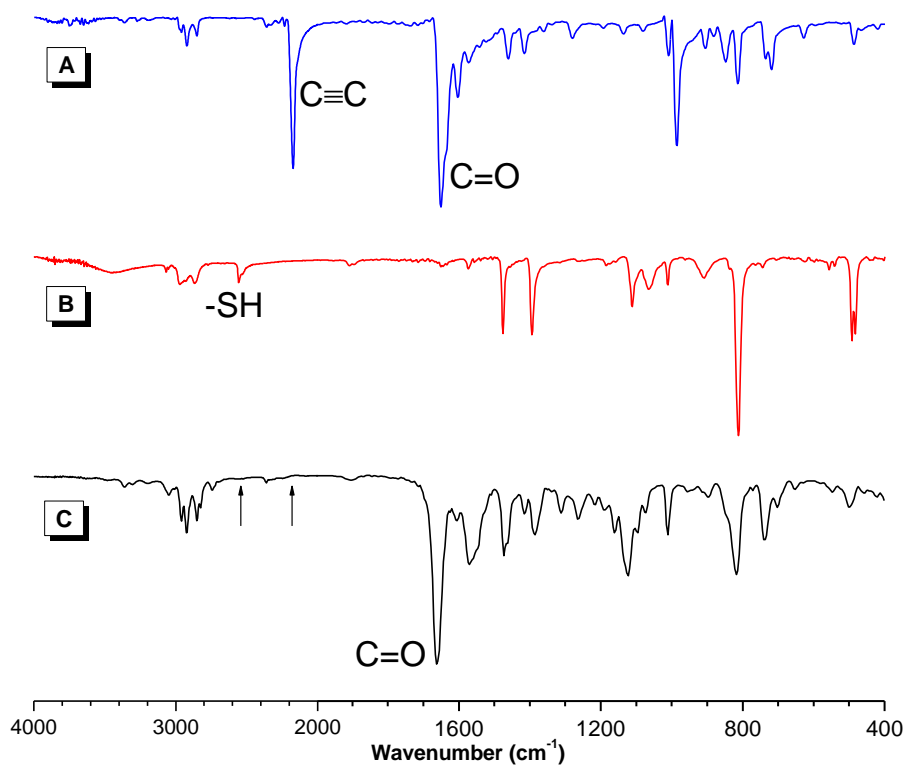


**Fig. S4** FT-IR spectra of **1b** (A), **2a** (B) and P**1b2a** (C).
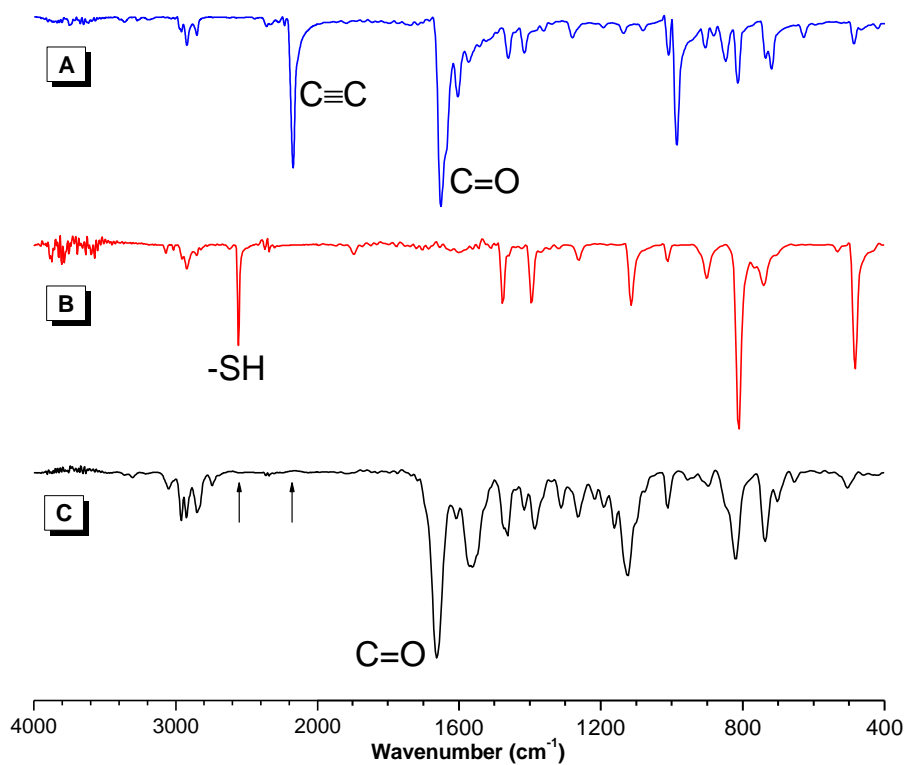
**Fig. S5** FT-IR spectra of **1b** (A), **2b** (B) and P**1b2b** (C).
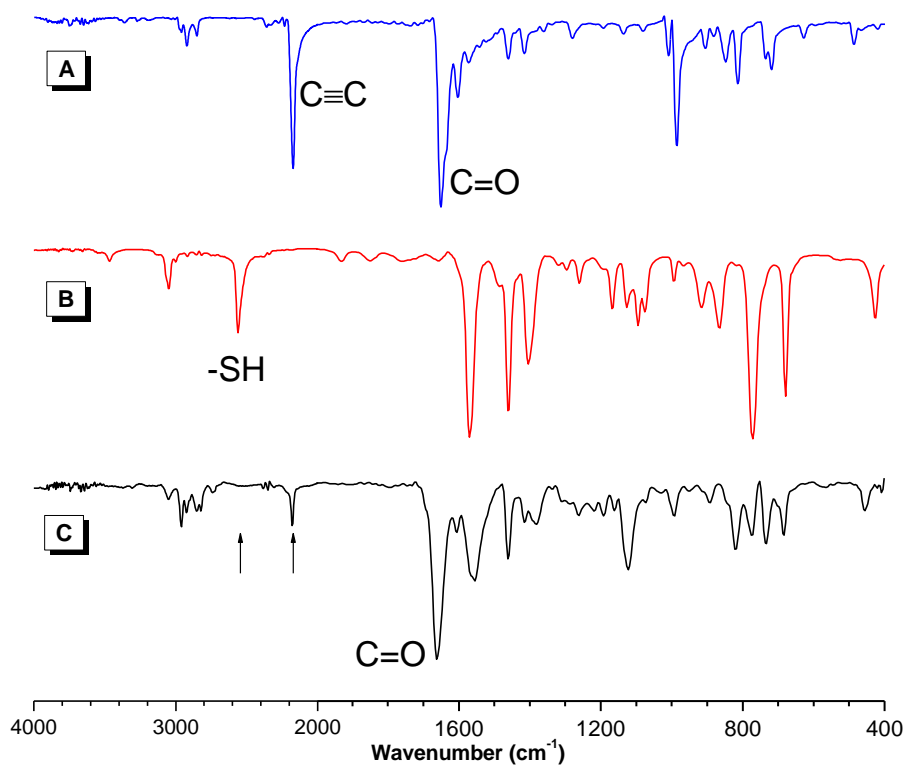


**Fig. S6** FT-IR spectra of **1b** (A), **2c** (B) and P**1b2c** (C).
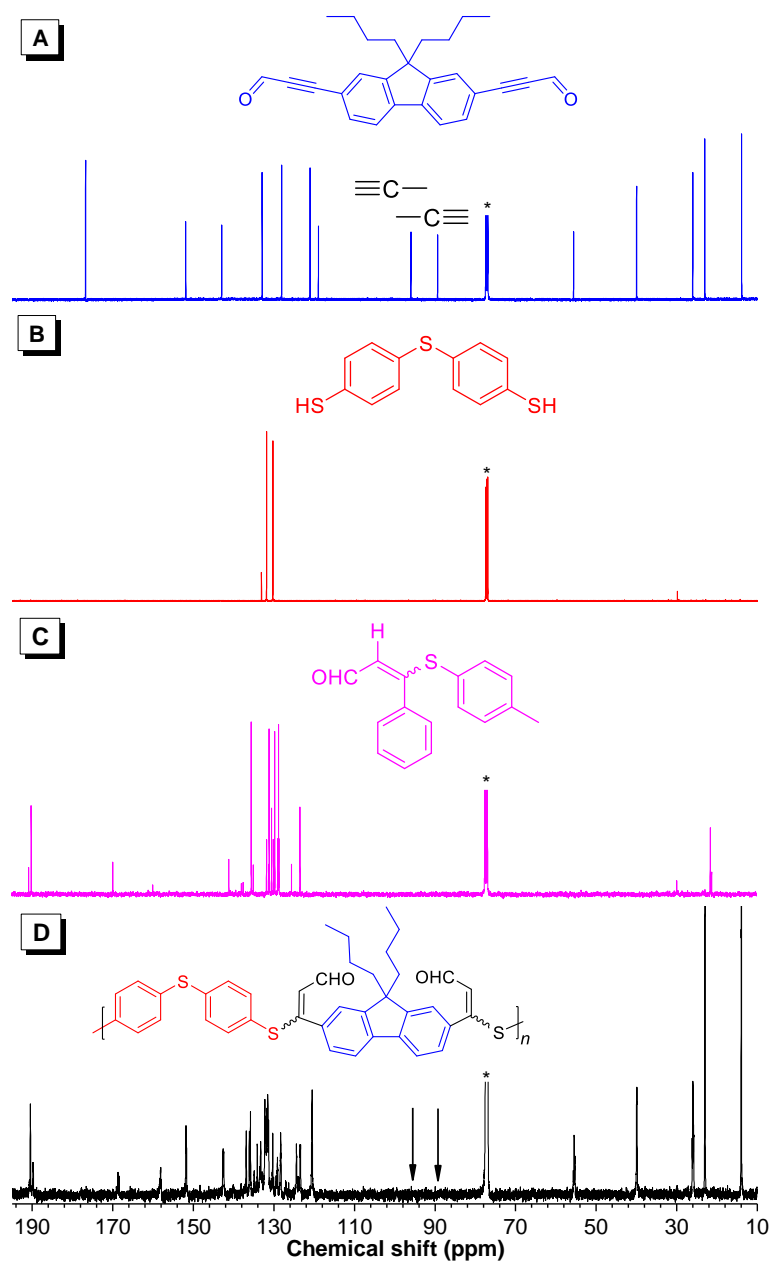
**Fig. S7** $^{13}$C NMR spectra of **1a** (A), **2a** (B), model compound **3** (C) and P**1a2a** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.
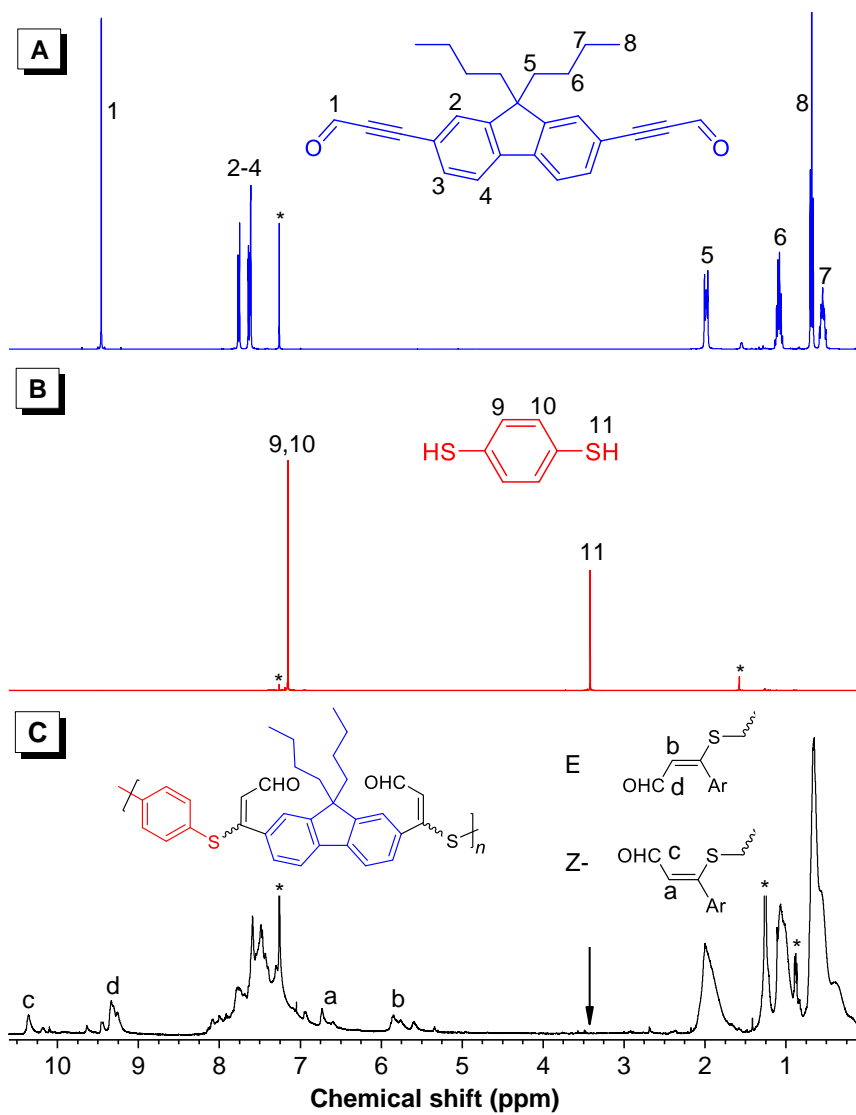
**Fig. S8** ^{1}H NMR spectra of **1a** (A), **2b** (B) and P**1a2b** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.
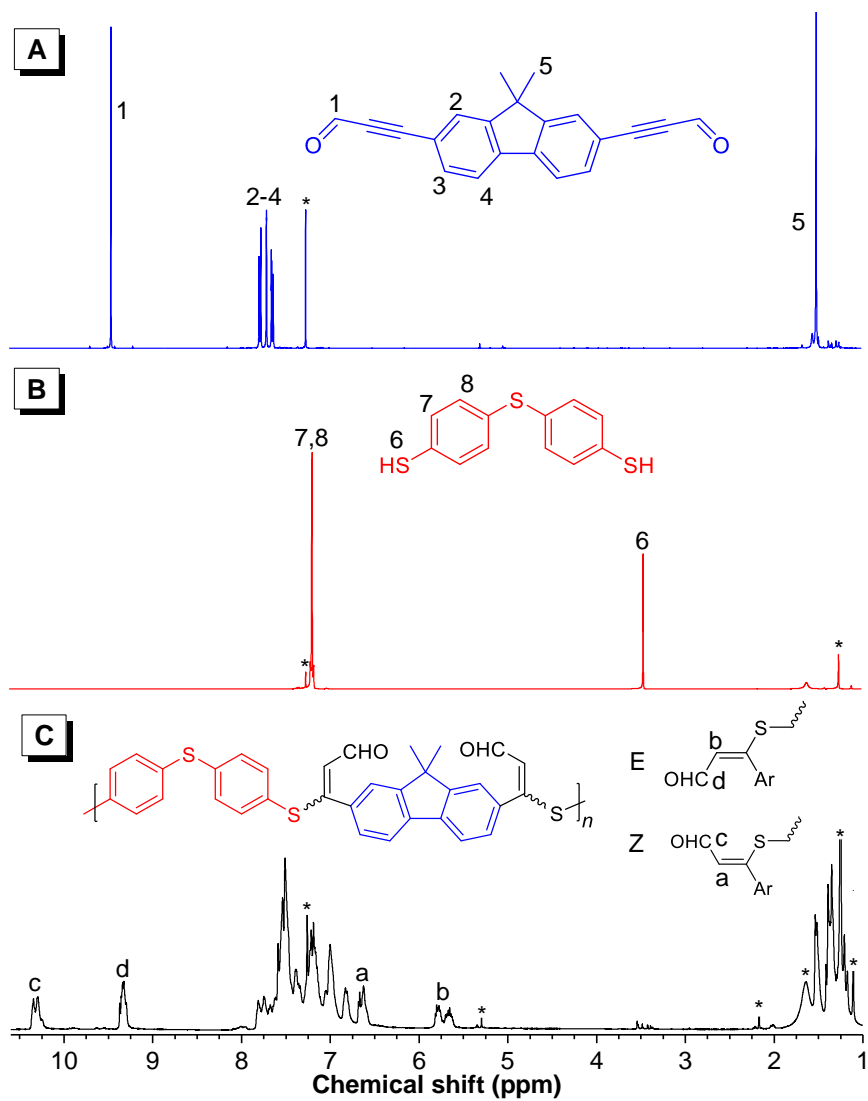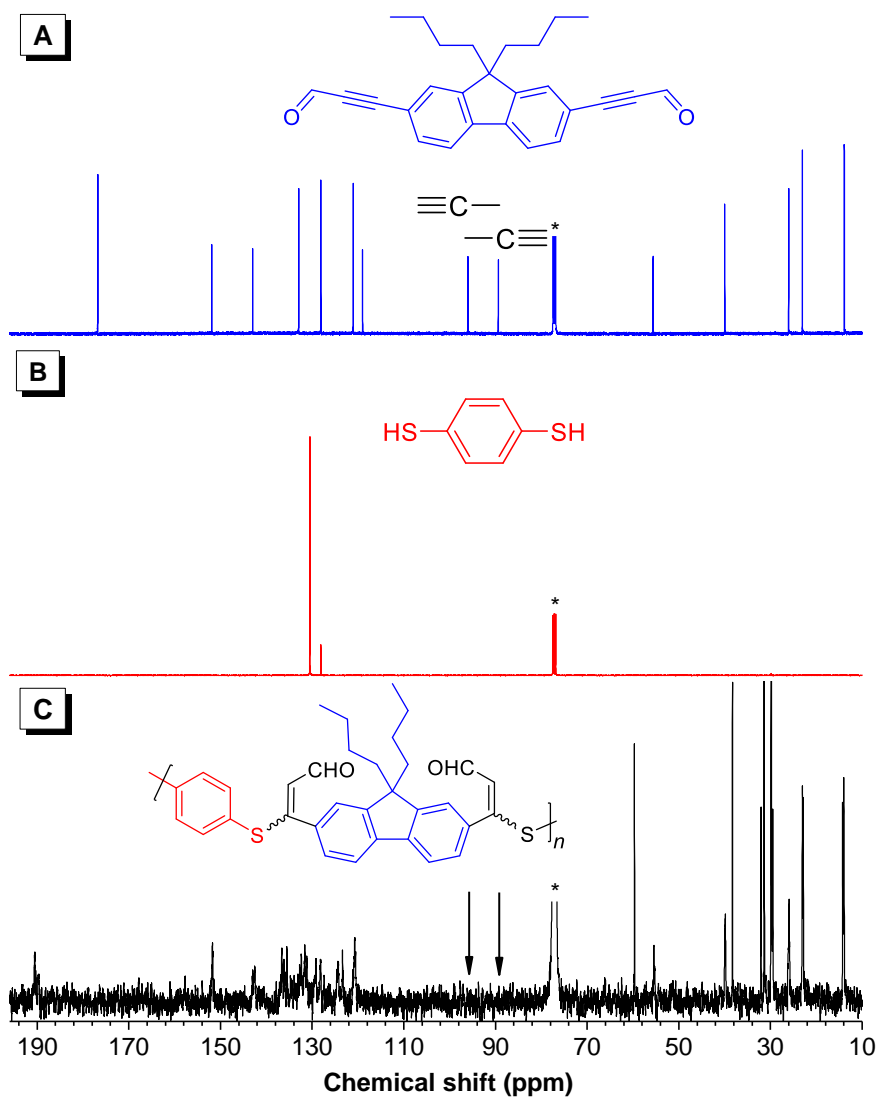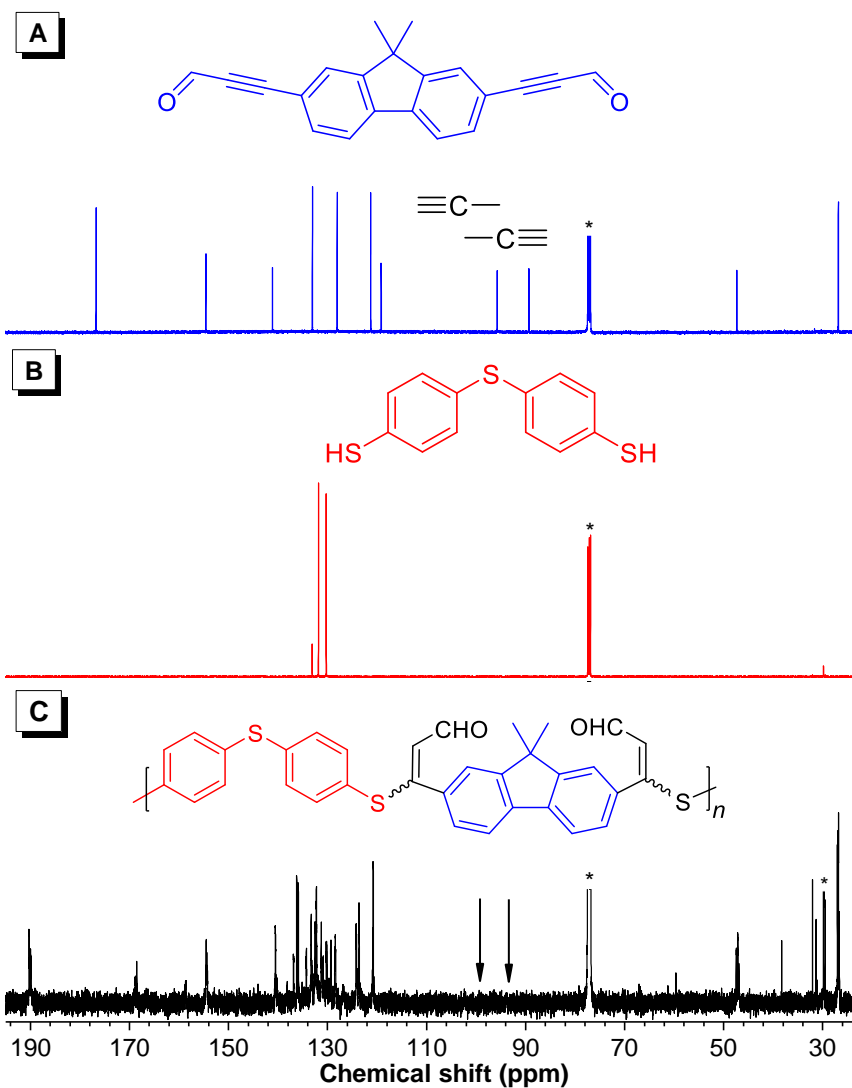
**Fig. S9** $^1$H NMR spectra of **1b** (A), **2a** (B) and P**1b2a** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.
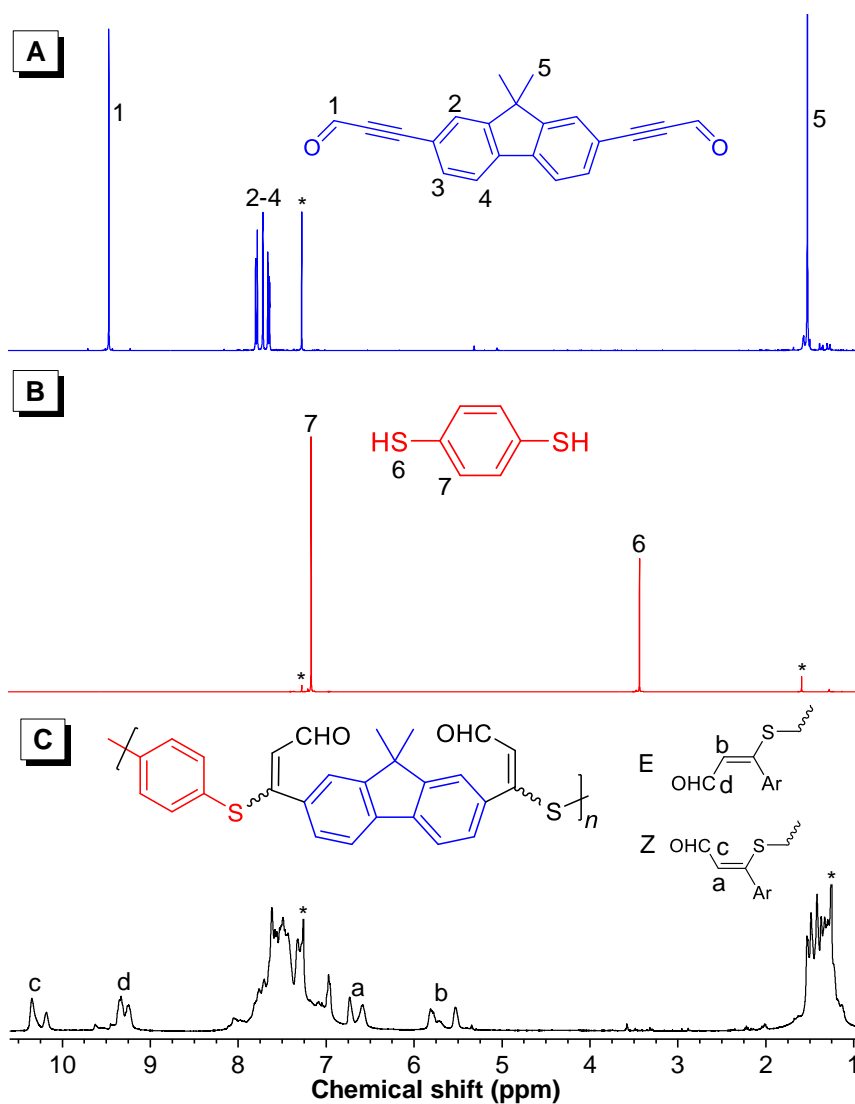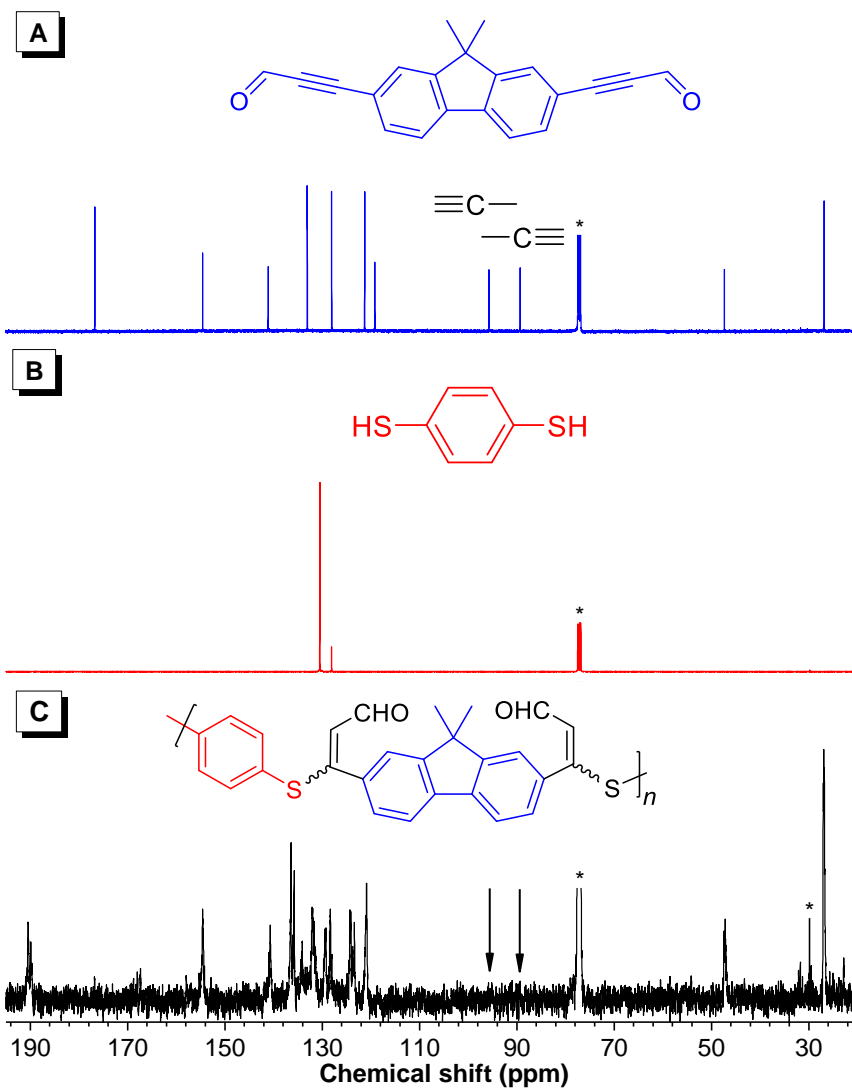
**Fig. S10** ^{1}H NMR spectra of **1b** (A), **2b** (B) and P**1b2b** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.
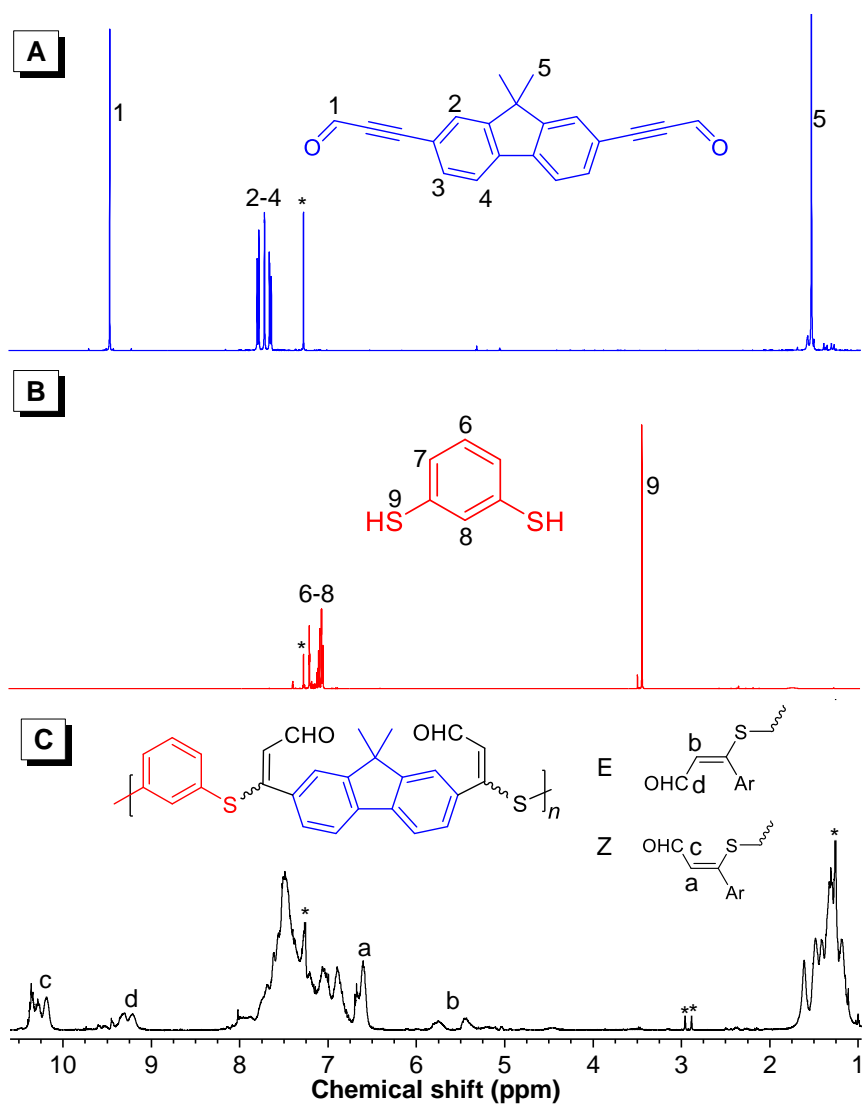
**Fig. S11** $^1$H NMR spectra of **1b** (A), **2c** (B) and **P1b2c** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.

**Fig. S12** ^{13}C NMR spectra of **1a** (A), **2b** (B) and **P1a2b** (D) in CDCl₃. The solvent peaks are marked with asterisks.
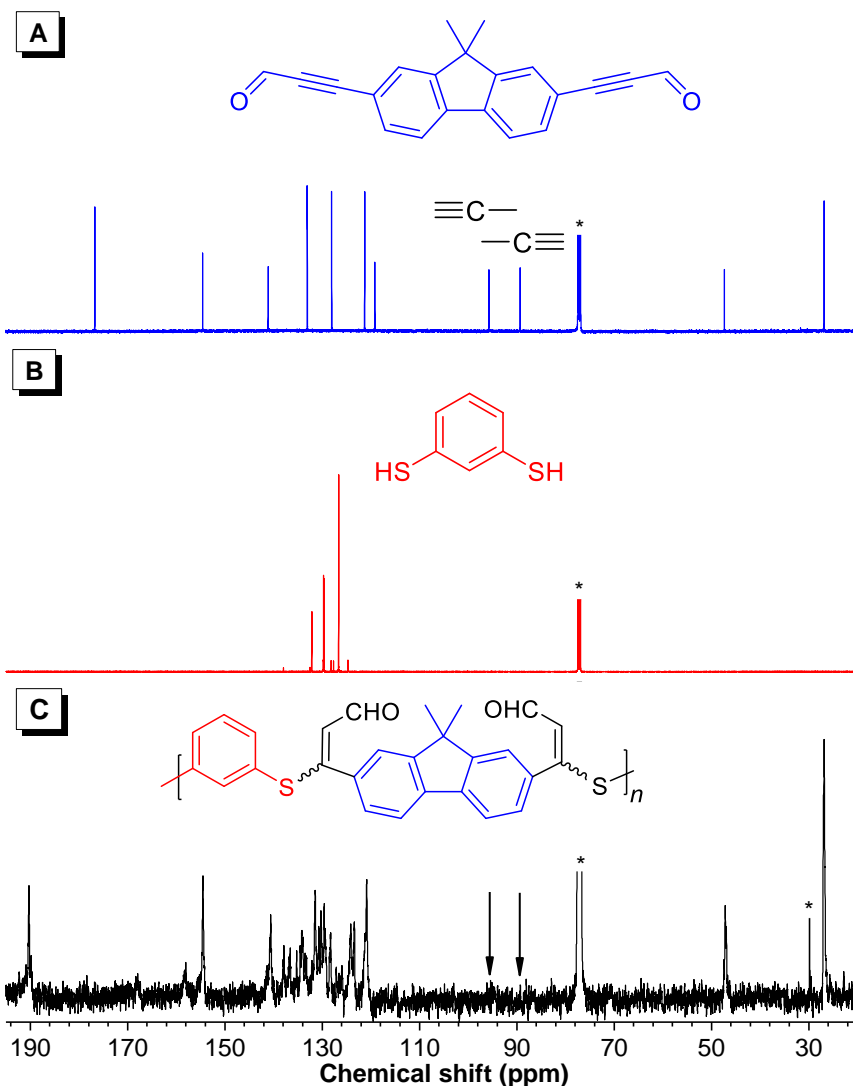
**Fig. S13** ^{13}C NMR spectra of **1b** (A), **2a** (B) and **P1b2a** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.

**Fig. S14** $^{13}$C NMR spectra of **1b** (A), **2b** (B) and **P1b2b** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.

**Fig. S15** $^{13}$C NMR spectra of **1b** (A), **2c** (B) and **P1b2c** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.

**Table S6** Refractive indices ($n_D$), Abbé numbers ($v_D$), optical dispersions ($D$) and thickness of thin films of polymers **P1a2a**-**P1b2c**, $n_D$ values of commercial polymers

| Polymer | $n_D{}^a$ | $v_D{}^b$ | $D^c$ | Thickness (nm) | Commercial polymer | $n_D{}^d$ |
|---|---|---|---|---|---|---|
| **P1a2a** | 1.7098 | 11.1393 | 0.0898 | 156.12 | Poly(ethyleneterephthalate) | 1.635 |
| **P1a2b** | 1.7117 | 8.1039 | 0.1234 | 263.02 | Polystyrene | 1.587 |
| **P1b2a** | 1.7552 | 8.3189 | 0.1202 | 225.43 | Polycarbonate | 1.581 |
| **P1b2b** | 1.7510 | 8.5600 | 0.1168 | 145.16 | Polyethylene | 1.499 |
| **P1b2c** | 1.7557 | 7.9536 | 0.1257 | 221.83 | Polyacrylate | 1.492 |

$^a$ Data of polymers at 632.8 nm. $^b$ $v_D = (n_{589.3}-1)/(n_{486.1}-n_{656.3})$. $^c$ $D = 1/v_D$. $^d$ Data of commercial polymers at 632.8 nm taken from refractive index database.
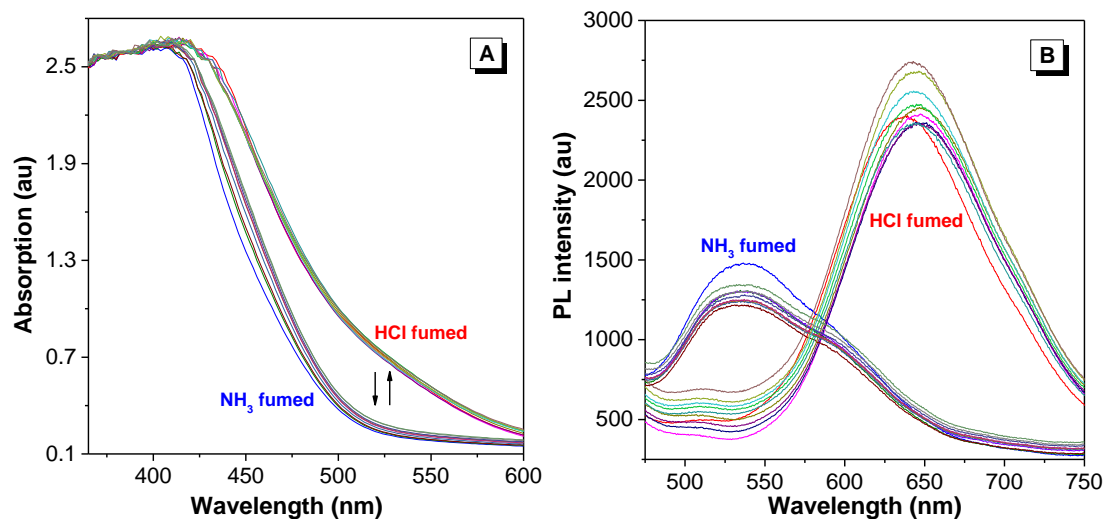
**Fig. S16** Absorption (A) and PL (B) spectra of imino-P**1a2a** film upon fumigation with HCl and NH₃ vapor.
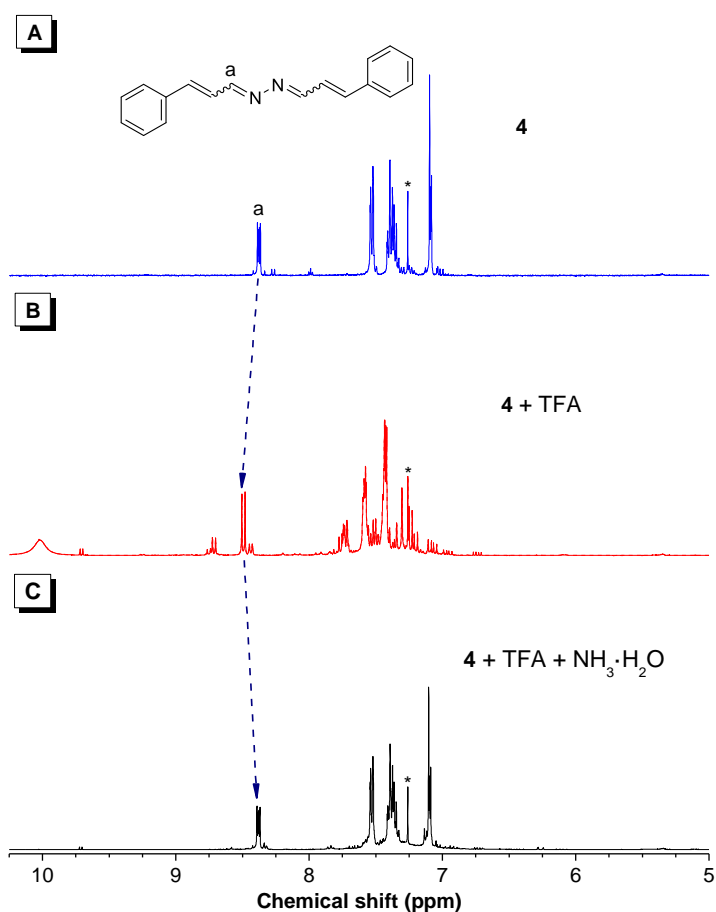


**Fig. S17** $^1$H NMR spectra of **4** (A) before and (B) after addition of one equivalent TFA and (C) a mixture of **4** and TFA after addition of one equivalent NH₃·H₂O in CDCl₃. The solvent peaks are marked with asterisks.
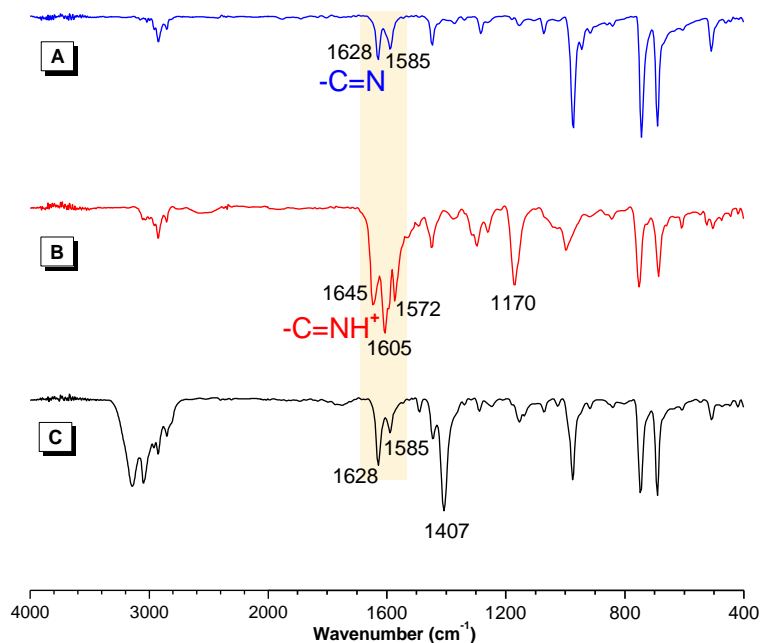
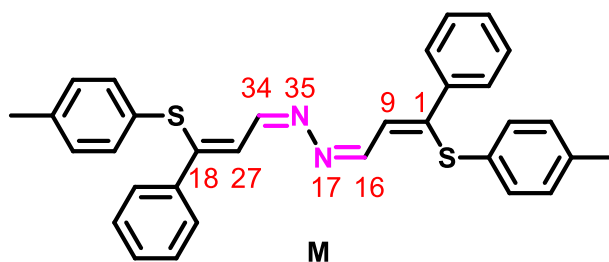**Fig. S18** FT-IR spectra of **4** (A), protonated (B) and deprotonated (C) analogues.



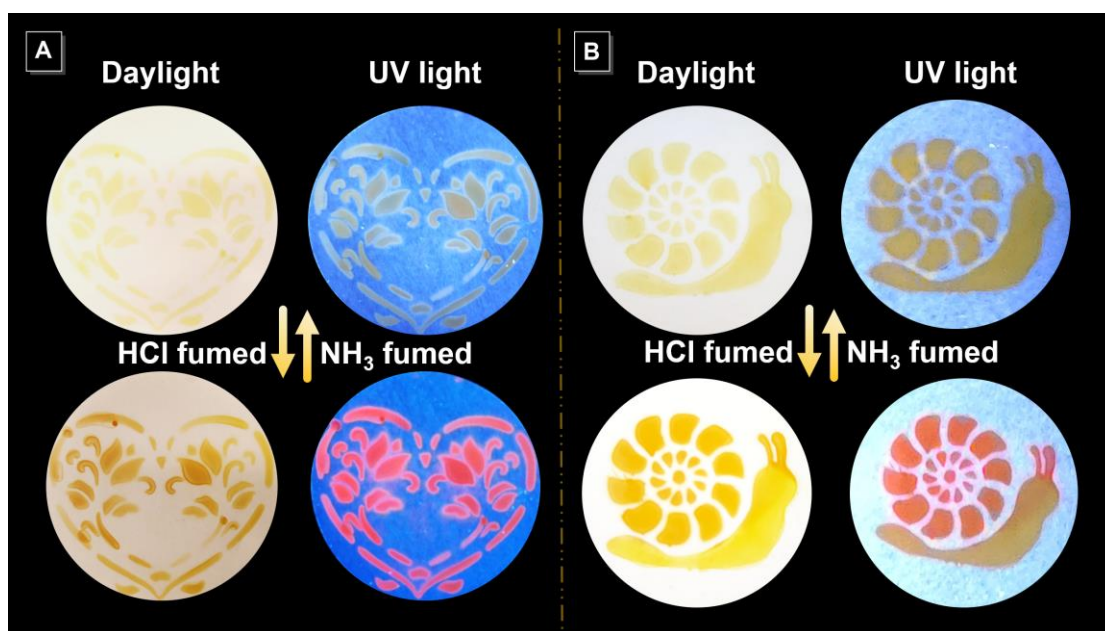**Fig. S19** Theoretical calculation model structure.



**Fig. S20** Responsive patten by spraying imino-P**1a2a** solution on the filter papers using photomask with HCl and NH$_3$ vapors.
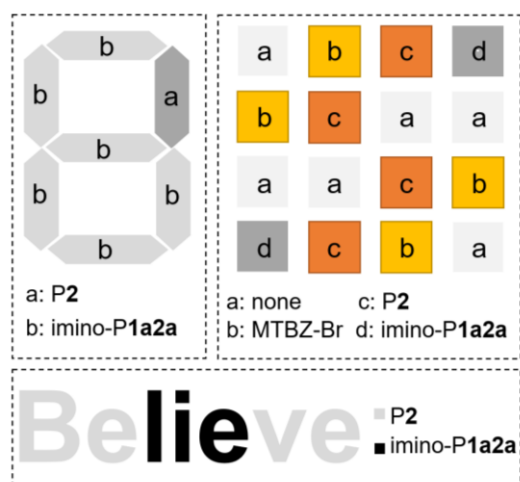
**Fig. S21** Schematic representation of the designed pattern in Fig. 8 using different fluorescent materials.
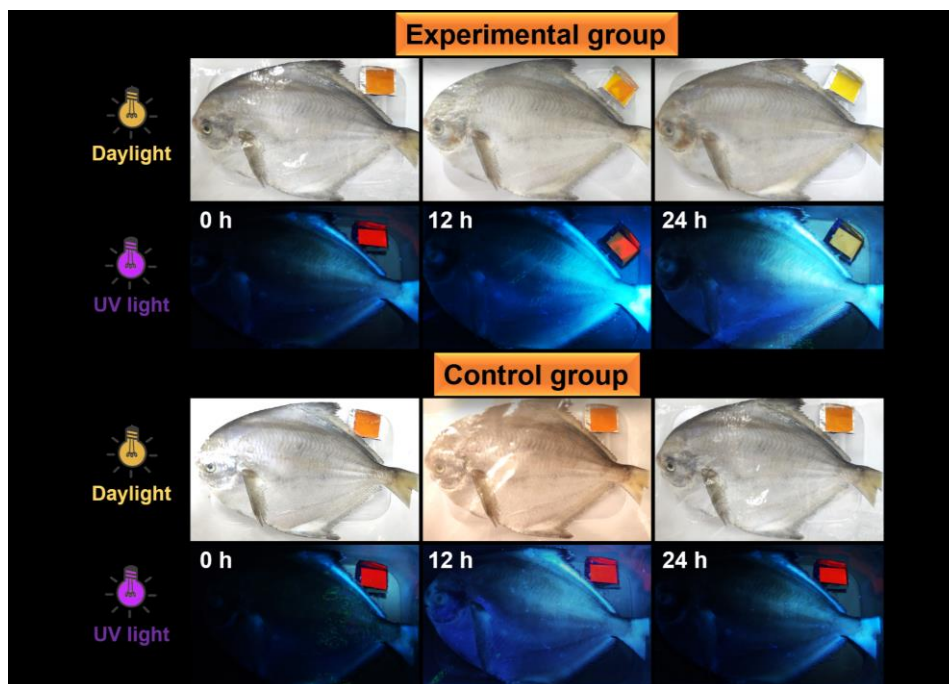


**Fig. S22** Spoilage detection of seafood in sealed packages for 24 h at room temperature (experimental group) and 4 °C (control group) using protonated imino-P**1a2a** filter papers. Photographs taken under normal room illumination and UV irradiation.

## References

1.  X. Lang, F. You, X. He, Y. Yu and L. He, *Green Chem.*, 2019, **21**, 509–514.

2.  J. M. Hoover and S. S. Stahl, *J. Am. Chem. Soc.*, 2011, **133**, 16901–16910.

3.  B. Li, A. Qin and B. Z. Tang, *Polym. Chem.*, 2020, **11**, 3075–3083.

4.  Q. Wan, R. Zhang, Z. Zhuang, Y. Li, Y. Huang, Z. Wang, W. Zhang, J. Hou and

B. Z. Tang, *Adv. Funct. Mater.*, 2020, **30**, 2002057.