Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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# Electronic Supplementary Information:

## Calix[4]resorcinarene-based branched macromolecues for all-optical photorefractive application

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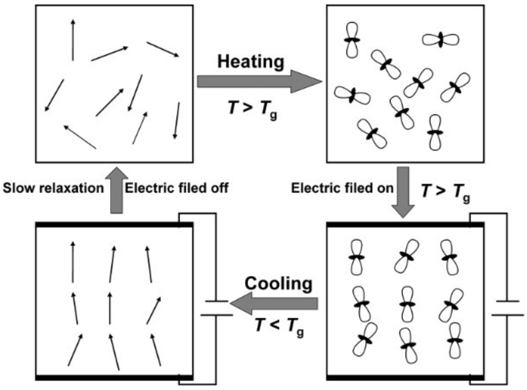


**Chart S1.** Graphical illustration of noncentrosymmetric alignment of NLO chromophores achieved by the high external electric field or poling process.

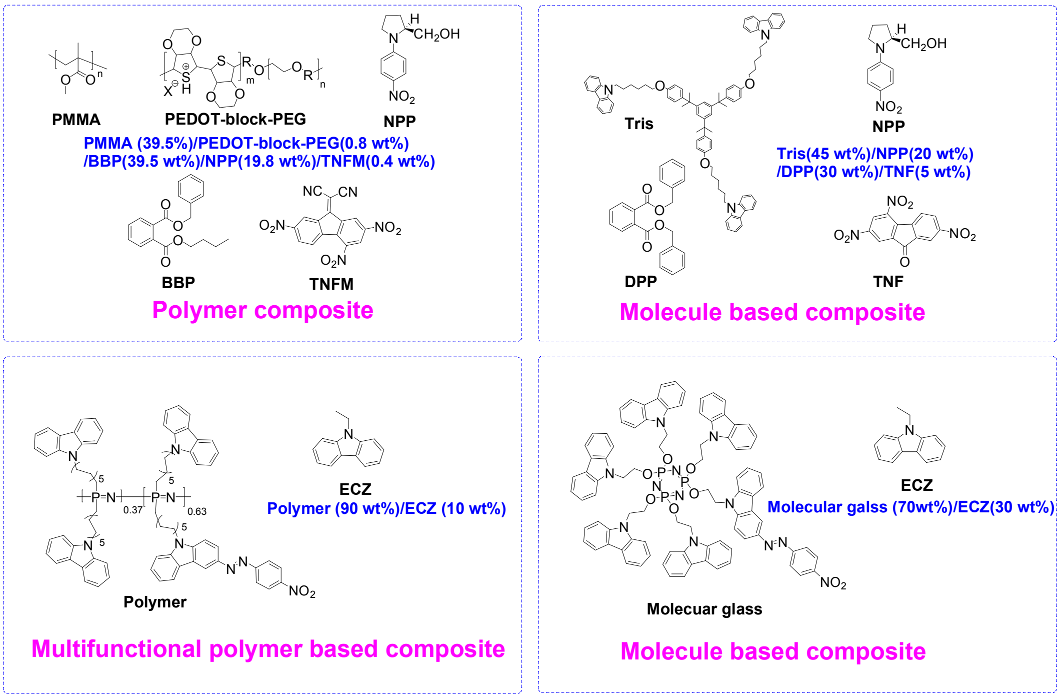


**Chart S2**. Different types of all-optical PR materials.

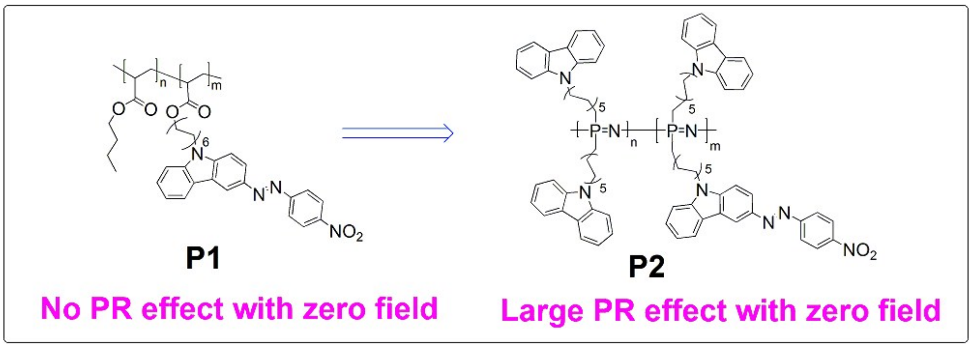


**Chart S3**. The example of similar polymer based composites with different PR performance.

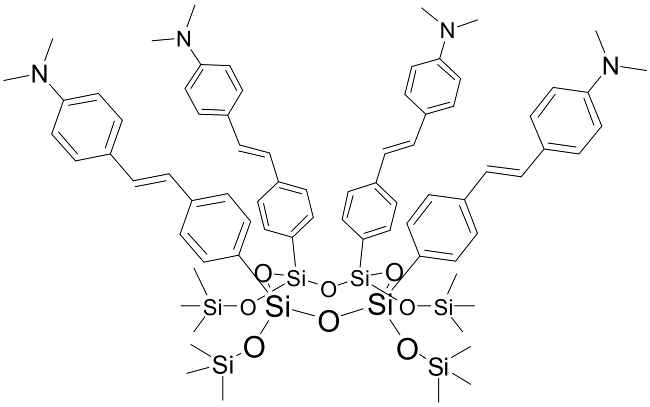
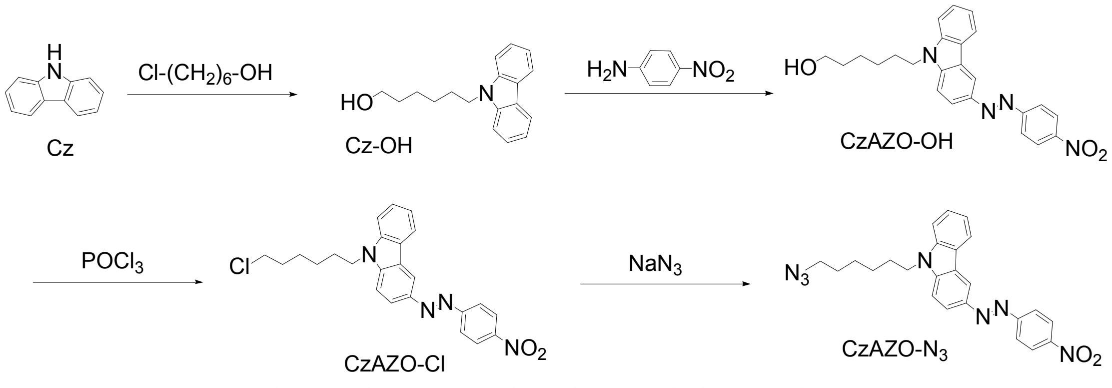


**Chart S4**. The structure with short-range ordered NLO chromophore.

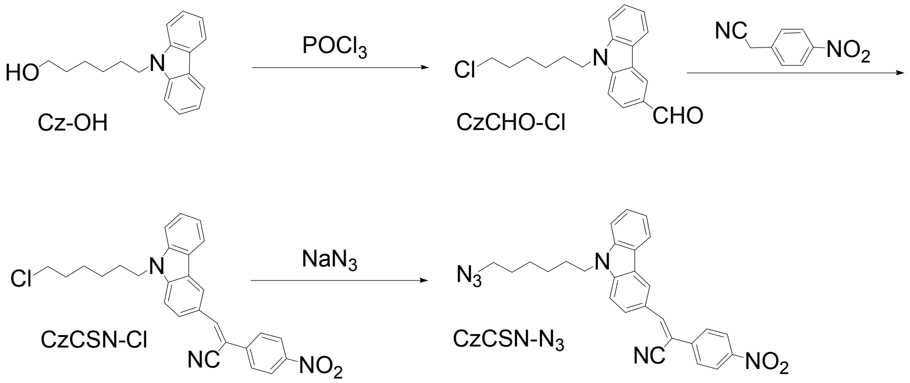
**Table S1**. The maximum absorption wavelengths of **CRA-Alk**, the chromophores and the target branched macromolecules.

| | $CH_2Cl_2$[a] | $CHCl_3$[a] | THF[a] | DMF[a] | Film[b] |
|---|---|---|---|---|---|
| **CRA-Alk** | 281 | 281 | 281 | 281 | -[c] |
| **CzAZO-Cl** | 437 | 438 | 434 | 439 | 450 |
| **CzCNS-Cl** | 420 | 423 | 416 | 420 | 434 |
| **CRA-CzAZO** | 436 | 437 | 433 | 437 | 449 |
| **CRA-CzCNS** | 420 | 421 | 415 | 420 | 434 |

[a] The maximum absorption wavelength of compound solutions with the concentrations fixed at 0.016 mg $mL^{-1}$. [b] The thickness of these thin films were both tested as around 80 μm. [c] Not obtained.



**Scheme S1**. The synthesis of carbazole-based chromophore **CzAZO-N$_3$**.



**Scheme S2**. The synthesis of carbazole-based chromophore **CzCNS-N$_3$**.

## Materials

*N,N*-Dimethylformamide (DMF) was dried over and distilled from $CaH_2$ under an atmosphere of dry nitrogen. Phosphorus oxychloride and piperidine are purchased from Aladdin Chemical Co. Ltd. Carbazole, sodium dodecyl sulfate and 1-chloro-6-hydroxyhexane were bought from Zhengzhou alpha chemical Co. Ltd. All other reagents were used as received.

## Synthesis of Cz-OH

Potassium hydroxide (8.42 g, 150 mmol) was added into 40 mL DMF. After stirring for 10 min, carbazole (5.02 g, 30.0 mmol) was added to the mixture and continued stirring for 45 min. Then, 1-chloro-6-hydroxyhexane (5.12 g, 37.5 mmol) was added slowly to the mixture and the reaction kept at 40 $^{o}$C for 28 hours. The resulting mixture was poured into a large amount of water and the precipitate was collected by filtration. Then silica gel chromatography with chloroform yielded **Cz-OH** (5.93 g, 70.2%) as a white needle solid. FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 3301 (-OH). $^1$H NMR (400 MHz, $CDCl_3$) , $\delta$ (TMS, ppm): 8.10 (d, 2H, ArH), 7.46 (t, 2H, ArH), 7.39 (d, 2H, ArH), 7.26-7.18 (m, 2H, ArH), 4.29 (t, 2H, -NCH$_2$-), 3.58 (t, 2H, -CH$_2$O-), 1.88 (m, 2H, -CH$_2$-), 1.58-1.44 (m, 2H, -CH$_2$-), 1.44-1.33 (m, 4H, -CH$_2$-), 1.31 (s, 2H, -OH). $^{13}$C NMR (100 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 140.9, 125.6, 122.8, 120.3, 118.7, 108.6, 62.7, 42.9, 32.5, 28.9, 27.0, 25.5. $C_{18}H_{21}NO$ (EA) (%, found/calcd): N 5.28/5.24, C 80.80/80.86, H 7.87/7.92.

## Synthesis of CzAZO-OH

A mixed solution of 4-nitroaniline (1.38 g, 10.0 mmol), concentrated hydrochloric acid (4.00 g, 37%) and deionized water (4 mL) was stirred below 4 $^{o}$C in an ice bath. Then, sodium nitrite (0.827 g, 12.0 mmol) dissolved in deionized water (4 mL) was slowly added dropwise to the above solution and stirring continued for an hour at 0-4 $^{o}$C. After the solution had become transparent, the mixture was filtered and the filtrate (diazonium salt solution) was kept in the ice bath. Sodium dodecyl sulfate (0.107 g, 0.370 mmol) was added into the filtrate. **Cz-OH** (2.81 g, 10.0 mmol) was dissolved in methylene chloride (100 mL), and then added dropwise to the above filtrate under intense stirring at room temperature for 48 hours. Dichloromethane was removed under reduced pressure, the mixture was filtered to get a red precipitate and this was rinsed with plenty of water. The crude product was purified through silica gel column with chloroform yielded **CzAZO-OH** (1.46 g, 33.9%) as a red solid. FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 3301 (-OH), 1518,1323 (-$NO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) , $\delta$ (TMS, ppm): 8.88 (d, 1H, ArH), 8.45 (d, 2H, ArH), 8.35 (d, 1H, ArH), 8.15 (d, 1H, ArH), 8.09 (d, 2H, ArH), 7.82 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.55 (t, 1H, ArH), 7.32 (t, 1H, ArH), 4.48 (t, 2H, -$NCH_2$-), 4.29 (t, 1H, -OH), 3.37-3.32 (m, 2H, -$CH_2O$-), 1.82 (s, 2H, -$CH_2$-), 1.47-1.21 (m, 6H, -$CH_2$-). $C_{24}H_{24}N_4O_3$ (EA) (%, found/calcd): N 13.33/13.45, C 69.28/69.21, H 5.80/5.81.

### Synthesis of CzAZO-Cl

**CzAZO-OH** (1.51 g, 3.50 mmol) was slowly added into phosphorus oxychloride (6 mL) with ice bath. After the addition was completed, the mixture was heated at 110 °C for 1 hour. After cooling to room temperature, the solution was then poured into chloroform (50 mL). After repeatedly washed with water and dried over anhydrous magnesium sulfate, the crude product was purified by silica gel chromatography eluted with petroleum ether/ethyl acetate (2/1, v/v) to give compound **CzAZO-Cl** (1.10 g, 70.0%). FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 1518, 1323（-$NO_2$）. $^1$H NMR (400 MHz, DMSO-$d_6$) , $\delta$ (TMS, ppm): 8.87 (s, 1H, ArH), 8.42 (t, 2H, ArH), 8.32 (t, 1H, ArH), 8.13 (d, 2H, ArH), 8.08 (d, 1H, ArH), 7.82 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.55 (t, 1H, ArH), 7.32 (t, 1H, ArH), 4.48 (t, 2H, -$NCH_2$-), 3.58 (t, 2H, -$CH_2Cl$), 1.88-1.72 (m, 2H, -$CH_2$-), 1.74-1.57 (m, 2H, -$CH_2$-), 1.39 (d, 10.8 Hz, 2H, -$CH_2$-), 1.39 (d, 2H, -$CH_2$-). $^{13}$C NMR (100 MHz, DMSO-$d_6$) , $\delta$ (TMS, ppm): 156.2, 148.1, 146.1, 143.2, 141.4, 127.3, 125.6, 123.5, 123.1, 121.6, 120.8, 120.6, 119.1, 110.7, 45.7, 43.1, 32.4, 28.9, 26.5, 26.1. $C_{24}H_{23}ClN_4O_2$ (EA) (%, found/calcd): N 12.35/12.88, C 66.33/66.28, H 5.46/5.33.

### Synthesis of CzAZO-N$_3$

A mixture of **CzAZO-Cl** (2.82 g, 6.30 mmol), sodium azide (2.00 g, 30.8 mmol), and DMF (20 mL) was stirred at 80 °C for 10 hours. After cooling to room temperature, the mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by chromatography with hexane/ethyl acetate (10:1, v/v) to give **CzAZO-N$_3$** (2.64 g, 92.0%) as a red solid. FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 2084 (-$N_3$), 1518, 1323(-$NO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) , $\delta$ (TMS, ppm): 8.87 (s, 1H, ArH), 8.44 (d, 2H, ArH), 8.35 (d, 1H, ArH), 8.12

(t, 3H, ArH), 8.07 (d, 1H, ArH), 7.81 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.56 (d, 1H, ArH), 7.37-7.25 (m, 4H, ArH), 4.47 (t, 2H, -$NCH_2$-), 3.26 (t, 2H, -$CH_2N_3$), 1.81 (s, 2H, -$CH_2$-), 1.46 (d, 2H, -$CH_2$-), 1.34 (s, 2H, -$CH_2$-), 1.22 (s, 2H, -$CH_2$-). $^{13}C$ NMR (100 MHz, DMSO-$d_6$), δ (TMS, ppm): 156.1, 148.1, 146.1, 143.2, 141.4, 127.2, 125.5, 123.4, 123.1, 121.5, 120.7, 120.6, 119.1, 110.6, 110.6, 51.0, 43.0, 28.9, 28.5, 26.4, 26.3. $C_{24}H_{23}ClN_7O_2$ (EA) (%, found/calcd): N 22.17/22.21, C 65.10/65.29, H 5.31/5.25. Melting Point: 121~122 °C.

**Synthesis of CzCHO-Cl**

Phosphorus oxychloride (6.13 g, 40.0 mmol) was added dropwise to DMF (25 mL) at 0 °C, and the mixture was stirred for 1 hour at this temperature. **Cz-OH** (5.63 g, 20.0 mmol) was added and the reaction mixture was stirred at 100 °C for 3 hours. Then, the mixture was cooled to room temperature, poured into ice water and carefully neutralized with sodium hydroxide. The solution was extracted with dichloromethane, then, the organic phase was washed with water and dried over anhydrous sodium sulfate. After filtration, the solvent was removed. The crude product was purified by silica gel chromatography eluted with chloroform to give **CzCHO-Cl** (4.80 g, 73.2%). FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 2747 (-CHO). $^1H$ NMR (400 MHz, DMSO-$d_6$) , $\delta$ (TMS, ppm): 10.06 (s, 1H, -CHO), 8.75 (s, 1H, ArH), 8.29 (d, 1H, ArH), 7.99 (d, 1H, ArH), 7.75 (t, 1H, ArH), 7.69 (d, 1H, ArH), 7.54 (t, 1H, ArH), 7.30 (t, 1H, ArH), 4.44 (t, 2H, -$NH_2$-), 3.55 (t, 2H, -$CH_2Cl$), 1.76 (m, 2H, -$CH_2$-), 1.62 (m, 2H, -$CH_2$-), 1.36 (d, 4H, -$CH_2$-). $^{13}C$ NMR (100 MHz, DMSO-$d_6$), δ (TMS, ppm): 192.3, 144.0, 141.3, 128.7, 127.2, 127.1, 124.5, 122.8, 122.7, 121.3, 120.6, 110.6, 110.3, 45.7, 43.0, 32.4, 28.8, 26.5, 26.1. $C_{19}H_{20}ClNO$ (EA) (%, found/calcd): N 4.13/4.46, C 72.94/72.71, H 6.34/6.42. Melting Point: 57~58 °C.

**Synthesis of CzCNS-Cl**

To the solution of compound **CzCHO-Cl** (3.27 g, 10.0 mmol) and 4-nitrophenylacetonitrile (1.95 g, 12.0 mmol) in 50 mL of ethanol was added piperidine (1.70 g, 20.0 mmol) at 60 °C. The mixture was stirred at reflux for 2 hours and poured into water. The precipitate was collected by filtration and washed with water. The crude product was purified by silica gel chromatography eluted with chloroform, then recrystallization from ethanol to yield **CzCNS-Cl** (3.30 g, 70.0%) as an orange solid. FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 2210 (-CN). $^1H$ NMR (400 MHz, DMSO-$d_6$) , δ (TMS, ppm): 8.83 (s, 1H, ArH), 8.45 (s, 1H, ArH), 8.37 (d, , 2H, ArH), 8.26 (d, 1H, ArH), 8.15 (d, 1H, ArH), 8.06 (d, 2H, ArH), 7.84 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.55 (t, 1H, ArH), 7.32 (t, 1H, ArH), 4.47 (t, 2H, -$NCH_2$-), 3.58 (t, 2H, -$CH_2Cl$), 1.92-1.72 (m, 2H, -$CH_2$-), 1.72-1.59 (m, 2H, -$CH_2$-), 1.53-1.24 (m, 4H, -$CH_2$-). $^{13}C$ NMR (100 MHz, DMSO-$d_6$), $\delta$ (TMS, ppm): 148.0, 147.3, 142.3, 141.6, 141.2, 127.7, 127.3, 126.9, 124.9, 124.6, 124.0, 122.9, 122.4, 120.8, 120.6, 118.9, 110.6, 104.3, 45.8, 43.0, 32.4, 28.9, 26.5, 26.1. $C_{27}H_{24}ClN_3O_2$ (EA) (%, found/calcd): N 9.05/9.18, C 70.96/70.81, H 5.29/5.28. Melting Point: 195~196 $^{o}$C.

**Synthesis of CzCNS-$N_3$**

A mixture of **CzCNS-Cl** (2.36 g, 5.00 mmol), sodium azide (0.975 g, 15.0 mmol), and DMF (20 mL) was stirred at 80 °C for 10 hours. After cooled to room temperature, the mixture was diluted with water and extracted with chloroform. The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by chromatography with chloroform, then recrystallization from ethanol to yield **CzCNS-$N_3$** (1.91 g, 79.8%) as an orange solid. FT-IR (KBr), $\upsilon$ (cm$^{-1}$): 2210 (-CN), 2087 (-$N_3$). $^1$H NMR (400 MHz, DMSO-$d_6$) , δ (TMS, ppm): 8.80 (s, 1H, ArH), 8.41 (s, 1H, ArH), 8.33 (d, 2H, ArH), 8.23 (d, 1H, ArH), 8.13 (d, 1H, ArH), 8.02 (d, 2H, ArH), 7.80 (d, 1H, ArH), 7.68 (d, 1H, ArH), 7.53 (t, 1H, ArH), 7.31 (t, 1H, ArH), 4.44 (s, 2H, -$NCH_2$-), 3.25 (s, 2H, -$CH_2N_3$), 1.80 (s, 2H, -$CH_2$-), 1.46 (s, 2H, -$CH_2$-), 1.33 (s, 4H, -$CH_2$-). $^{13}$C NMR (100 MHz, DMSO-$d_6$), δ (TMS, ppm): 147.9, 147.3, 142.3, 141.5, 141.2, 127.7, 127.2, 126.8, 124.8, 124.6, 123.9, 122.9, 122.5, 120.8, 120.5, 118.8, 110.5, 104.3, 51.0, 43.0, 28.8, 28.5, 26.4, 26.3. $C_{27}H_{24}N_6O_2$ (EA) (%, found/calcd): N 18.34/18.09, C 69.89/69.81, H 5.16/5.21. Melting Point: 168~169 $^{o}$C.

**The $^1$H NMR and $^{13}$C NMR spectra of related compounds.**

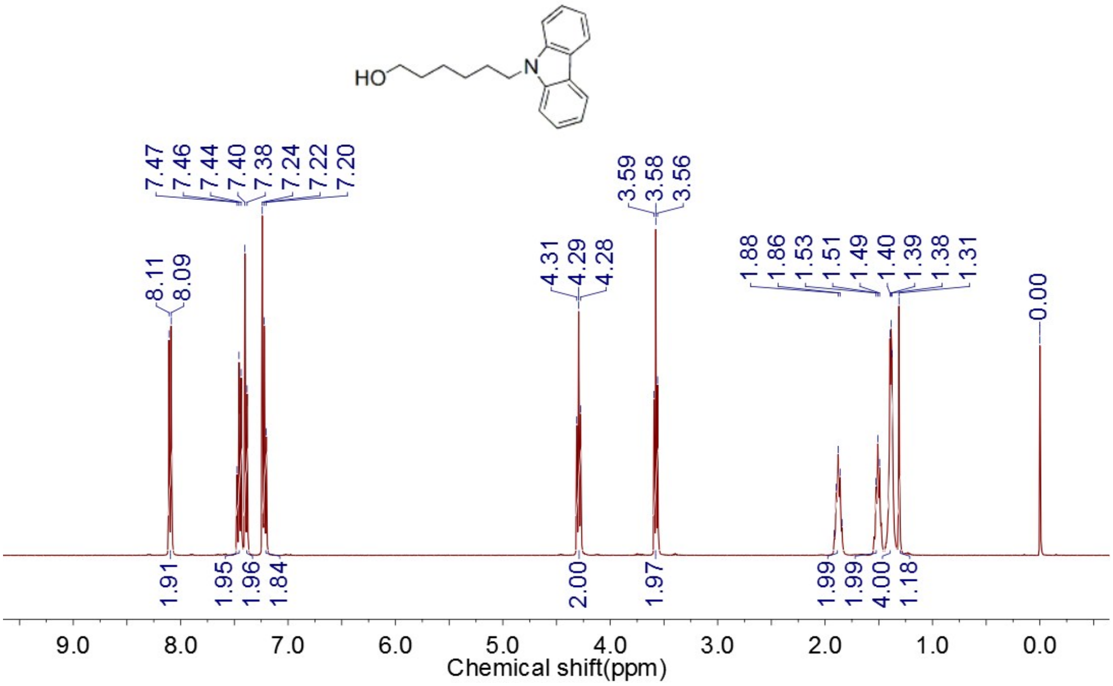


**Fig. S1** $^1$H NMR spectrum of **Cz-OH** in chloroform-*d*.

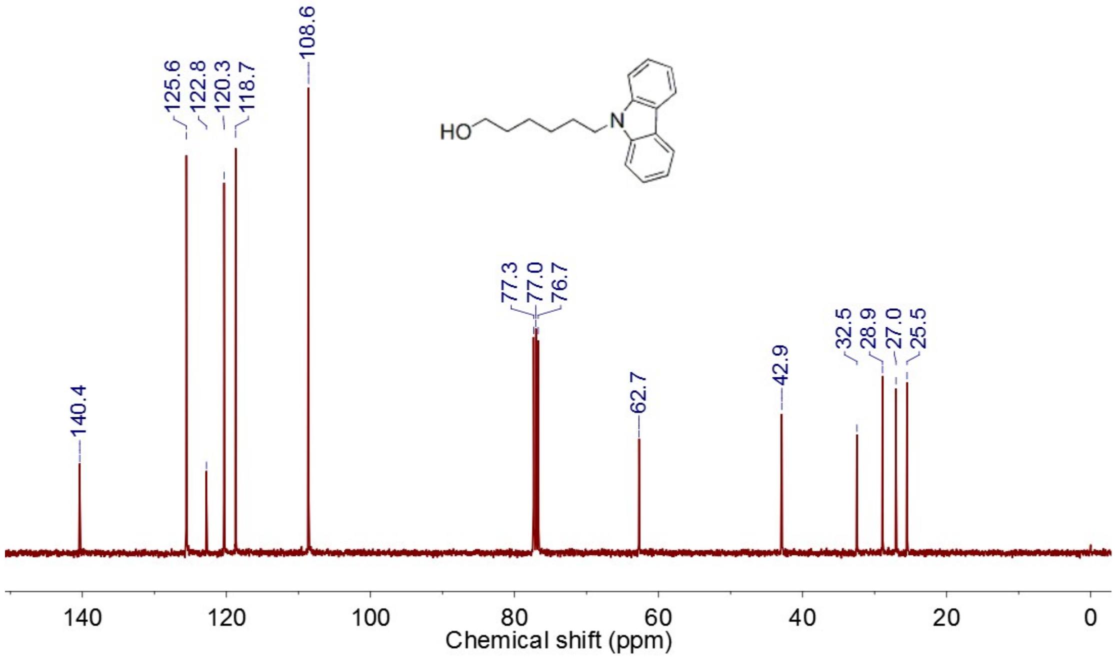


**Fig. S2** $^{13}$C NMR spectrum of **Cz-OH** in chloroform-*d*.

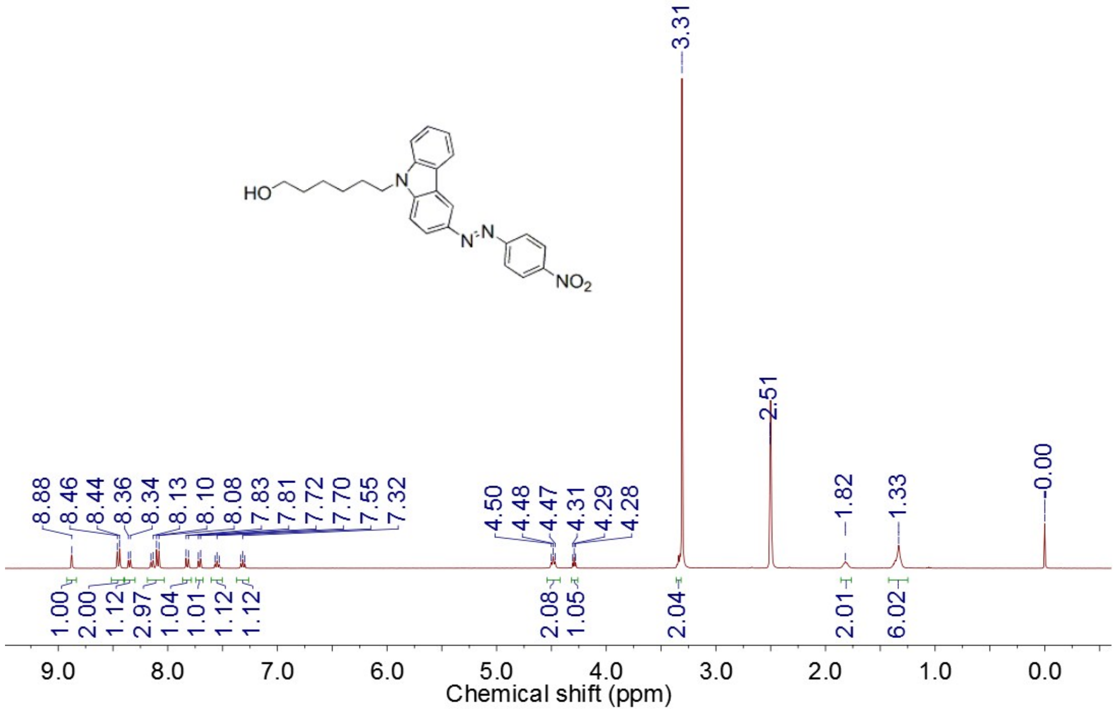


**Fig. S3** $^{1}$H NMR spectrum of **CzAZO-OH** in DMSO-$d_6$.

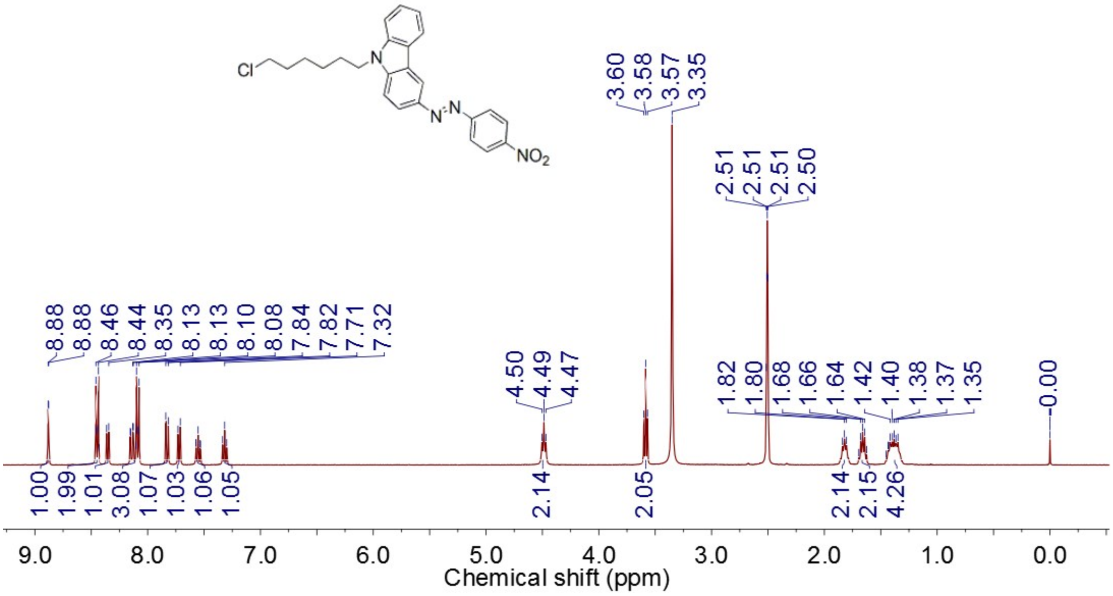


**Fig. S4** $^{1}H$ NMR spectrum of **CzAZO-Cl** in DMSO-$d_6$.

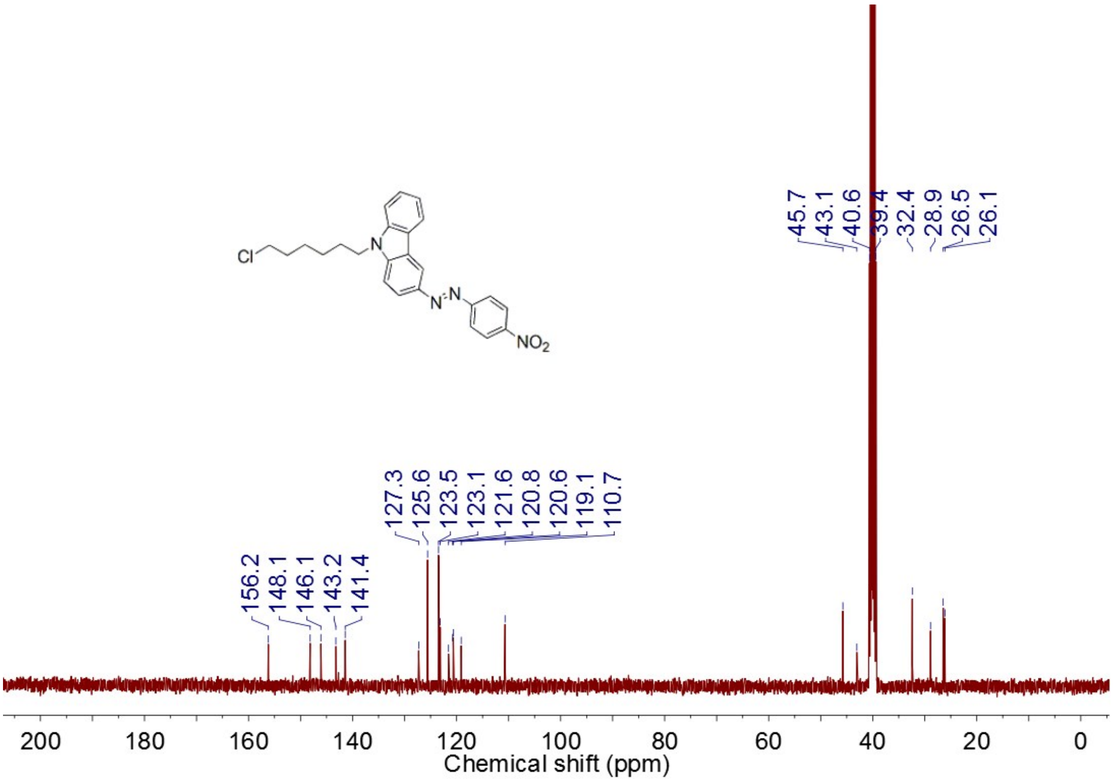


**Fig. S5** $^{13}C$ NMR spectrum of **CzAZO-Cl** in DMSO-$d_6$.

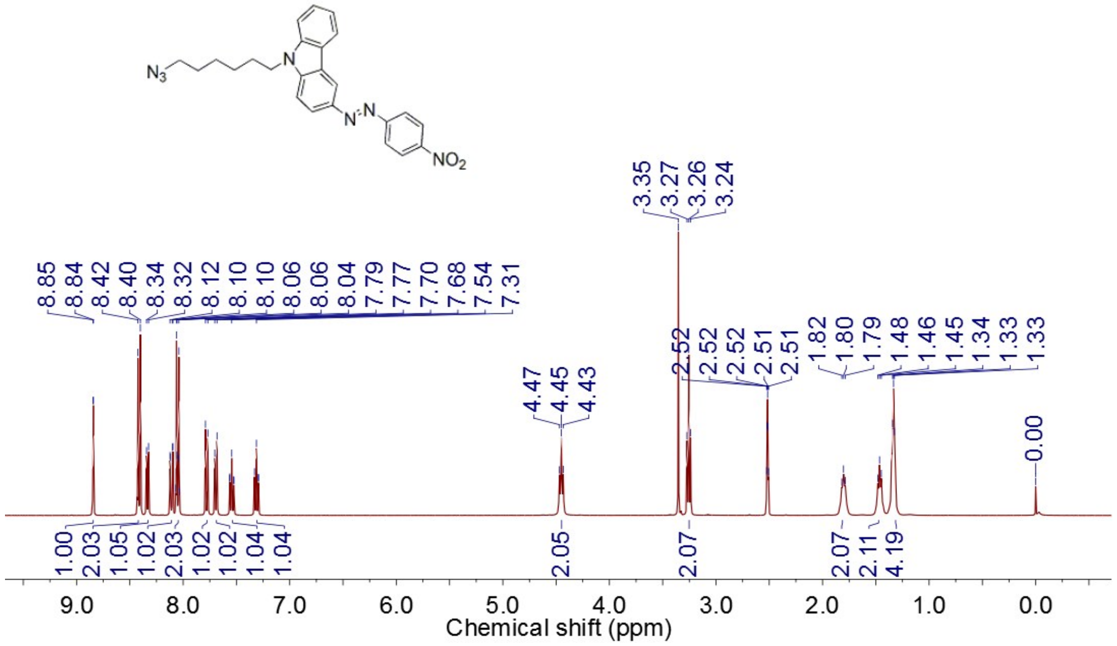


**Fig. S6** $^{1}$H NMR spectrum of **CzAZO-N$_3$** in DMSO-$d_6$.

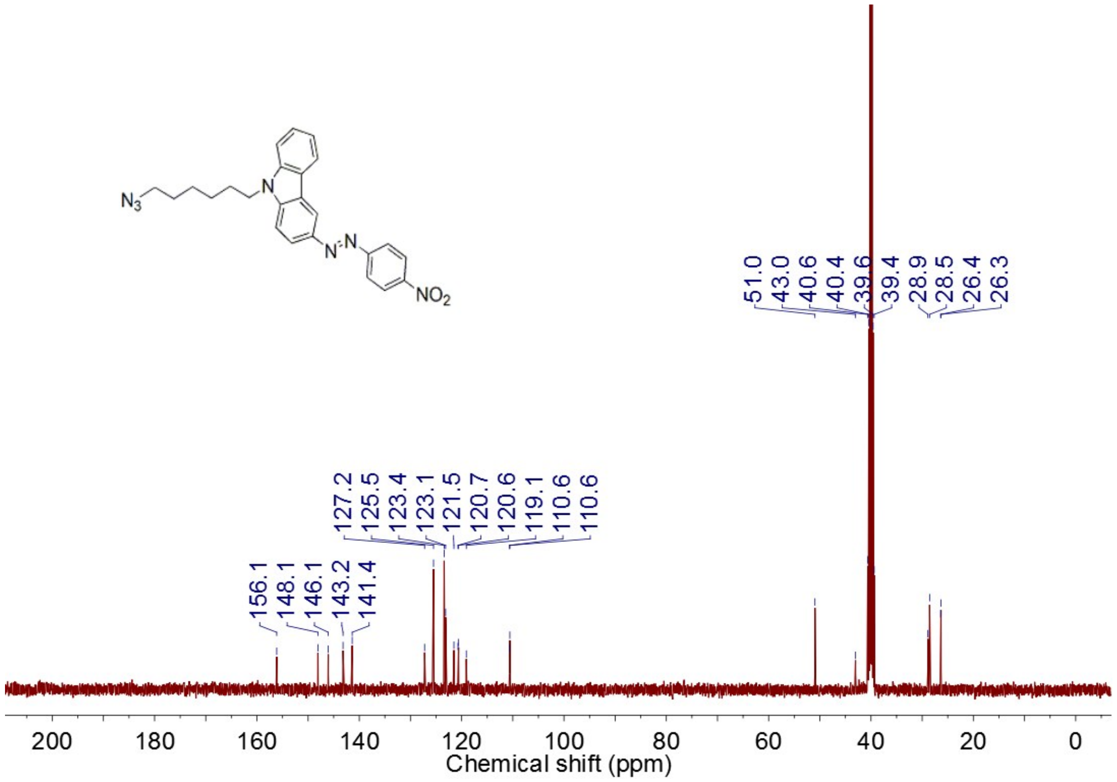


**Fig. S7** $^{13}$C NMR spectrum of **CzAZO-N$_3$** in DMSO-$d_6$.

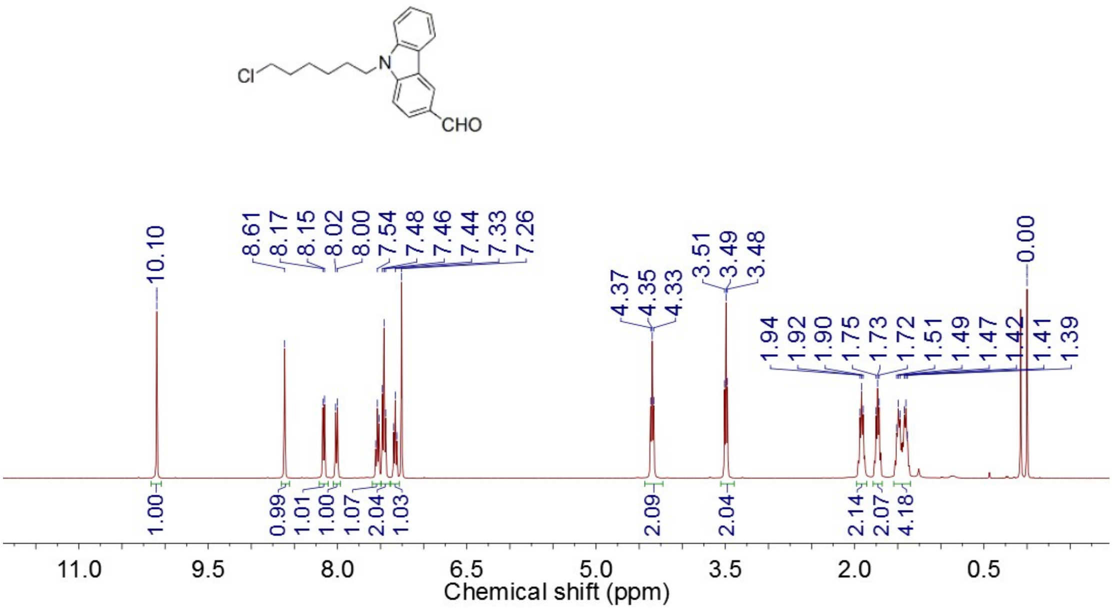


**Fig. S8** $^{1}$H NMR spectrum of **CzCHO-Cl** in DMSO-$d_6$.

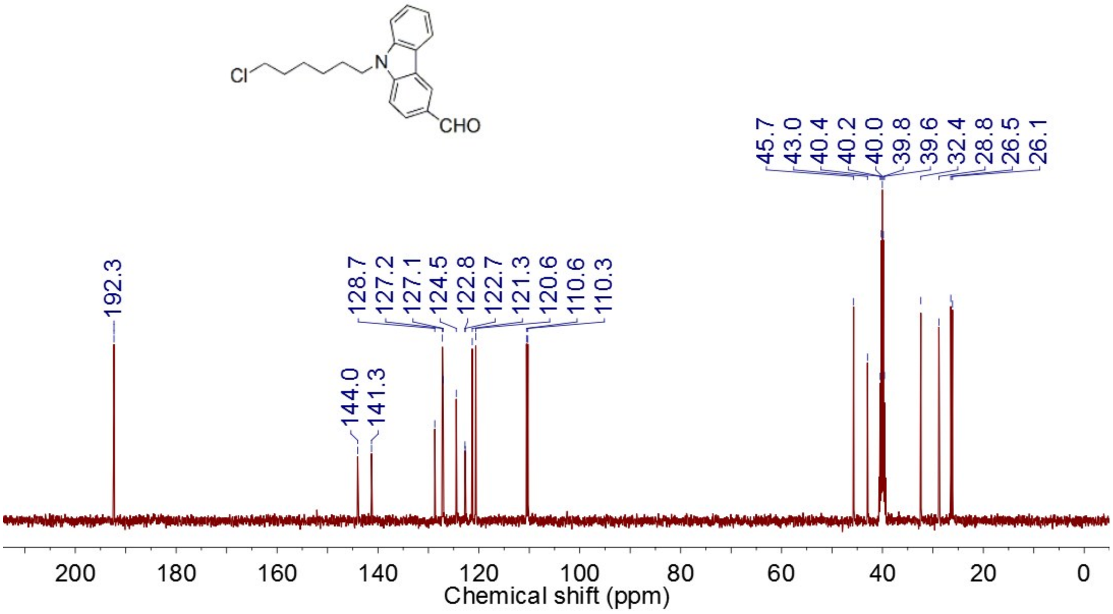


**Fig. S9** $^{13}$C NMR spectrum of **CzCHO-Cl** in DMSO-$d_6$.

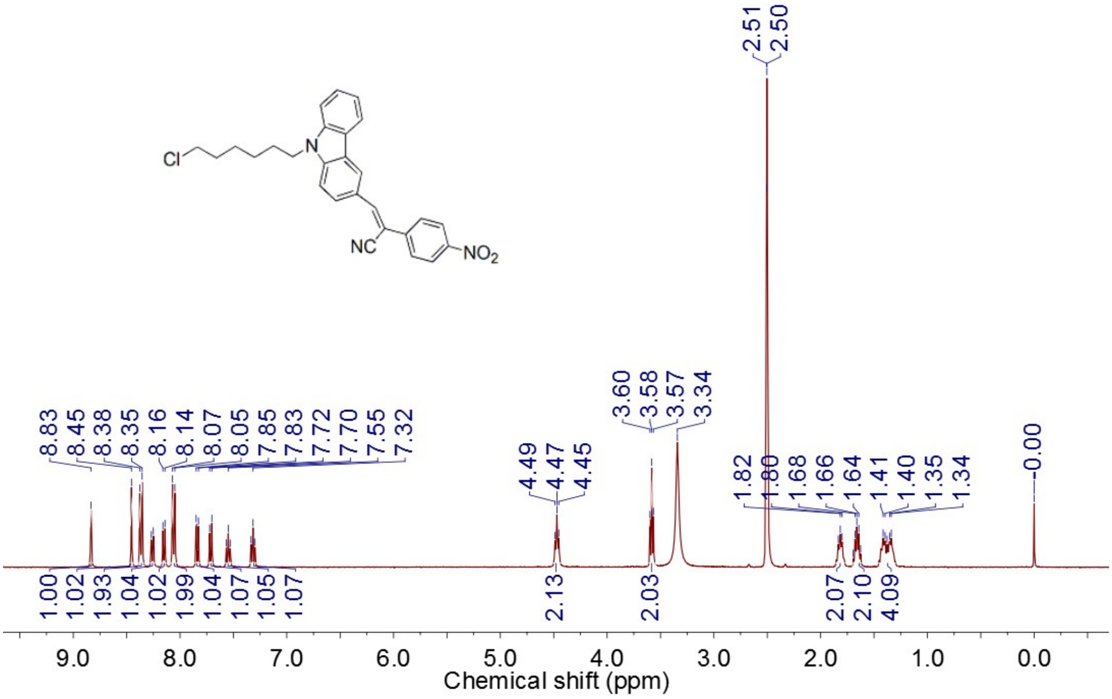


**Fig. S10** $^{1}$H NMR spectrum of **CzCNS-Cl** in DMSO-$d_6$.

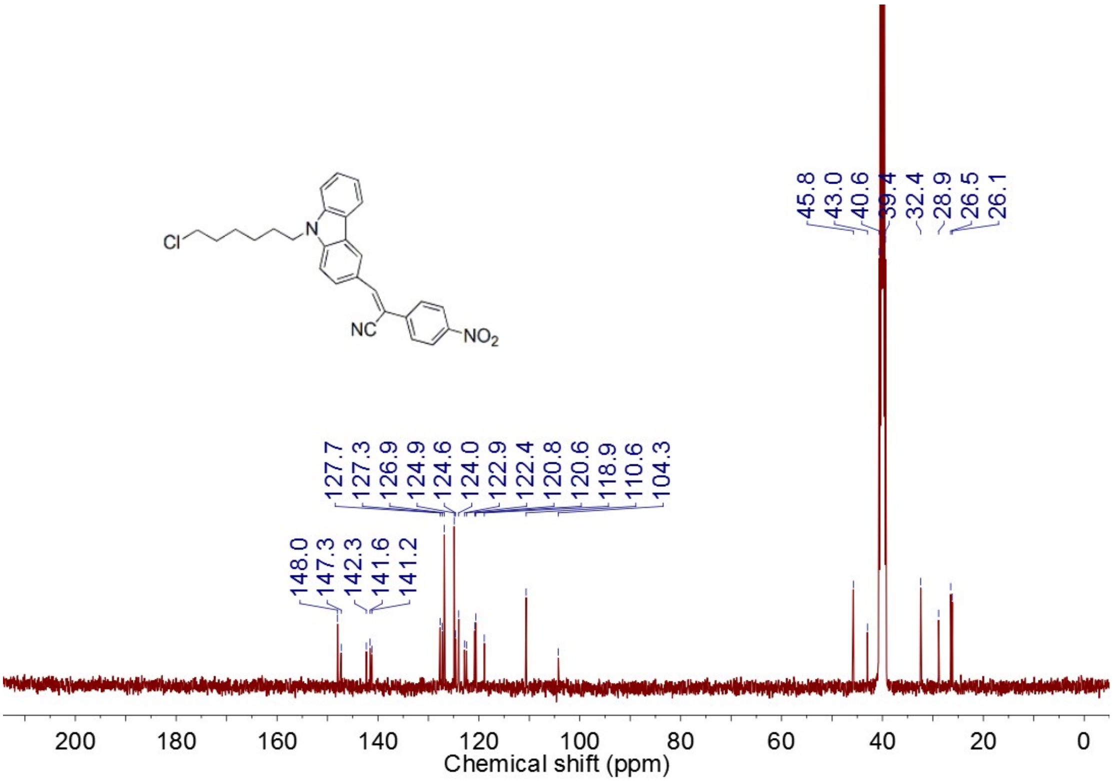


**Fig. S11** $^{13}$C NMR spectrum of **CzCNS-Cl** in DMSO-$d_6$.

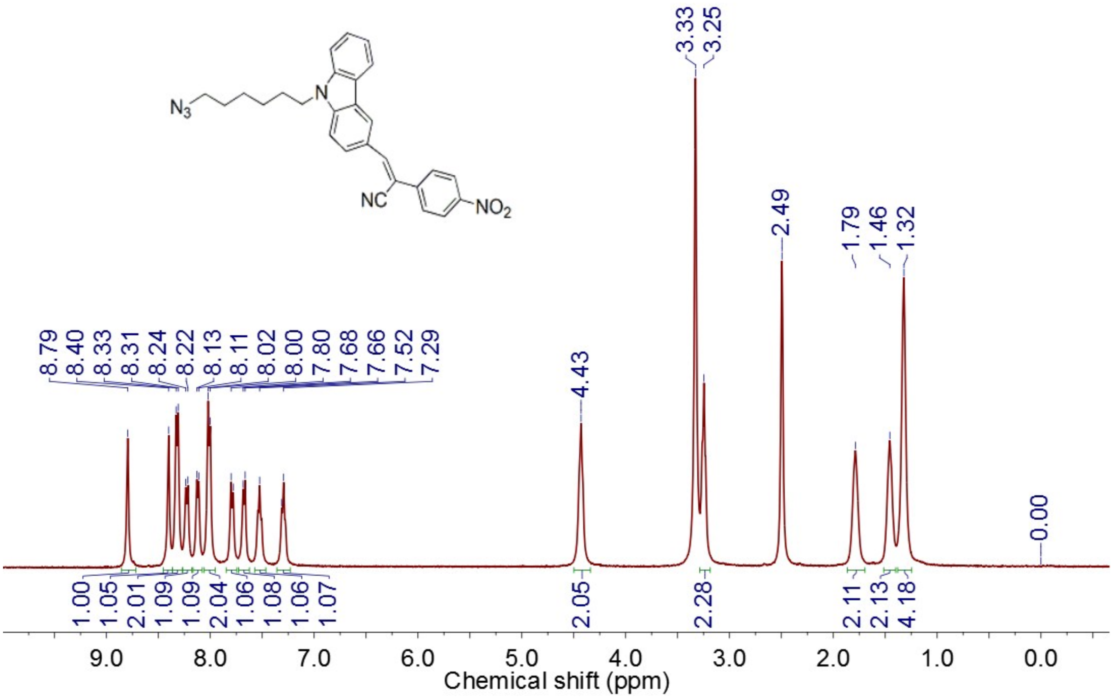


**Fig. S12** $^{1}$H NMR spectrum of **CzCNS-N$_3$** in DMSO-*d$_6$*.

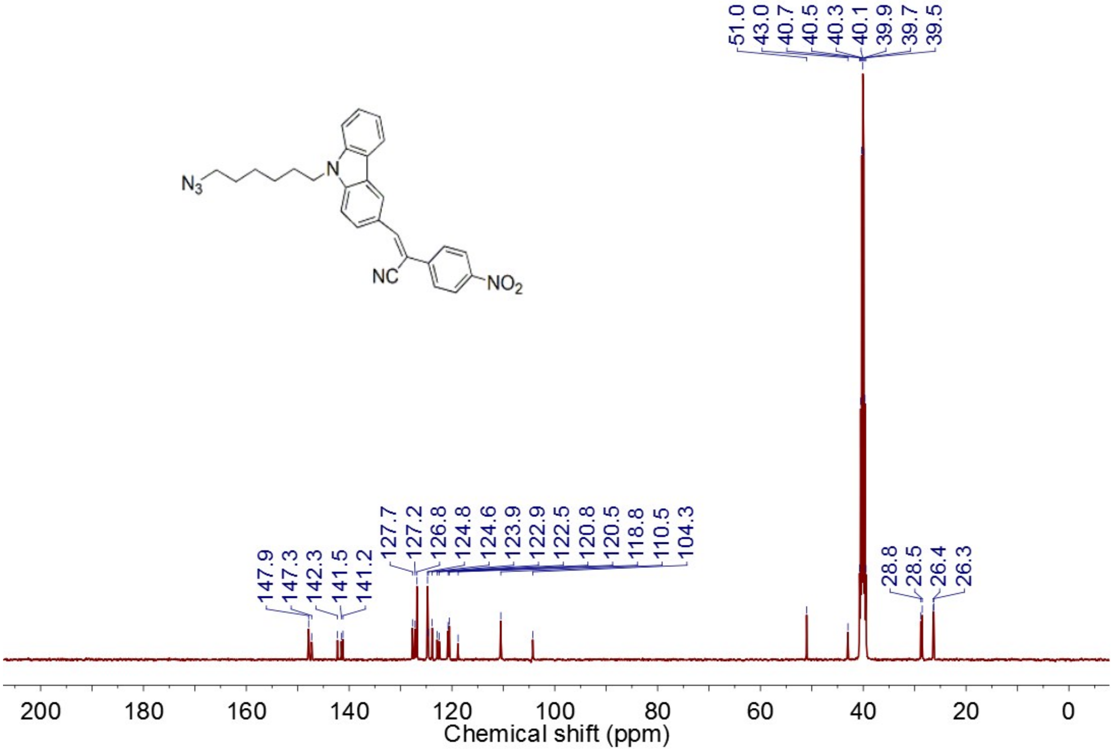


**Fig. S13** $^{13}$C NMR spectrum of **CzCNS-N$_3$** in DMSO-*d$_6$*.

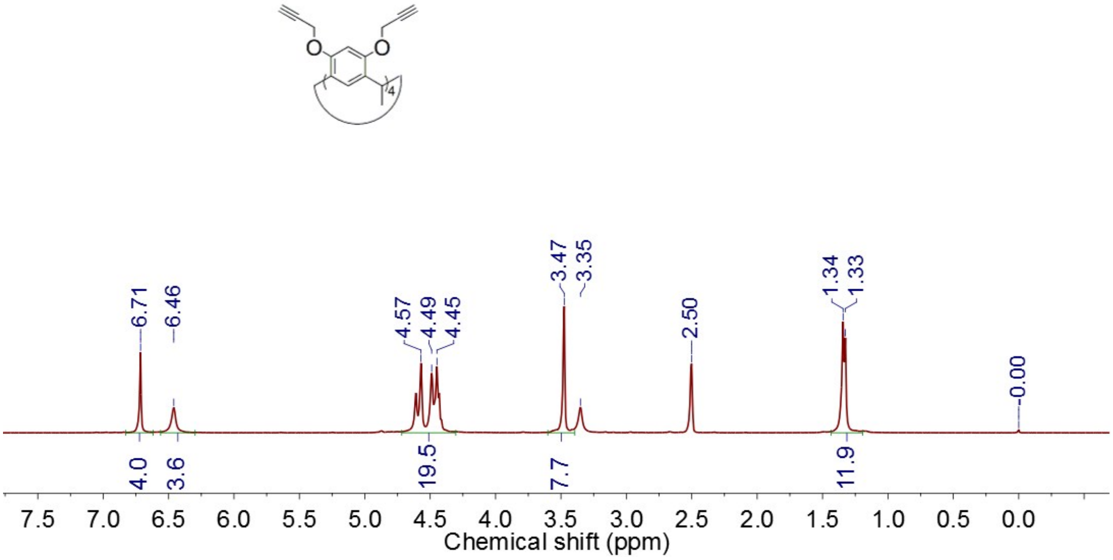


**Fig. S14** $^{1}H$ NMR spectrum of **CRA-Alk** in DMSO-$d_6$.

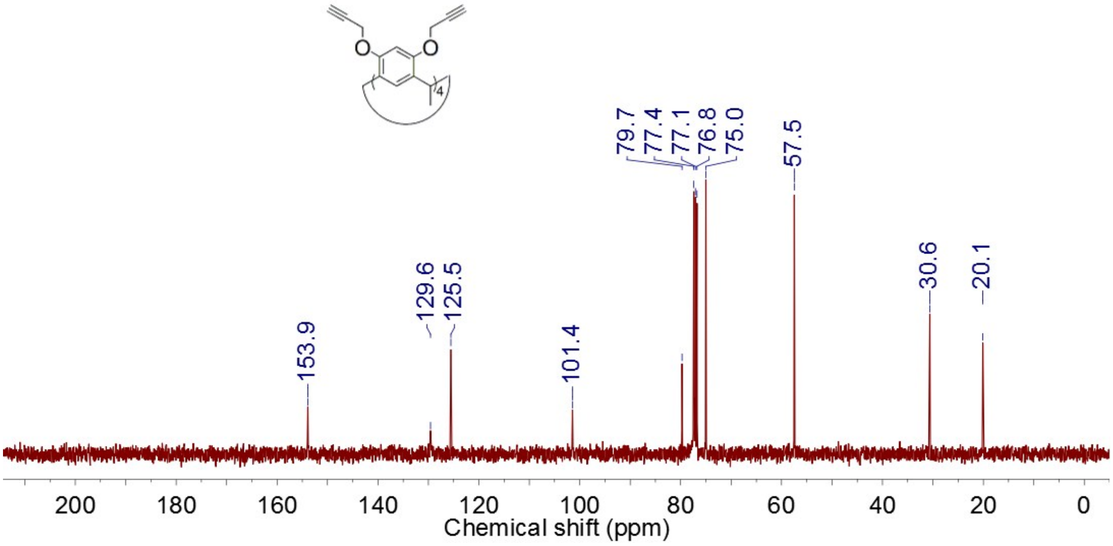


**Fig. S15** $^{13}C$ NMR spectrum of **CRA-Alk** in chloroform-$d$.

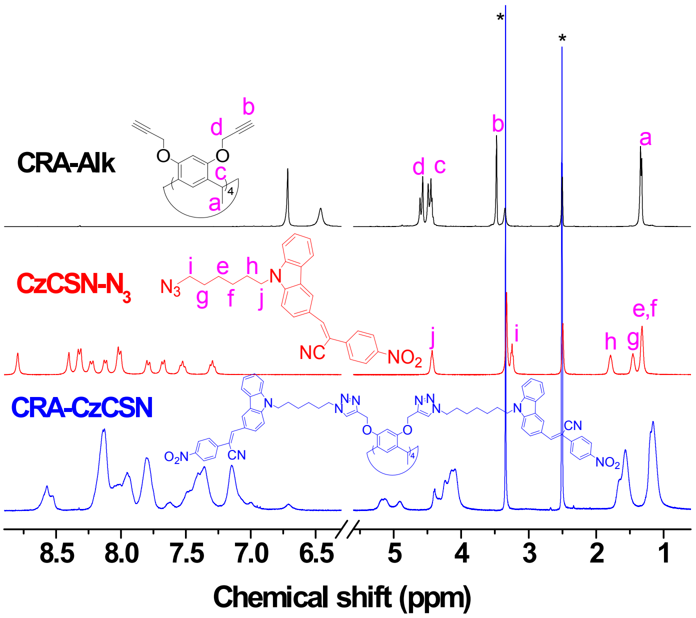


**Fig. S16** $^1$H NMR spectra of **CRA-Alk, CzCNS-N$_3$** and **CRA-CzCNS** in DMSO-$d_6$.

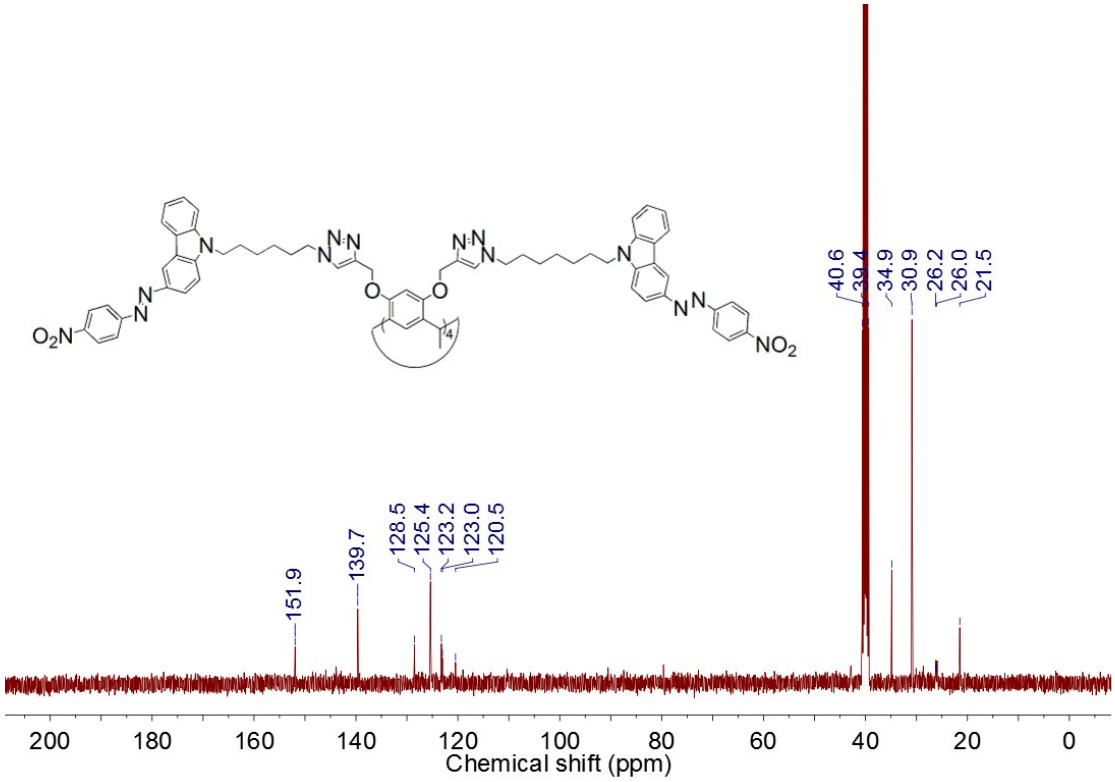


**Fig. S17** $^{13}$C NMR spectra of **CRA-CzAZO** in DMSO-$d_6$.

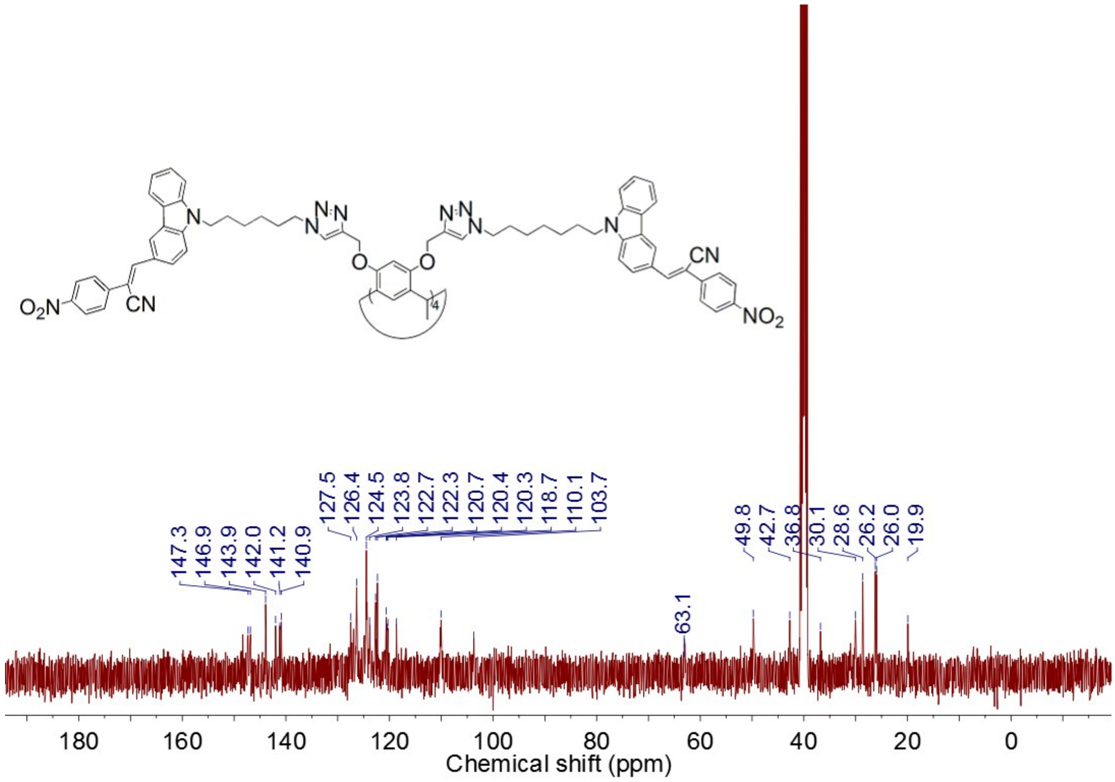


**Fig. S18** $^{13}$C NMR spectra of **CRA-CzCNS** in DMSO-$d_6$.

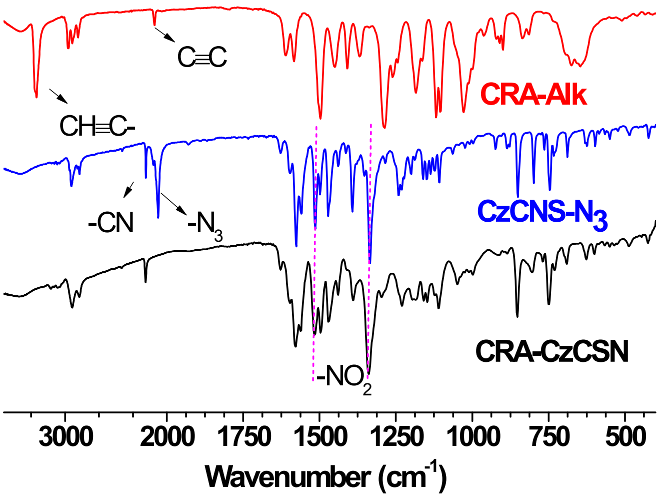


**Fig. S19** The FT-IR spectra of **CRA-Alk, CzCNS-N$_3$** and **CRA-CzCNS.**

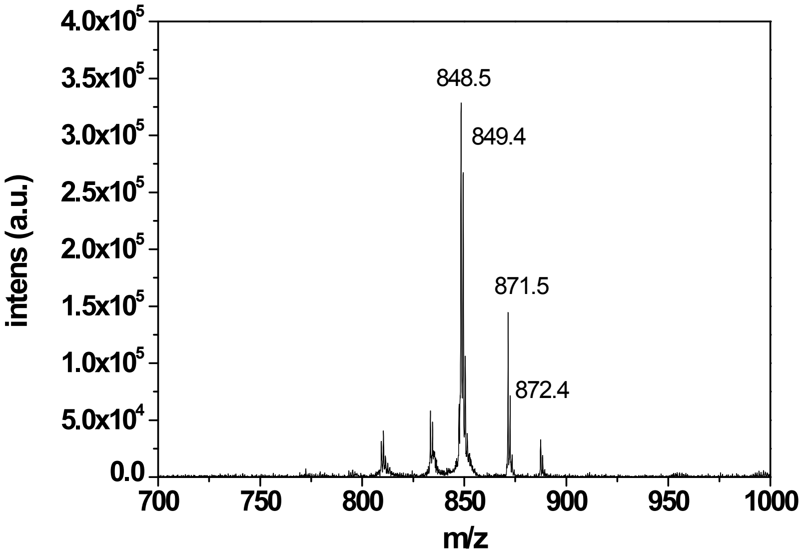


**Fig. S20** The MALDI-TOF mass spectrum of **CRA-Alk.**

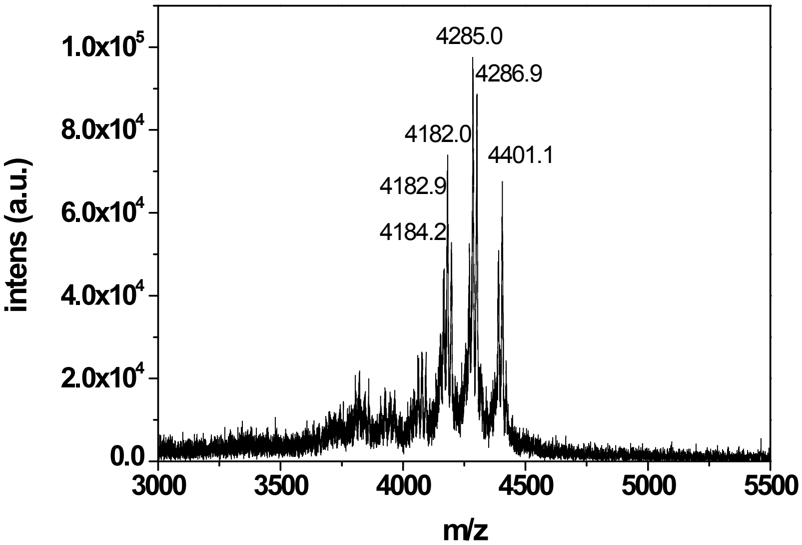


**Fig. S21** The MALDI-TOF mass spectrum of **CRA-CzAZO.**

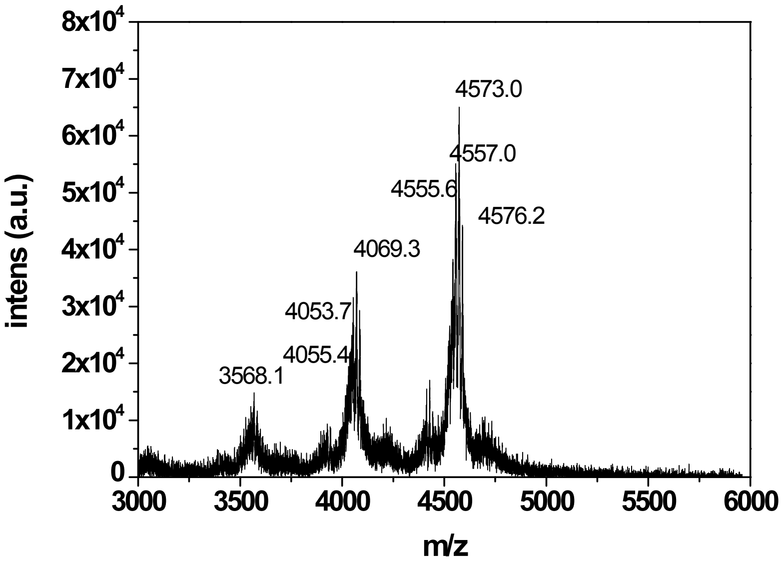


**Fig. S22** The MALDI-TOF mass spectrum of **CRA-CzCSN.**

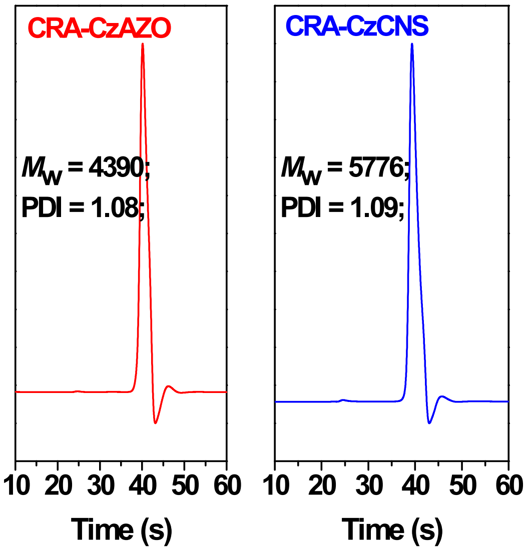


**Fig. S23**. The GPC chromatograms of **CRA-CzAZO** and **CRA-CzCNS**.

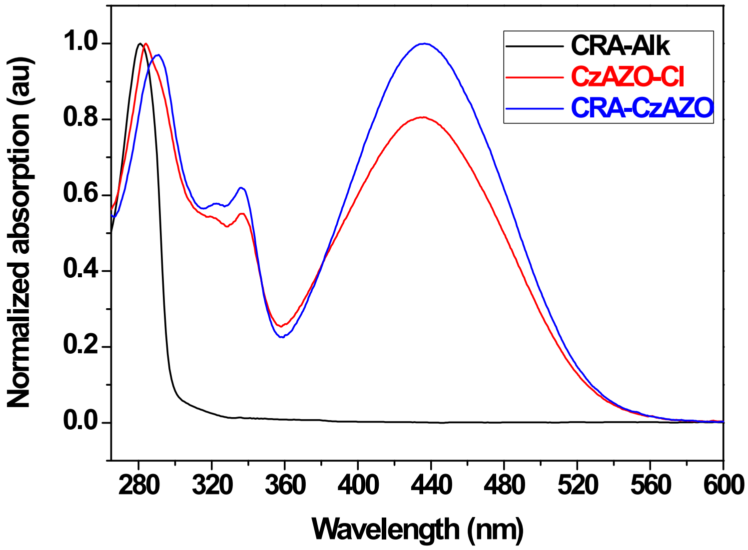


**Fig. S24** UV-Vis spectra of **CRA-Alk**, **CzAZO-Cl** and **CRA-CzAZO** in $CH_2Cl_2$.

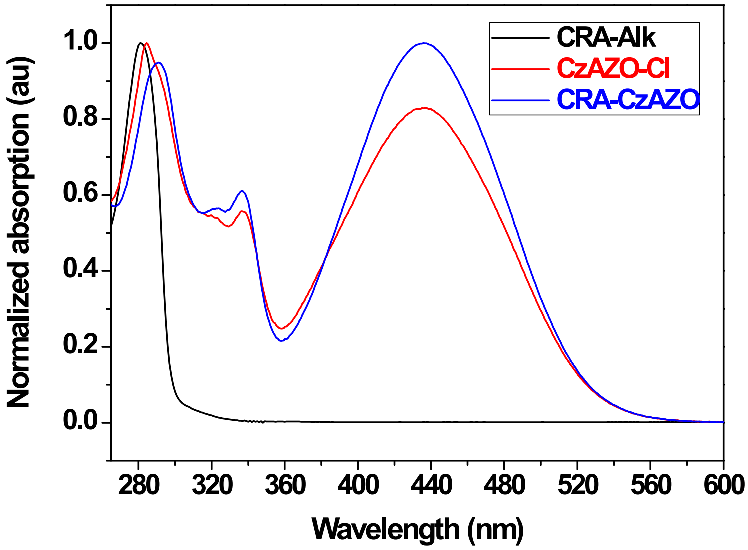


**Fig. S25** UV-Vis spectra of **CRA-Alk**, **CzAZO-Cl** and **CRA-CzAZO** in $CHCl_3$.

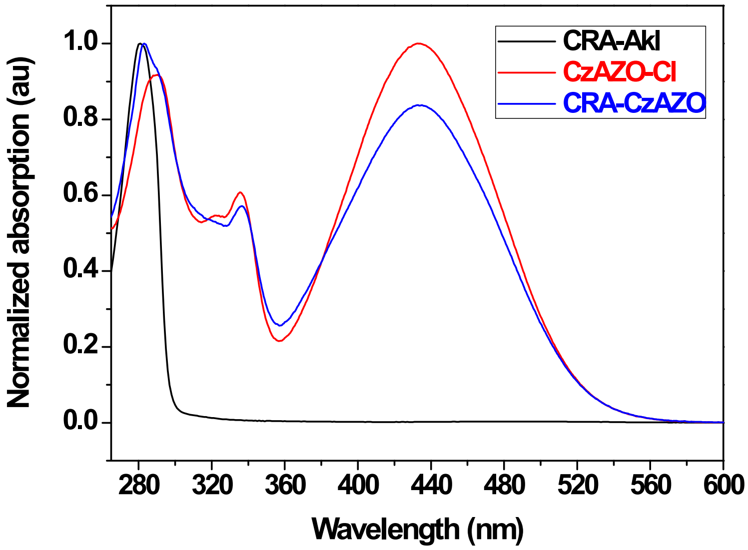


**Fig. S26** UV-Vis spectra of **CRA-Alk**, **CzAZO-Cl** and **CRA-CzAZO** in THF.

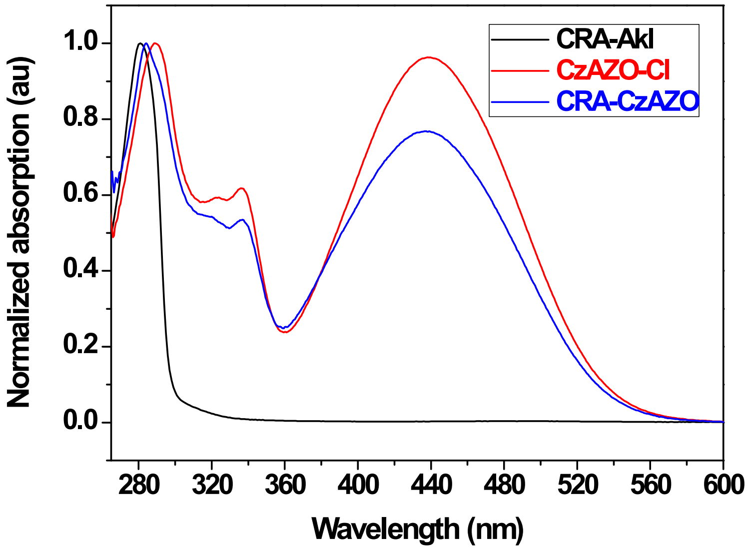


**Fig. S27** UV-Vis spectra of **CRA-Alk**, **CzAZO-Cl** and **CRA-CzAZO** in DMF.

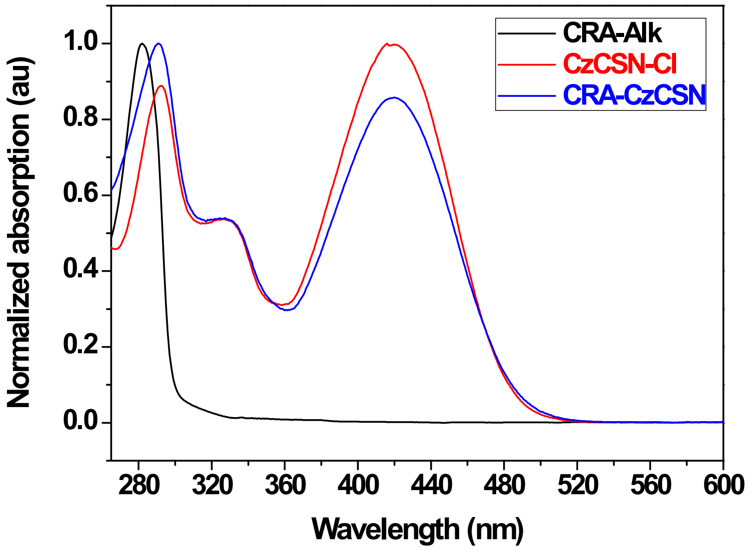


**Fig. S28** UV-Vis spectra of **CRA-Alk**, **CzCSN-Cl** and **CRA-CzCSN** in $CH_2Cl_2$.

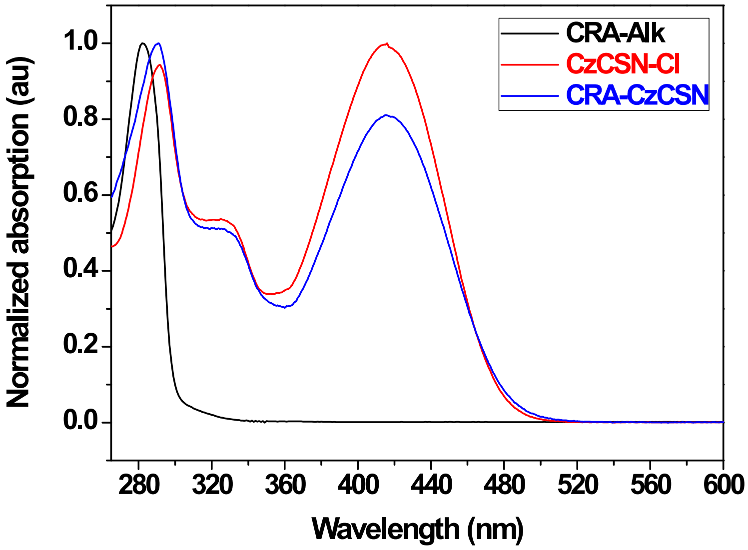


**Fig. S29** UV-Vis spectra of **CRA-Alk**, **CzCSN-Cl** and **CRA-CzCSN** in $CHCl_3$.

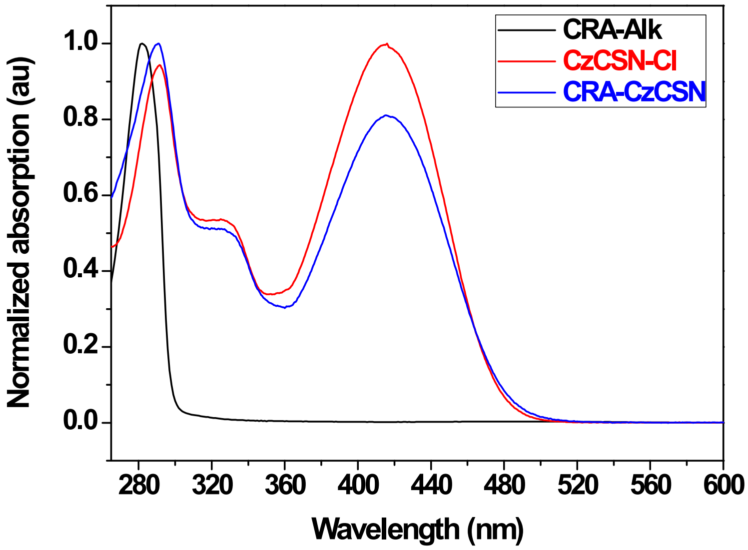


**Fig. S30** UV-Vis spectra of **CRA-Alk**, **CzCSN-Cl** and **CRA-CzCSN** in THF.

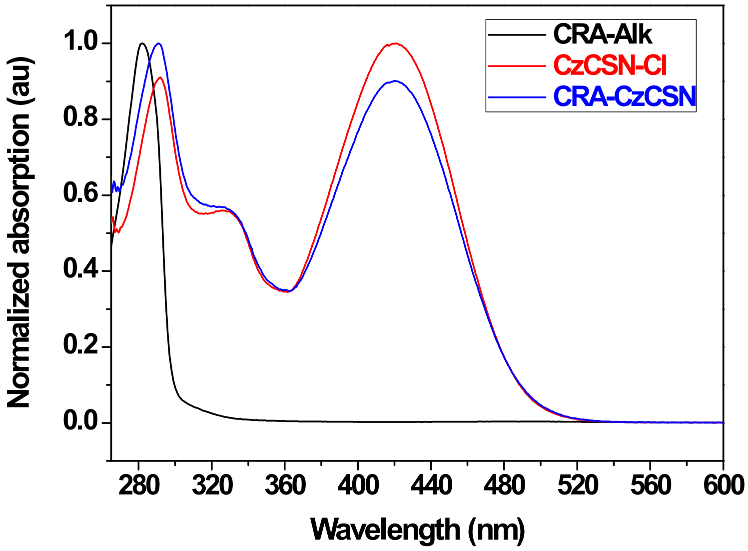


**Fig. S31** UV-Vis spectra of **CRA-Alk**, **CzCSN-Cl** and **CRA-CzCSN** in DMF.

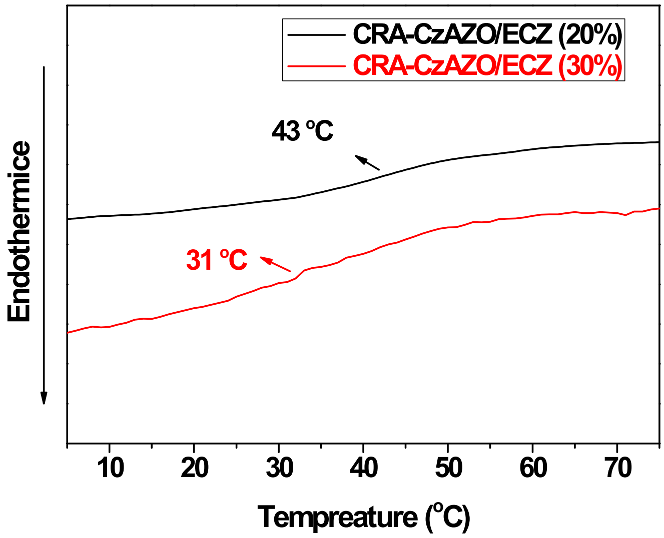


**Fig. S32** DSC thermogram of the composites of **CRA-CzAZO/ECZ**(20%) and **CRA-CzAZO/ECZ**(30%).

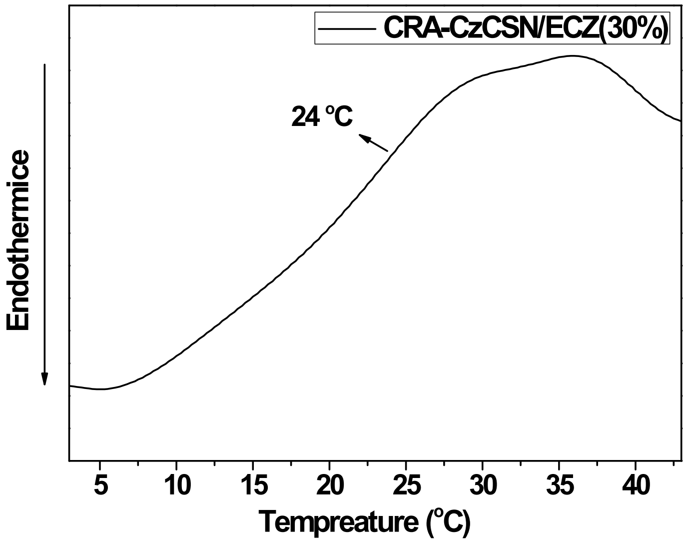


**Fig. S33** DSC thermogram of the composites of **CRA-CzCNS/ECZ**(30%).

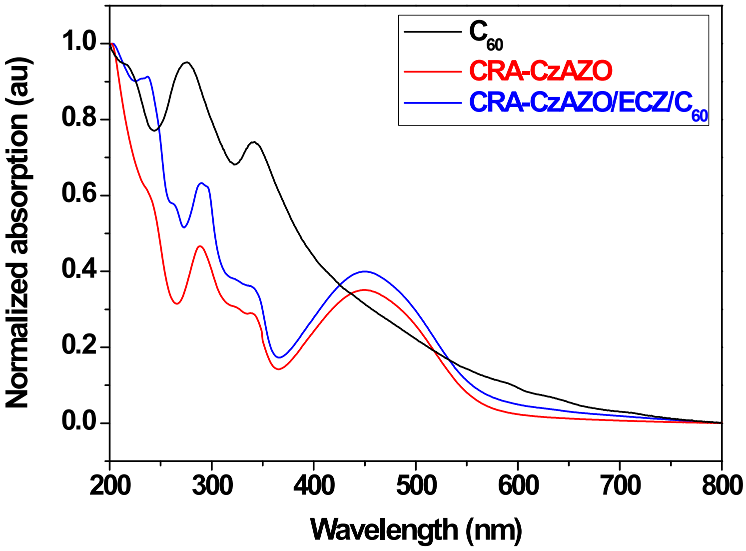


**Fig. S34** UV-Vis spectra of the film of **$C_{60}$**, **CRA-CzAZO** and **CRA-CzAZO/ECZ/$C_{60}$**.

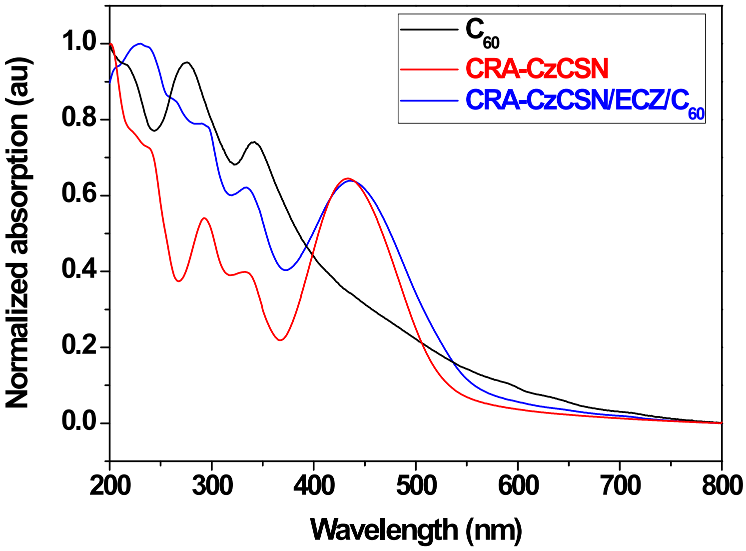


**Fig. S35** UV-Vis spectra of the film of **$C_{60}$**, **CRA-CzCSN** and **CRA-CzCSN/ECZ/$C_{60}$**.

### Calculation of the coupling gain coefficients:

The PR effect of 80 μm-thick films of branched macromolecules were measured by two-beam-coupling (TBC) experiments employing an oblique geometry as shown in Fig. S34. Two coherent *p*-polarized He-Ne laser beams at a wavelength of 633 nm overlapped in the sample to produce an interference pattern. The normal of the sample surface was tilted at an angle $\phi_{ext} = 35^{o}$ (in air) with respect to the symmetric axis of the two incident beams, and the angle between the two writing beams $2\theta_{\mathrm{ext}} = 20^{\circ}$ (in air). In the TBC experiment, the initial power of two writing beams (beam 1 and beam 2) was measured to be 15 and 10 mW, respectively. The TBC coefficient $\Gamma$ could be estimated from the following expression:

$$\Gamma = \frac{\cos\phi_{in}}{d}\left(\ln\left(\gamma_0\beta\right) - \ln(\beta + 1 - \gamma_0)\right)$$

Where $d = 80$ μm is the thickness of the sample, $\phi_{\mathrm{in}}$ is the incident angle of the beam 1 inside the sample, $\beta$ is the initial intensity ratio of beams after the sample (in the absence of coupling), and $\gamma_0 = I/I_0$ is the beam coupling ratio where $I_0$ is the signal intensity without the pump beam, and $I$ is the signal intensity with the pump beam.

All the photorefractive measurements were employed on the unpoled samples under room temperature.

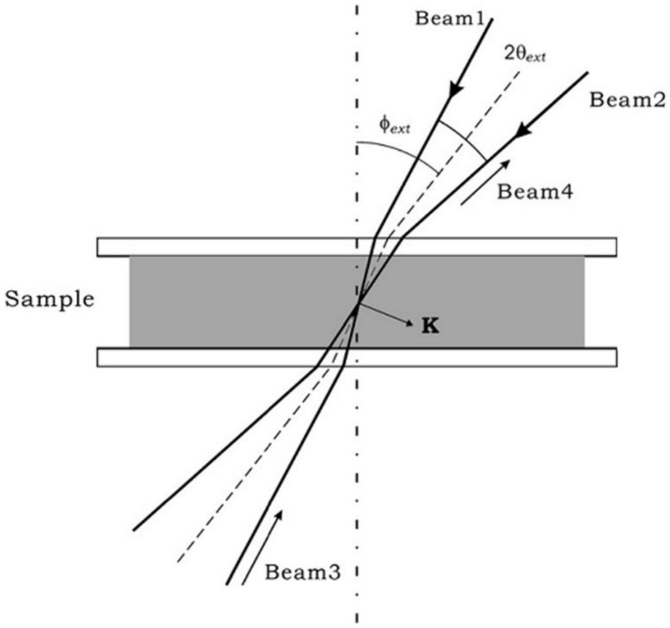


**Fig. S36** Experimental setup for two-beam coupling. Only beam 1 and beam 2 are present in two-beam coupling experiment, which are *p*-polarized He-Ne laser beams. Beam 3 is the *s*-polarized probe beam and beam 4 is the diffractive beam. $\phi_{\mathrm{ext}} = 35^{\circ}$ is the tilted angle of the symmetric axis of the two incident beams with respect to the sample normal, and $2\theta_{\mathrm{ext}} = 20^{\circ}$ is the external interbeam angle. **K** is the grating wave vector.