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*Electronic Supplementary Material (ESI) for*

## **Wavelength-Focused Organic Molecule Materials with Diazoacetate or Fumarate as Monofluorophore**

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## 1. Materials

(-)-Menthyl diazoacetate was prepared by the literature method.<sup>1</sup> PEG 1000 ( $M_n = 1000$ ) was purchased from Alfa-Aesar. PEG 3000 ( $M_n = 3000$ ) was purchased from Sigma-Aldrich. PEG 800 ( $M_n = 800$ ) was purchased from Aladdin. Polyvinyl alcohol (PVA, 98% hydrolyzed,  $M_w = 16000$ ) was purchased from Acros Organics. Allyl acrylate (AA, 98%) and Fumaryl Chloride (95%) were purchased from Tokyo Chemical Industry Co., Ltd. Acrylyl chloride (98%) and Ethyl diazoacetate (EDA, 90%) were purchased from Energy Chemical Industry Co., Ltd. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

## 2. Instrumentation

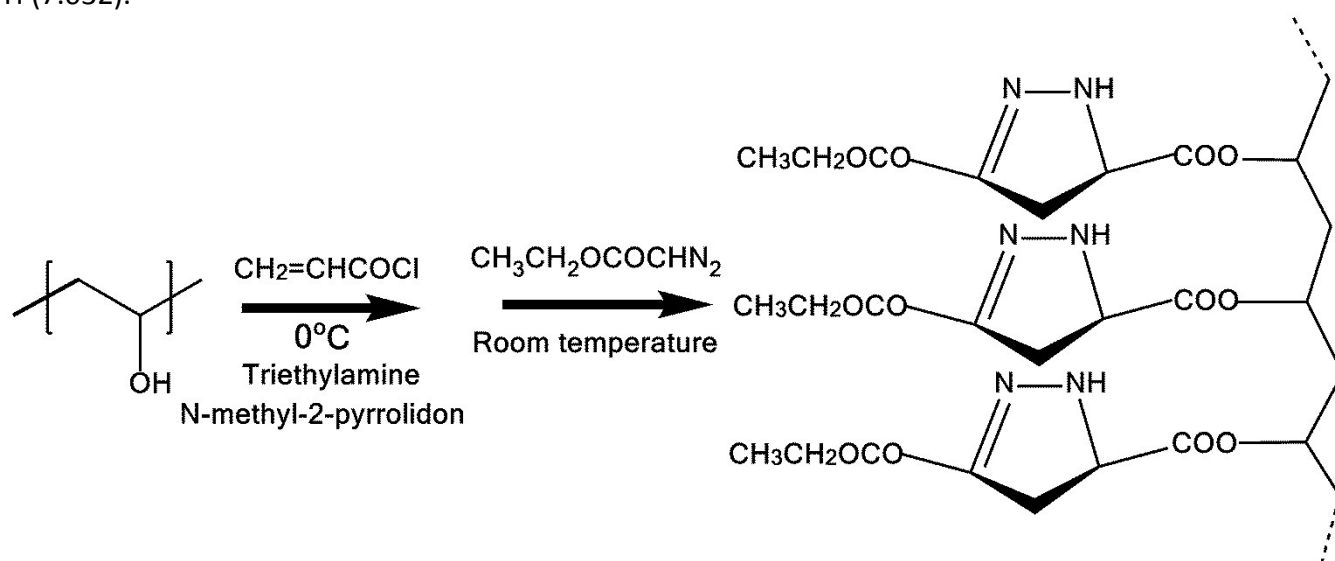
<sup>1</sup>H-NMR spectra were recorded using a Mercury VX-300 spectrometer (300 MHz) using CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as a solvent and TMS as the internal standard. The number-average molecular weight ( $M_n$ ) and polydispersity index (PDI,  $M_w/M_n$ ) of the CoPF samples were determined by gel permeation chromatography calibrated with polystyrene standards with DMF as eluent at 30 °C. Fourier transform infrared spectra were recorded using a Thermo iS10 spectrometer. Elemental analysis data were collected using a Vario EL instrument. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) spectra were obtained using a Bruker Biflex III mass spectrometer equipped with a 337 nm nitrogen laser. The melting point and glass transition temperature data were collected using a Q20 (TA Instruments) with nitrogen as the protecting gas (50 mL min<sup>-1</sup>). Fluorescence emission spectra were recorded on an RF-5301PC (Shimadzu) fluorescence spectrophotometer with a 150 W Xe lamp as the light source and the average intensity of incident light of 3.5-4.0 mW cm<sup>-2</sup>, measured by UVA light meter (Model UVA-365). The upconversion emission spectra were obtained using a 720 nm continuous-wave (CW) diode laser and recorded by a spectrometer (Spectrapro 2500i, Acton) with a liquid nitrogen cooled CCD (SPEC-10: 100B, Princeton). Broadband excitation spectra were excited by Laser-Driven Light Source EQ-99FC and recorded with Ideaoptics PG2000-EX fiber optic spectrometer (Ideaoptics Technology Ltd., China). Confocal fluorescence micrographs were recorded by confocal laser scanning microscopy (CLSM; Nikon C1-si, Japan, BD Laser) at 405 nm, 700 nm and 750 nm. The optical rotation was measured in ethanol, using a WZZ-3 automatic polarimeter.

## 3. Cell culture and cell imaging

Human cervix carcinoma (HeLa) cells and African green monkey kidney (Cos7) cells were purchased from China Center for Type Culture Collection and incubated in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% antibiotics with 5% CO<sub>2</sub> at 37 °C. Cells were seeded in a 6-well plate at a density of 3×10<sup>5</sup> cells per well and cultured in 1mL DMEM with 10% FBS for 24 h. Then, a solution of the 5R-CCMP (50 μg), CEP-g-PVA (50 μg) and EDA-CEC-AA (50 μg) dissolved in DMEM (1 ml) with the addition of 10% FBS, 1% antibiotics and 5% dimethyl sulfoxide was added and further incubated for another 4 h at 37 °C, respectively. The cells were washed with PBS (1 mL) upon removing the medium and confocal laser scanning microscopy (CLSM) was carried out at 405 nm, 700 nm and 750 nm.

## 4. Synthesis of CEP-g-PVA

In a three-necked flask (250 ml) fitted with a stirrer, a dropping funnel, and a thermometer was placed a solution of PVA (0.54 g) in N-methyl-2-pyrrolidon (100 ml). After this solution had been heated to 90 °C with stirring over 1 h, a solution of triethylamine, prepared from triethylamine (2.5 ml, 0.018 mol) and N-methyl-2-pyrrolidon (10 ml), was added with stirring at 25 °C for 1 h. After the addition was completed, the mixture was stirred in an ice bath for an additional 30 minutes, a solution of acryloyl chloride, prepared from acryloyl chloride (1 ml, 0.012 mol) and N-methyl-2-pyrrolidon (10 ml), was added dropwise with stirring at such a rate that the reaction mixture remains within the temperature range 0-5 °C (about 30 minutes was required for the addition). After the addition was completed, the mixture was added with EDA (1 ml, 0.01 mol) and stirred over 16 h. Then, the mixture was dialyzed with de-ionized water and freeze-dried, the yellow product was CEP-g-PVA with 12.12% grafting ratio.  $T_g$  (glass transition temperature) = 79.11 °C;  $^1\text{H-NMR}$  (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 8.47-8.58 (m, 1H), 5.02-5.18 (m, 1H), 4.72-4.79 (m, 1H), 4.10-4.25 (m, 2H), 3.21-3.28 (m, 2H), 1.46-1.69 (m, 2H), 1.25-1.34 (m, 3H); IR (KBr):  $\nu$  = 3388 (m, NH), 1718 (s, C=O), 1583 (m, C=N); Elemental analysis: N (5.119), C (50.82), H (7.032).



**Figure S1.** The synthesis process of CEP-g-PVA

### 5. Synthesis of 2-pyrazolines<sup>2</sup>

Typical preparation: EDA (0.114 g, 0.001 mol) was added to acrylonitrile (0.064 g, 0.0012 mol) at ambient temperature and the mixture was stirred for 16 hours. The crude product was purified by silica gel chromatography (petroleum ether /ethyl acetate was 3:1). The obtained product was CCEP (68.5mg, 41.01%).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.82 (s, 1H), 4.75 (t, 1H), 4.41 (q, 2H), 3.42 (d, 2H), 1.41 (t, 3H); IR (KBr),  $\nu$  = 3351 (m, NH), 2282 (w, C $\equiv$ N), 1724 (s, C=O); 1671 (m, C=N).

DCEP and TCEP were synthesized following the same process.

### 6. Synthesis of CoPF<sup>3</sup>

PEG 1000 (10 g, 0.01 mol, 8 g for PEG 800 and 30 g for PEG 3000) was dried by azeotropic distillation as follows. After dissolving PEG in toluene (250 mL), toluene (150 mL) was distilled off, and the remaining toluene was further removed under reduced pressure. The dried PEG 1000 was dissolved in anhydrous methylene chloride (250 mL). Fumaryl chloride (0.94 ml, 0.009 mol) and triethylamine (2.77 ml, 0.02 mol) were simultaneously added to the PEG solution in an ice bath over 5 h while the reaction mixture was vigorously stirred. For the oligomerization of PEG 3000, anhydrous methylene chloride (500 mL) was used. After dropwise addition of fumaryl chloride and triethylamine into the PEG solution, the reaction was run overnight at room temperature. Upon completion of the reaction, the solvent was removed by a rotary evaporator, and the residue was dialyzed with de-ionized water and freeze-dried

to obtain the product as a yellow liquid (0.47).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.95-6.83 (m, 2H), 4.48-4.03 (m, 2H), 3.75-3.47 (m, 4H), 2.75-2.64 (m, 1H); IR (KBr),  $\nu = 3004$  (m, =CH), 1721 (s, C=O), 1640 (m, C=C); 1100 (s, -C-O-C-); CoP<sub>800</sub>F:  $M_n$  (g/mol) = 3900,  $M_w$  (g/mol) = 19200, PDI = 4.96; CoP<sub>1000</sub>F:  $M_n$  (g/mol) = 2700,  $M_w$  (g/mol) = 9800, PDI = 3.69; CoP<sub>3000</sub>F:  $M_n$  (g/mol) = 5100,  $M_w$  (g/mol) = 15200, PDI = 2.97 (Detected by GPC).

## 7. Synthesis of 5R-CCMP

(-)-Menthyl diazoacetate (0.12 g, 0.0005 mol) was added to acrylonitrile (0.04 ml, 0.0006 mol) at ambient temperature and the mixture was stirred for 16 hours. The crude product was purified by silica gel chromatography (petroleum ether /ethyl acetate was 3:1) and then recrystallized from ethanol, by which the transparent rhabdolithes (59.6mg, 43.03%) were obtained. mp 36 °C;  $[\alpha]_D^{20} = -87$   $\text{cm}^3 \text{g}^{-1} \text{dm}^{-1}$  ( $c = 0.1$  in ethanol);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.80 (s, 1H), 4.73 (t, 1H), 4.51-4.45 (m, 1H), 3.22 (d, 2H), 2.18 (d, 1H), 1.96 (t, 1H), 1.73 (t, 1H), 1.62-1.53 (t, 1H), 1.25-1.10 (t, 1H), 0.96 (t, 1H), 0.85 (t, 1H);  $^{13}\text{C-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 186.78, 163.89, 134.74, 132.62, 129.90, 128.88, 76.98, 46.87, 40.67, 34.08, 31.55, 26.20, 23.40, 21.94, 20.65; IR (KBr),  $\nu = 3359$  (m, NH), 2223 (w,  $\text{C}\equiv\text{N}$ ), 1730 (s, C=O), 1667 (m, C=N). CCDC 1444757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/getstructures](http://www.ccdc.cam.ac.uk/getstructures)

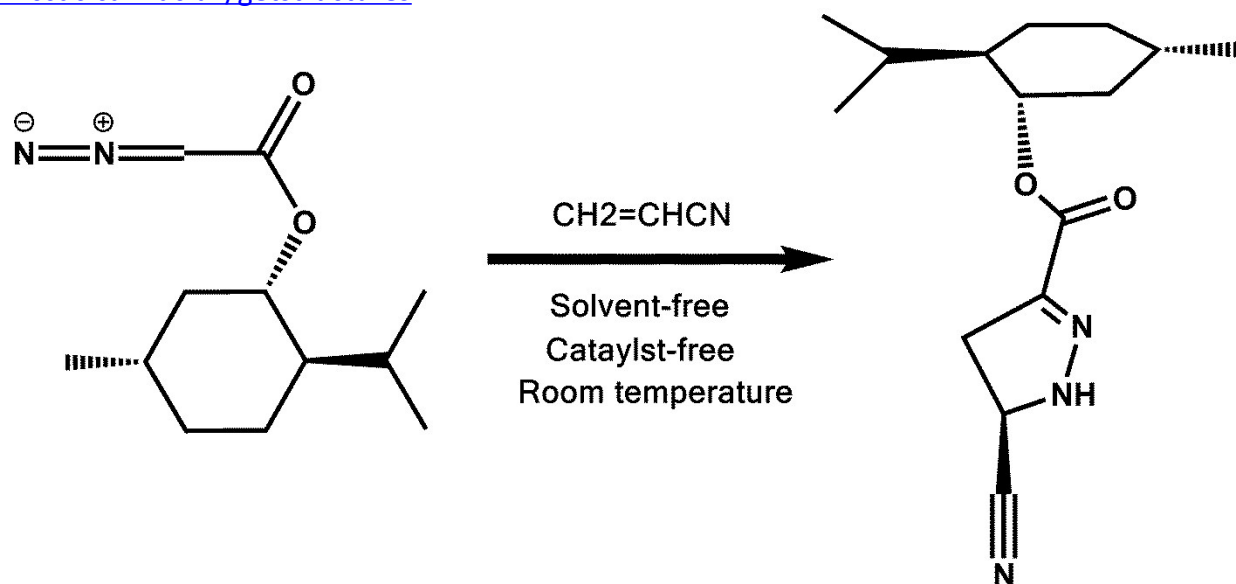
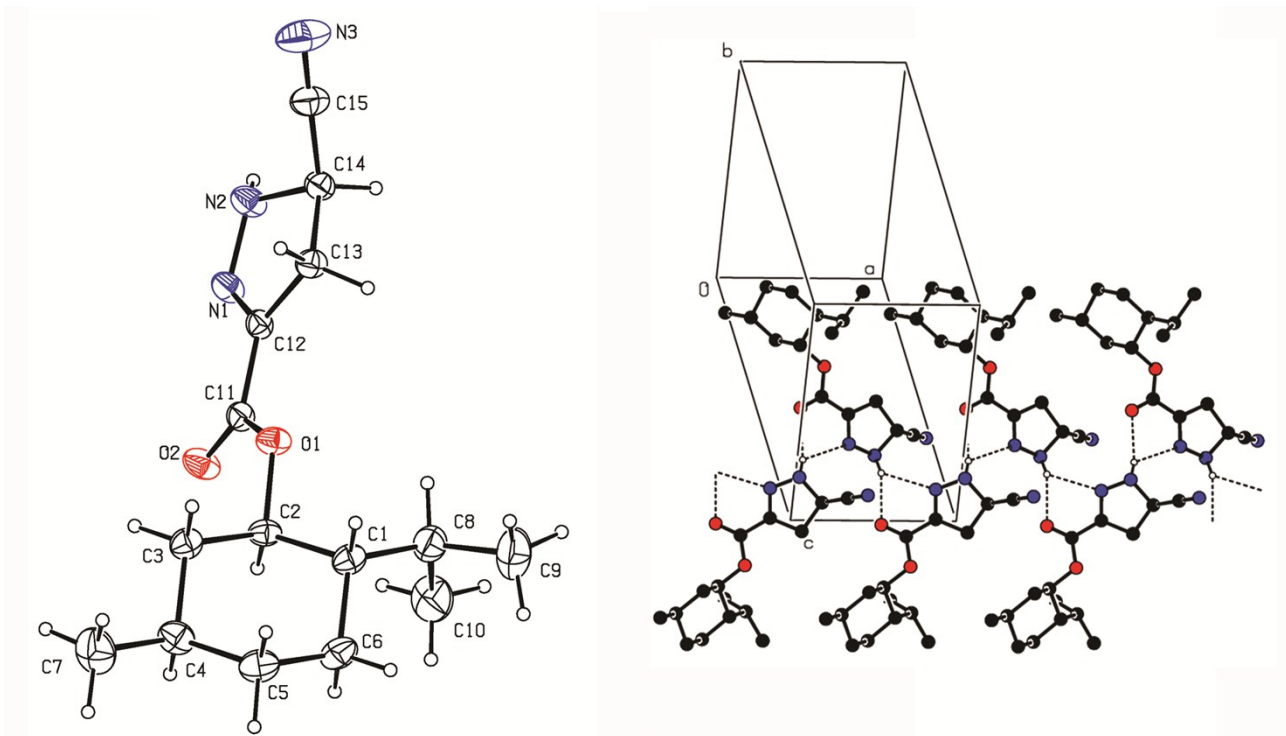


Figure S2. The synthesis process of the 5R-CCMP.



**Figure S3.** The crystal structure of 5R-CCMP and a stereoview of part of the packing of 5R-CCMP, showing the double-chains of 5R-CCMP. Hydrogen bonds were shown as dashed lines.

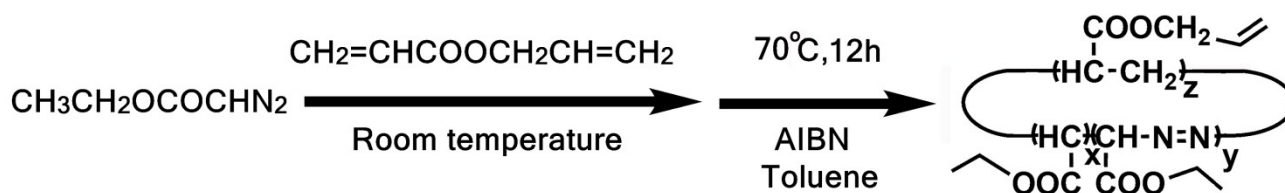
**Table S1.** Crystal data and structure refinement for 5R-CCMP.

Empirical formula	C <sub>15</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub>	
Formula weight	277.36	
Temperature	297(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.2202(2) Å	a = 90°.
	b = 10.6578(3) Å	b = 90°.
	c = 20.9068(5) Å	g = 90°.
Volume	1608.81(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.145 Mg/m <sup>3</sup>	

Absorption coefficient	0.619 mm <sup>-1</sup>
F (000)	600
Crystal size	0.20 x 0.20 x 0.20 mm <sup>3</sup>
Theta range for data collection	4.23 to 63.44°.
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24
Reflections collected	37839
Independent reflections	2620 [R (int) = 0.0383]
Completeness to theta = 63.44°	99.7%
Absorption correction	Multi-scan (SABABS; Bruker, 2001)
Max. and min. transmission	0.8862 and 0.8862
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2620 / 1 / 188
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indices [I > 2σ(I)]	R1 = 0.0276, wR2 = 0.0750
R indices (all data)	R1 = 0.0335, wR2 = 0.0753
Absolute structure parameter	0.0 (2)
Extinction coefficient	0.0068 (6)
Largest diff. peak and hole	0.202 and -0.205 e.Å <sup>-3</sup>

### 8. Synthesis of EDA-CEC-AA

In a three-necked flask (250 ml) fitted with a stirrer, a dropping funnel, and a thermometer were placed EDA (1.5 ml, 0.014 mol), AA (1.6 ml, 0.013 mol) and toluene (25 ml) under dry argon atmosphere with stirring over 16 h at room temperature. Then, the temperature of the mixture was adjusted to 70 °C, and 2, 2'-Azobis (2-methylpropionitrile) (16.4 mg, 0.0001 mol) was added with stirring over 12 h (CEC was formed via the nitrogen releasing of EDA), most of the solvent was removed at 70 °C with a rotary evaporator. Subsequently, the crude product was purified by silica gel chromatography to obtain the product as a yellow liquid (82.3mg). TCL (petroleum ether : ethyl acetate, 9:1 v/v): R<sub>f</sub> = 0.90; T<sub>g</sub> = -11.27 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 5.99-5.83 (m, 1H), 5.40-5.23 (m, 2H), 4.80-4.55 (m, 2H), 4.41-4.10 (m, 2H), 3.32-3.15 (m, 1H), 1.99-1.61 (m, 2H), 1.40-1.18 (m, 3H); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>, δ): 161.01, 139.87, 131.34, 119.09, 109.26, 77.01, 65.95, 61.56, 13.90; IR (KBr), ν = 3004 (m, =CH), 1728 (s, C=O), 1659 (m, C=C), 1633 (m, N=N).



**Figure S4.** The synthesis process of EDA-CEC-AA.

### 9. Analysis of MALDI-TOF-MS spectrum of EDA-CEC-AA

MALDI-TOF-MS spectrum of EDA-CEC-AA with  $m/z$  from 300 to 700 was shown in Figure. S2. Regular  $m/z$  86,  $m/z$  112 and  $m/z$  114 spaced repeating patterns were observed, which indicate the repeating units in the polymer chain were  $-\text{CH}(\text{COOEt})-$  ( $m/z=86$ ),  $-\text{CH}_2-\text{CH}(\text{COOCH}_2\text{CH}=\text{CH}_2)-$  ( $m/z=112$ ) and  $-\text{N}=\text{N}-\text{CH}(\text{COOEt})-$  ( $m/z=114$ ). The main  $m/z$  peaks of EDA-CEC-AA in the range of 320 to 630 can be sorted as series  $\text{Na}^+ + \text{EDA-CEC-AA}$  and series  $\text{K}^+ + \text{EDA-CEC-AA}$  and series  $\text{H}^+ + \text{EDA-CEC-AA}$  match quite well with the three mass formulae below:

For series  $\text{Na}^+ + \text{EDA-CEC-AA}$ :

$$m/z = 23 + 114x + 86y + 112z$$

$$m/z = 333, x = 0, y = 1, z = 2$$

$$m/z = 359, x = 0, y = 0, z = 3$$

$$m/z = 393, x = 0, y = 3, z = 1$$

$$m/z = 419, x = 0, y = 2, z = 2$$

$$m/z = 447, x = 1, y = 1, z = 2$$

$$m/z = 475, x = 2, y = 0, z = 2$$

$$m/z = 531, x = 0, y = 2, z = 3$$

$$m/z = 559, x = 1, y = 1, z = 3$$

$$m/z = 587, x = 2, y = 0, z = 3$$

For series  $\text{K}^+ + \text{EDA-CEC-AA}$ :

$$m/z = 39 + 114x + 86y + 112z$$

$$m/z = 349, x = 0, y = 1, z = 2$$

$$m/z = 375, x = 0, y = 0, z = 3$$

$$m/z = 409, x = 0, y = 3, z = 1$$

$$m/z = 603, x = 2, y = 0, z = 3$$

For series  $\text{H}^+ + \text{EDA-CEC-AA}$ :

$$m/z = 1 + 114x + 86y + 112z$$

$$m/z = 431, x = 0, y = 5, z = 0$$

$$m/z = 459, x = 1, y = 4, z = 0$$

$$m/z = 485, x = 1, y = 3, z = 1$$

$$m/z = 515, x = 3, y = 2, z = 0$$

$$m/z = 543, x = 4, y = 1, z = 0$$

$$m/z = 573, x = 2, y = 4, z = 0$$

$$m/z = 629, x = 4, y = 2, z = 0$$

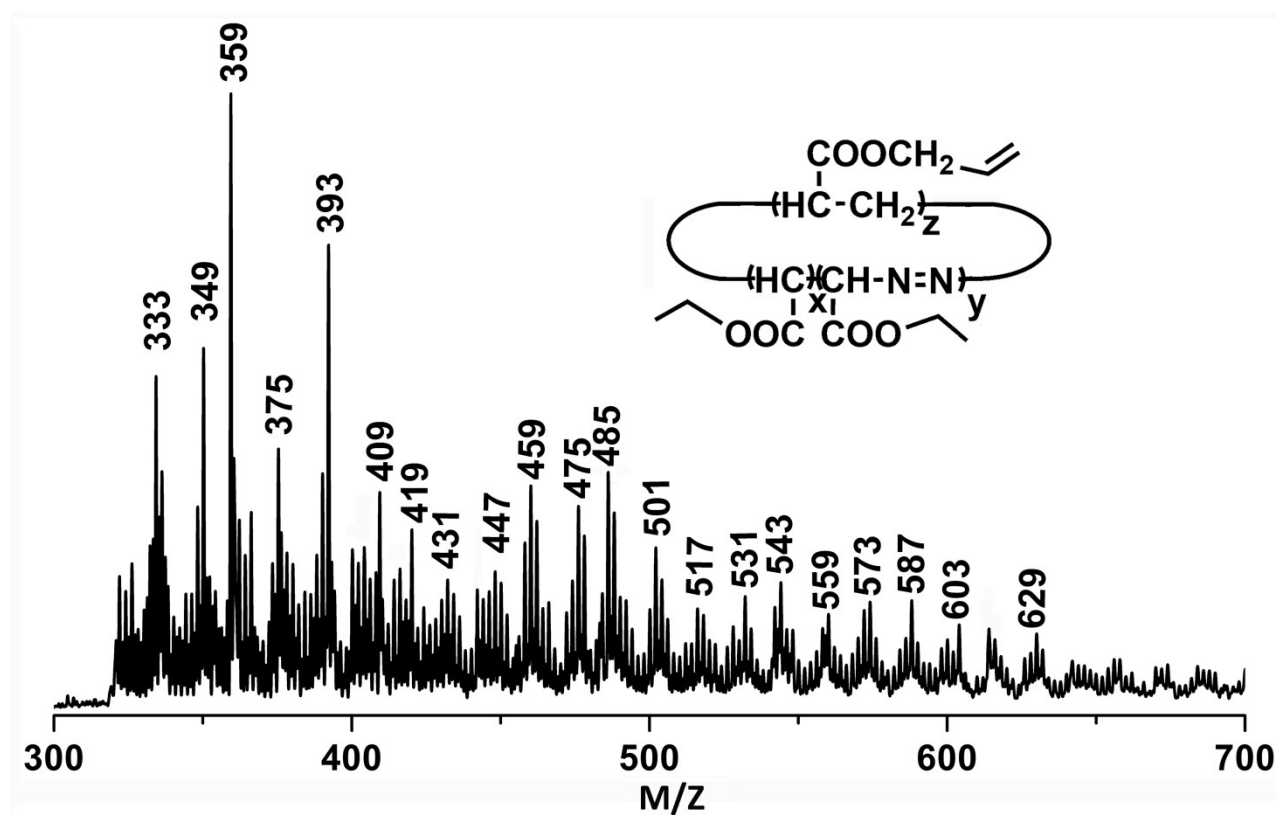


Figure S5. MALDI-TOF-MS spectrum of EDA-CEC-AA with m/z from 300 to 700.

## 10. References

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