Electronic Supplementary Material (ESI) for Polymer Chemistry.

One-Pot Catalyst-Free Synthesis of Down- and Upconversion Fluorescent Oligopyrazolines from Diazoacetates and Maleic Anhydride

Xiangxiang Jia, Yan Li, Jinlong Wu, Cheng Chen, Lijian Liu*
Key Laboratory of Biomedical Polymers, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, China.
Correspondence to: Lijian Liu (E-mail: liulj@whu.edu.cn)

Supporting Information

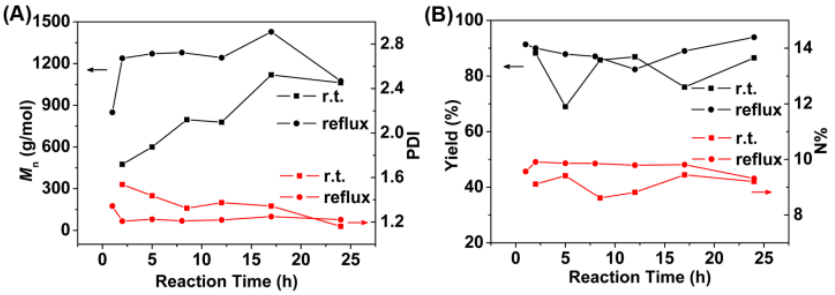

Figure S1. The polymerization of MA and EDA at different reaction time in $CHCl_3$. (A) black: M_n; red: PDI. (B) black: yield; red: N%.

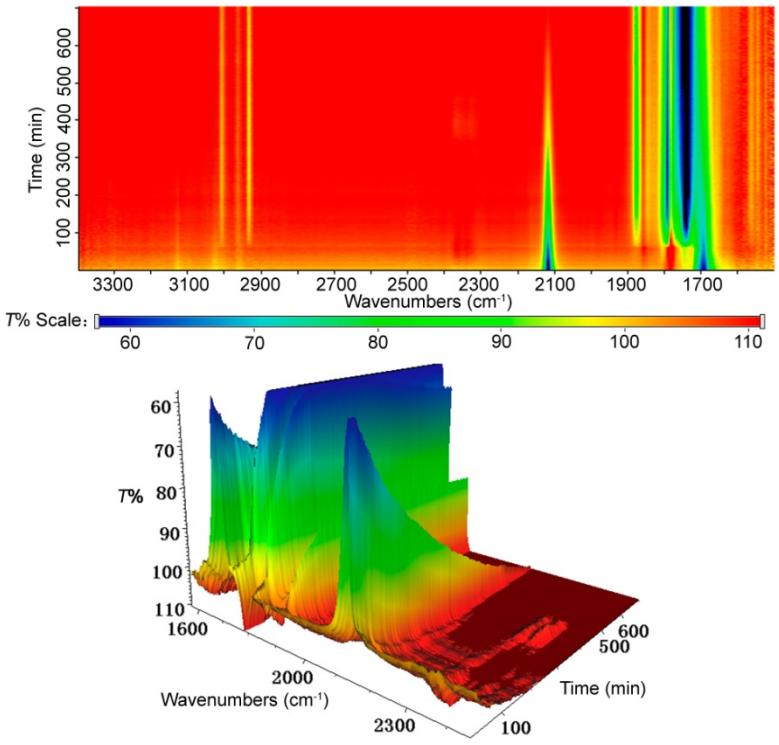

Figure S2. The on-line FT-IR spectra of MA polymerized with MDA.

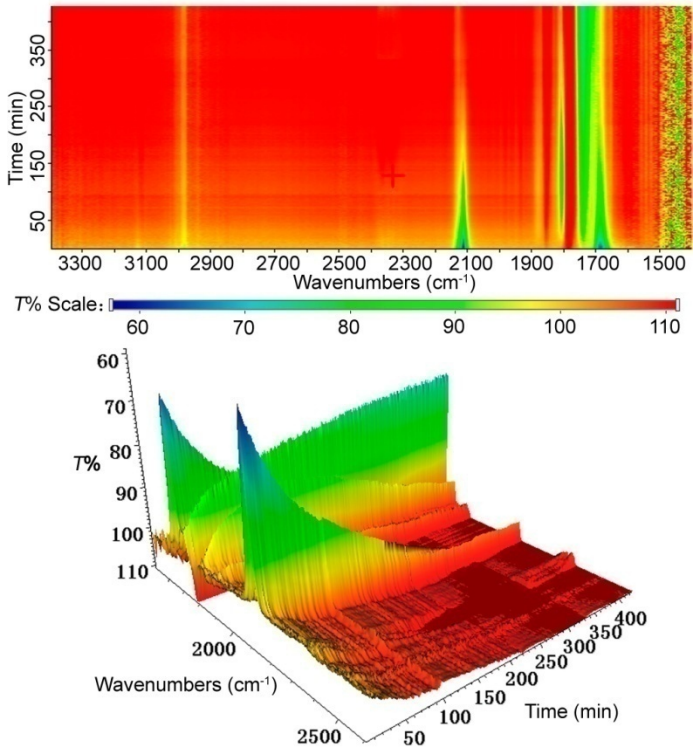

Figure S3. The on-line FT-IR spectra of MA polymerized with *t*-BDA.

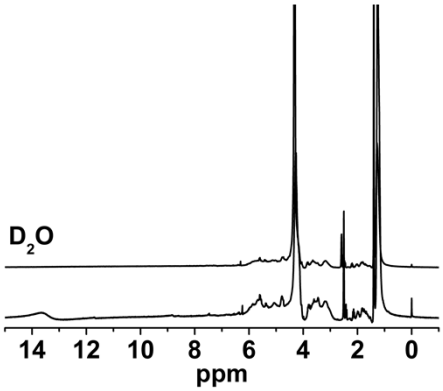

Figure S4. The ^{1}H NMR spectra of the oligomer of [**1a**]:[**2a**]=1:1 with the addition of deuteroxide.

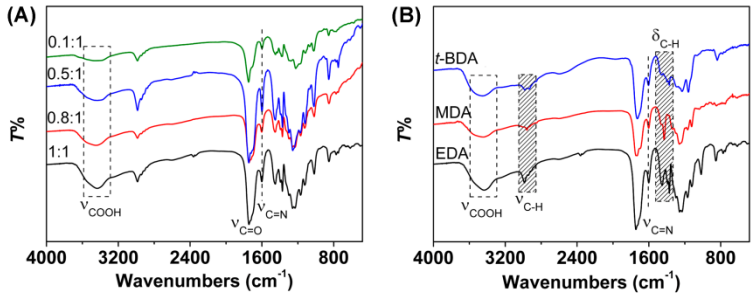

Figure S5. The FT-IR spectra of the oligomers. (A) The oligomers with different feed ratios of [**1a**]:[**2a**]; (B) The oligomers derived from MA and **2a-c** with the feed ratio of [**1a**]:[**2**]=1:1.

Here, in Figure S5A, the ratio of absorption at 3434 cm^{-1} to that at 1744 cm^{-1}, defined as A_{3434}/A_{1744} (A_{3434}: the peak area of 3708-3283 cm^{-1}; A_{1744}: the peak area of 1631-1869 cm^{-1}), could be used to express the change of COOH group in the oligomer with different feed ratios in some way. The values of A_{3434}/A_{1744} for the reactions with the ratio of 1-0.1 are 0.66, 0.72, 0.35 and 0.33, respectively.

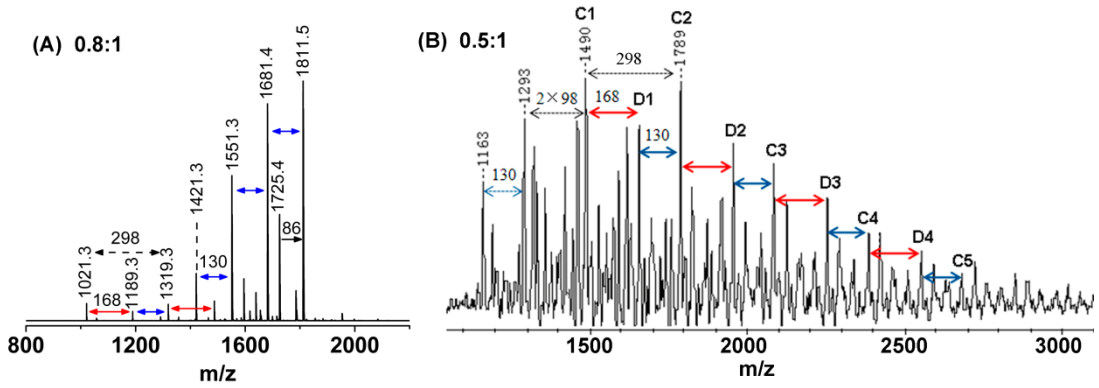

Figure S6. The MALDI-TOF-MS spectra of oligomers with [**1a**]:[**2a**]=0.8:1 (A) and 0.5:1 (B).

The spectrum analysis for Figure S6A is shown as follows:

298+168×6+114+1 {[-**U1**-(**U2**)$_6$-**U5**-]H^+} for *m/z*=1421.3;

298×2+168×5+114+1 {[-(**U1**)$_2$-(**U2**)$_5$-**U5**-]H^+} for *m/z*=1551.3;

298×3+168×4+114+1 {[-(**U1**)$_3$-(**U2**)$_4$-**U5**-]H^+} for *m/z*=1681.4;

298×4+168×3+114+1 {[-(**U1**)$_4$-(**U2**)$_3$-**U5**-]H^+} for *m/z*=1811.5.

The spectrum analysis for Figure S6B is shown as follows:

series C1-C5 are made up of **U1**+H^+, *m/z*=298*n*+1, *n*=5-9;

series D1-D4 are made up of **U1**+**U2**+H^+, *m/z*=298*n*+168+1, *n*=5-8.

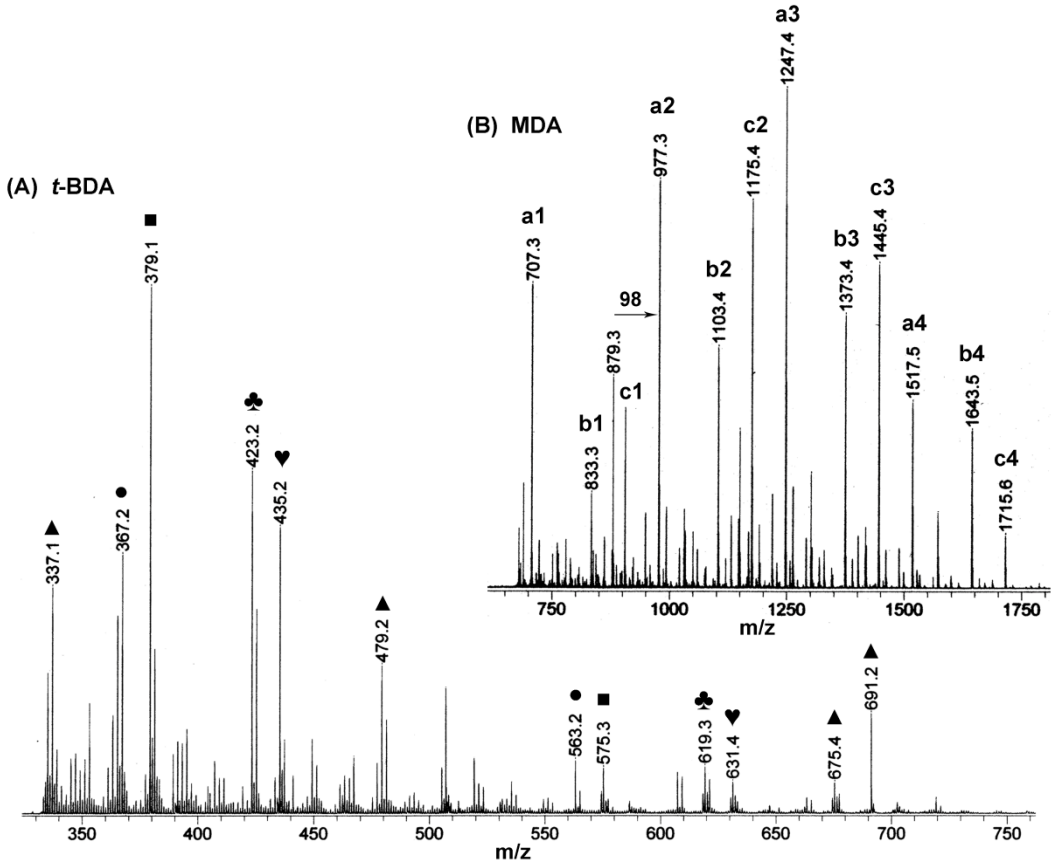

Figure S7. The MALDI-TOF-MS spectra of oligomers derived from *t*-BDA (A) and MDA (B).

For monomer *t*-BDA, $M_{\mathbf{U1}}$=354, $M_{\mathbf{U2}}$=196, $M_{\mathbf{U4}}$=114, $M_{\mathbf{U5}}$=142. Here *M* represents molecular weight. As shown in Figure S7A, series 337.1+142 (for *m/z*=479.2), 337.1+142+196 (for *m/z*=675.4) and 337.1+354 (for *m/z*=691.2) are recorded, marked as ▲. Other series (marked as ●, ■, ♣, and ♥) all possess an *m/z* difference of 196 (**U2**). The formula for *m/z*=379.1 is 354+2+23 (*i.e.* [H-**U1**-H]Na^+).

For monomer MDA, $M_{\mathbf{U1}}$=270, $M_{\mathbf{U2}}$=154, $M_{\mathbf{U4}}$=72, $M_{\mathbf{U5}}$=100. Here *M* represents molecular weight. The formulae for the calculation of measured *m/z* are expressed as follows:

series a1-a4 are made up of **U1**+**U4**+Na^+, *m/z*=270*n*+72×2+23, *n*=2-5;

series b1-b4 are made up of **U1**+Na^+, *m/z*=270*n*+23, *n*=3-6;

series c1-c4 are made up of **U1**+**U4**+Na^+, *m/z*=270*n*+72+23, *n*=3-6.

Here, 23 is the *m/z* value of Na^+. The differential value between series b and c is 72 (**U4**). Another deviation between 879.3 and 977.3 is 98, in agreement with the unit **U3**.

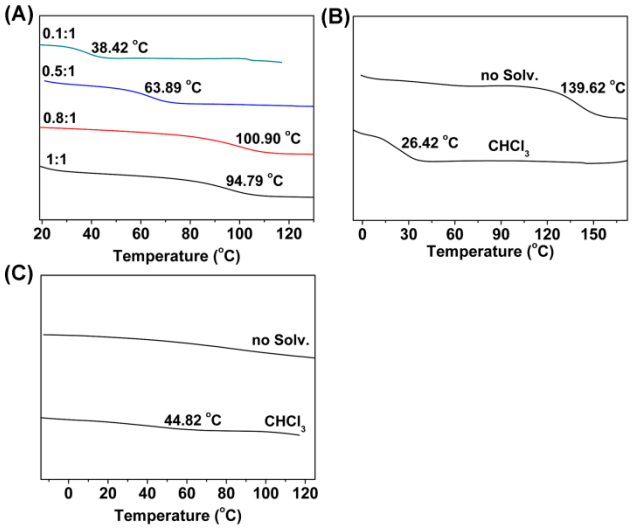

Figure S8. The DSC curves of the obtained oligomers. (A) Oligomers from MA and EDA without any solvent with feed ratio of 1-0.1; (B) Oligomers from MA and MDA at two different conditions: in $CHCl_3$ at room temperature and without the addition of solvents; (C) Oligomers from MA and *t*-BDA at two different conditions: in $CHCl_3$ at room temperature and without the addition of solvents.

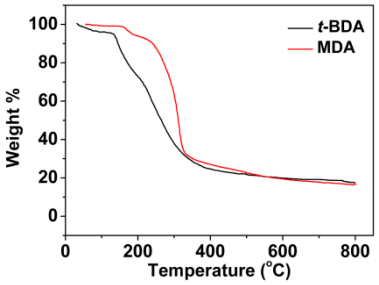

Figure S9. The TG curves of the oligomers obtained from MDA and *t*-BDA without solvents.

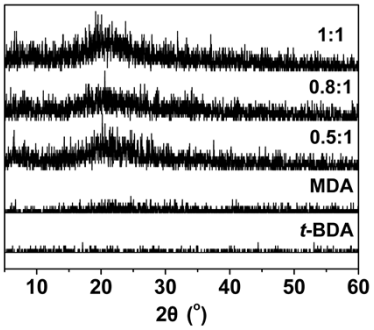

Figure S10. The XRD patterns of the oligomers.

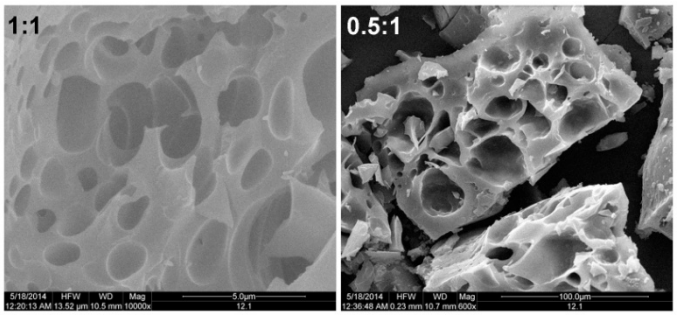

Figure S11. The SEM images of the oligomers with feed ratio of [**1a**]:[**2a**]=1:1 and 0.5:1.

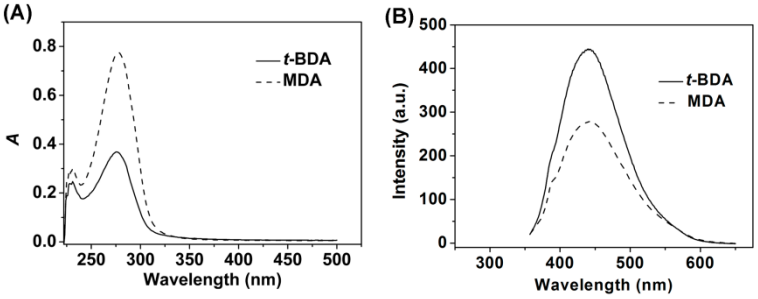

Figure S12. UV-Vis (A) and fluorescent spectra (B) of oligomers from MDA and *t*-BDA.

Table S1. The quantum yield (QY) of the oligomers.

Oligomer	[**1a**]:[**2a**]=1:1	[**1a**]:[**2a**]=0.8:1	[**1a**]:[**2a**]=0.5:1	[**1a**]:[**2a**]=0.1:1	[**1a**]:[**2b**]=1:1	[**1a**]:[**2c**]=1:1
QY (%)	19	15	14	12	12	17

The QY is measured with quinine sulfate as the standard (0.1 M H_2SO_4 at 22 °C, QY=58% with excitation at 350 nm), using the following formula:

$$Q = Q_R \frac{I\ OD_R n^2}{I_R\ OD\ n_R^2}$$

where Q, I, OD and n are the quantum yield, the integrated fluorescence intensity, the optical density and the refractive index, respectively. The subscript R represents the standard fluorophore.

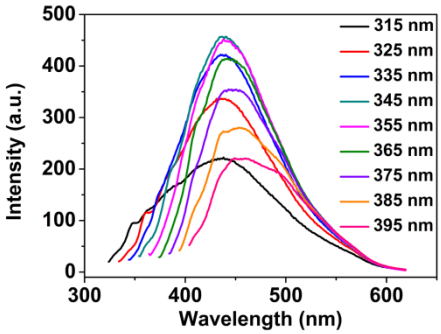

Figure S13. Fluorescent spectra of the oligomer from EDA with the ratio of 1:1 at different excitation wavelengths.

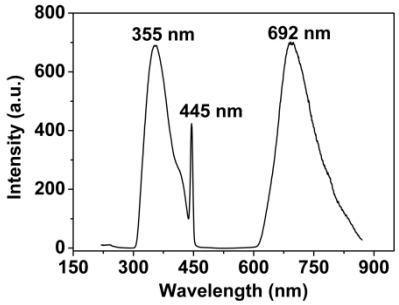

Figure S14. The excitation spectrum with the emission at 445 nm.

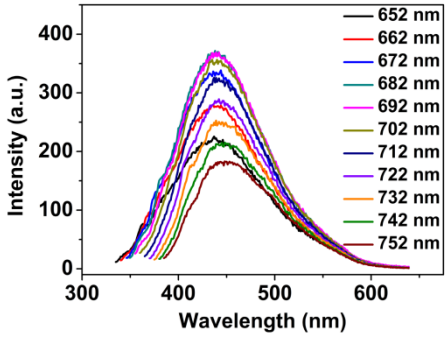

Figure S15. Upconversion fluorescent spectra of the oligomer from EDA with the ratio of 1:1 at different excitation wavelengths.

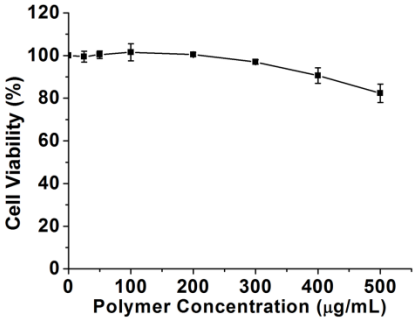

Figure S16. Cytotoxicity of the oligomer from EDA with the ratio of 1:1 in Hela cells.

Cytotoxicity Assay. Hela cells in the medium of DMEM containing 10% FBS (1 mL) were seeded directly in a 24-well plate (5×10^4 cells per well) and then incubated at 37 ^oC for 24 h. After the cells were incubated at 37 ^oC for another 24 h with the addition of the sample to be detected, 1 mL of DMEM containing 10% FBS and MTT (60 μL, 5 mg/mL) were added into each well with the following incubation at 37 ^oC for 4 h. After that, the supernatant was removed and DMSO (850 μL) was added in. The absorbance of the solution at 570 nm was measured with a microplate reader (Bio-Rad 550) to obtain the OD value. The relative cell viability was calculated as followed:

Relative cell viability = $(OD_{(sample)}/OD_{(control)}) \times 100\%$

where $OD_{(sample)}$ was obtained from the cells in the presence of the oligomer and $OD_{(control)}$ was obtained from the cells without the addition of oligomer. The data was given as mean ± standard deviation (SD) based on triplicate independent experiments.