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

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Supporting Information

Figure S1. The polymerization of MA and EDA at different reaction time in CHCl₃. (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 deuter oxide.
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:

- \(298+168\times6+114+1\) \([-\text{U1}-(\text{U2})_6\text{-U5}]+\) for \(m/z=1421.3\);
- \(298\times2+168\times5+114+1\) \([-\text{U1}-(\text{U2})_5\text{-U5}]+\) for \(m/z=1551.3\);
- \(298\times3+168\times4+114+1\) \([-\text{U1}-(\text{U2})_4\text{-U5}]+\) for \(m/z=1681.4\);
- \(298\times4+168\times3+114+1\) \([-\text{U1}-(\text{U2})_3\text{-U5}]+\) for \(m/z=1811.5\).

The spectrum analysis for Figure S6B is shown as follows:

- series C1-C5 are made up of \(\text{U1}+\text{H}^+\), \(m/z=298n+1, n=5-9\);
- series D1-D4 are made up of \(\text{U1}+\text{U2}+\text{H}^+\), \(m/z=298n+168+1, n=5-8\).
Figure S7. The MALDI-TOF-MS spectra of oligomers derived from t-BDA (A) and MDA (B).

For monomer t-BDA, $M_{U1}=354$, $M_{U2}=196$, $M_{U4}=114$, $M_{U5}=142$. 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, $M_{U1}=270$, $M_{U2}=154$, $M_{U4}=72$, $M_{U5}=100$. 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 $U1+U4+Na^+$, $m/z=270n+72\times2+23$, $n=2-5$;
series b1-b4 are made up of $U1+Na^+$, $m/z=270n+23$, $n=3-6$;
series c1-c4 are made up of $U1+U4+Na^+$, $m/z=270n+72+23$, $n=3-6$.
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.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>[1a]:[2a]=1:1</th>
<th>[1a]:[2a]=0.8:1</th>
<th>[1a]:[2a]=0.5:1</th>
<th>[1a]:[2a]=0.1:1</th>
<th>[1a]:[2b]=1:1</th>
<th>[1a]:[2c]=1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>QY (%)</td>
<td>19</td>
<td>15</td>
<td>14</td>
<td>12</td>
<td>12</td>
<td>17</td>
</tr>
</tbody>
</table>

The QY is measured with quinine sulfate as the standard (0.1 M H$_2$SO$_4$ at 22 °C, QY=58% with excitation at 350 nm), using the following formula:

$$Q = \frac{I_{OD}n^2}{I_RODn_R^2}$$

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 (5×10⁴ cells per well) and then incubated at 37 °C for 24 h. After the cells were incubated at 37 °C 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 °C 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}) × 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.