Electronic Supplementary Information

BINOLs as visible light photocatalyst for metal-free atom transfer radical polymerization

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Reaction setup

The 6W purple LED reactor (Fig. S1) was purchased from Wuhan GEAO Chemical Technology Co. Ltd and were used as shown above (Fig. S1). The reaction vessel (Schlenk tube) was placed in the hole of the reactor, where the light intensity was measured to be ca. 25.5 mW/cm².
Synthesis and characterization of BINOL photocatalysts

Preparation of BINOL 2-6

\[
\begin{align*}
\text{BINOL 1: } & R = H \\
\text{BINOL 2: } & R = \text{Ph} \\
\text{BINOL 3: } & R = 4-t\text{-BuC}_6\text{H}_4 \\
\text{BINOL 4: } & R = 4\text{-MeOC}_6\text{H}_4 \\
\text{BINOL 5: } & R = 4\text{-CF}_3\text{C}_6\text{H}_4 \\
\text{BINOL 6: } & R = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3
\end{align*}
\]

Into a 150 mL dry round bottom flask containing a magnetic stirring bar was weighed the 3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (1.59 mmol, 1 eq.),\textsuperscript{1,2} Ba(OH)\textsubscript{2}·8H\textsubscript{2}O (5.59 mmol, 3.5 eq.) and Pd(PPh\textsubscript{3})\textsubscript{4} (0.16 mmol, 0.1 eq.) under argon. 1, 4-dioxane/ H\textsubscript{2}O (90 mL, 3:1) and aryl boric acid (5.59 mmol, 3.5 eq.) were added sequentially at room temperature. The reaction mixture was refluxed for 12 h at 100 °C. At the end of the reaction, the 1, 4-dioxane was removed, and the residue was extracted in CH\textsubscript{2}Cl\textsubscript{2} (3 × 100 mL), washed with saturated NaCl (75 mL) and dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}. The crude was purified by silica gel column chromatography to afford product. (75 - 92% yield)

On the bench-top, a 50 mL round bottom was charged with 3,3'-disubstituted -2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (3.0 mmol). The reagent was dissolved in dioxane (15 mL) and 6 M HCl (6.5 mL) were added successively. The mixture was heated at reflux for 12 h after which the resulting yellow solution was cooled to room temperature, concentrated in vacuo, and combined with water (30 mL). The resulting solution was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 mL) and the combined organics were dried over Na\textsubscript{2}SO\textsubscript{4}. The drying agent was removed via filtration and the solvents were removed in vacuo. The crude residue was purified by column chromatography on silica gel to give product as white needle crystals (75% - 90% yield).
BINOL 2: \(^2\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (s, 2H), 7.92 (d, \(J = 8.0\) Hz, 2H), 7.73 (d, \(J = 8.0\) Hz, 4H), 7.49 (t, \(J = 7.6\) Hz, 4H), 7.40 (dd, \(J = 14.4, 7.7\) Hz, 4H), 7.32 (dd, \(J = 8.0, 7.1\) Hz, 2H), 7.24 (dd, \(J = 6.1, 4.5\) Hz, 2H), 5.35 (s, 2H).

BINOL 3: \(^4\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (s, 2H), 7.90 (d, \(J = 7.9\) Hz, 2H), 7.67 (d, \(J = 7.4\) Hz, 4H), 7.51 (d, \(J = 7.5\) Hz, 4H), 7.37 (t, \(J = 7.2\) Hz, 2H), 7.29 (t, \(J = 7.4\) Hz, 2H), 7.22 (t, \(J = 6.7\) Hz, 2H), 5.38 (s, 2H), 1.38 (s, 18H).

BINOL 4: \(^2\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (s, 2H), 7.90 (d, \(J = 8.0\) Hz, 2H), 7.67 (d, \(J = 7.4\) Hz, 4H), 7.37 (t, \(J = 7.1\) Hz, 2H), 7.29 (t, \(J = 7.4\) Hz, 2H), 7.21 (d, \(J = 8.2\) Hz, 2H), 7.02 (d, \(J = 7.4\) Hz, 4H), 5.35 (s, 2H), 3.87 (s, 6H).

BINOL 5: \(^3\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 2H), 7.94 (d, \(J = 8.0\) Hz, 2H), 7.86 (d, \(J = 7.9\) Hz, 4H), 7.73 (d, \(J = 7.9\) Hz, 4H), 7.39 (dt, \(J = 15.1, 7.1\) Hz, 4H), 7.22 (d, \(J = 8.4\) Hz, 2H), 5.31 (s, 2H).

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.50 (s).

BINOL 6: \(^2\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.23 (s, 4H), 8.11 (s, 2H), 8.00 (d, \(J = 8.0\) Hz, 2H), 7.91 (s, 2H), 7.45 (dt, \(J = 15.1, 7.0\) Hz, 4H), 7.23 (d, \(J = 8.3\) Hz, 2H), 5.37 (s, 2H).

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.73 (s).
UV-Vis Spectra of BINOL 1-6
Fig. S2. UV-Vis Spectra of BINOL1-6 in DMA.
Fig. S3. Emission spectra of BINOL 1-6, BINOL 2-OMe and BINOL 5-OMe in DMA.
Fig. S4. Cyclic voltammograms (vs. Ag/AgCl) of BINOL 1-6 in DMA.
<table>
<thead>
<tr>
<th>catalyst</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>$\varepsilon_{\lambda_{\text{max}}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Ex (nm)</th>
<th>Em $\lambda_{\text{max}}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BINOL 1</td>
<td>340</td>
<td>8500</td>
<td>338</td>
<td>366</td>
</tr>
<tr>
<td>BINOL 2</td>
<td>345</td>
<td>9150</td>
<td>334</td>
<td>392</td>
</tr>
<tr>
<td>BINOL 3</td>
<td>346</td>
<td>9280</td>
<td>336</td>
<td>388</td>
</tr>
<tr>
<td>BINOL 4</td>
<td>346</td>
<td>9880</td>
<td>333</td>
<td>382</td>
</tr>
<tr>
<td>BINOL 5</td>
<td>348</td>
<td>7270 ($\varepsilon_{412\text{nm}}=480$)</td>
<td>347</td>
<td>482</td>
</tr>
<tr>
<td>BINOL 6</td>
<td>350</td>
<td>6820 ($\varepsilon_{415\text{nm}}=985$)</td>
<td>348</td>
<td>509</td>
</tr>
<tr>
<td>BINOL 2-OMe</td>
<td>/</td>
<td>/</td>
<td>309</td>
<td>372</td>
</tr>
<tr>
<td>BINOL 5-OMe</td>
<td>/</td>
<td>/</td>
<td>340</td>
<td>392</td>
</tr>
</tbody>
</table>

**Determination of excited state reduction potential**

Fig. S5. Cyclic voltammograms (vS. Ag/AgCl) of BINOL 5 in DMA.

Cyclic voltammetry was conducted using 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte in DMA at 25 °C with a Ag/AgCl reference electrode. It is known that naphthols are difficult to obtain a reversible CV due to the acidic proton,$^{5-6}$ the first peak value ($E^{\text{ox}} = +0.45$ V vs. SCE) was thus employed for the following estimation:
Fig. S6. Emission spectra of BINOL 5 in DMA.

Photoluminescence max was estimated to be 482 nm (see Fig. S4). Using photoluminescence maximum and $E_{\text{ox}}$, the excited state reduction potential was estimated for BINOL 5 ($E_{\text{red}} (\text{BINOL 5}^+/\text{BINOL 5}^\ast) = -2.12 \text{ V})$ according to the following equations:

$$E_{\text{red}} (\text{BINOL 5}^+/\text{BINOL 5}^\ast) = E_{\text{ox}} - E_{0,0}$$

where $E_{0,0} = \frac{hc}{\lambda_{\text{max}}} = 1240 \text{ nm} / \lambda_{\text{max}}$
MALDI-TOF-MS

$20 \times 100.14 + 326 + 23 = 2351.8$

$21 \times 100.14 + 243 + 23 = 2368.9$

$22 \times 100.14 + 164 + 23 = 2390.0$

$M_w$ of monomer$(100) \times n + M_w$ of PC(574) + Na (23)

$\ast M_w$ (polymer initiated by catalyst)

$2397$
Supplemental Polymerization Results

Table S1. Effect of solvents on the photoinduced metal-free ATRP of MMA

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Solvent</th>
<th>Conv.</th>
<th>$M_n^b$</th>
<th>$M_n^c$</th>
<th>$D^b$</th>
<th>$D^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EBP</td>
<td>Toluene</td>
<td>72.5%</td>
<td>12700</td>
<td>15200</td>
<td>1.49</td>
<td>1.47</td>
</tr>
<tr>
<td>2</td>
<td>EBP</td>
<td>DCM</td>
<td>56.8%</td>
<td>11500</td>
<td>13800</td>
<td>1.47</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>EBP</td>
<td>THF</td>
<td>92.3%</td>
<td>11300</td>
<td>13900</td>
<td>1.50</td>
<td>1.47</td>
</tr>
<tr>
<td>4</td>
<td>EBP</td>
<td>CH$_3$CN</td>
<td>68.9%</td>
<td>12800</td>
<td>15500</td>
<td>1.39</td>
<td>1.37</td>
</tr>
<tr>
<td>5</td>
<td>EBP</td>
<td>DMF</td>
<td>73.6%</td>
<td>8300</td>
<td>10300</td>
<td>1.22</td>
<td>1.22</td>
</tr>
</tbody>
</table>

$^a$ [MMA]$_0$/[initiator]$_0$/[BINOL 5]$_0$ = 1000/20/0.5.  $^b$ Determined by gel permeation chromatography using polystyrene standards.  $^c$ Determined by gel permeation chromatography using PMMA standards.

Table S2. Supplementary results to Table 1 of photoinduced metal-free ATRP of methyl methacrylate with using BINOL-type photocatalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>photocatalyst</th>
<th>Conv. $^b$</th>
<th>$M_n^c$</th>
<th>$D^c$</th>
<th>$M_n^d$</th>
<th>$D^d$</th>
<th>$I^*$(%) $^{d,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BINOL 1</td>
<td>57.0%</td>
<td>44.8</td>
<td>1.64</td>
<td>48.5</td>
<td>1.58</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>BINOL 2</td>
<td>70.2%</td>
<td>11.7</td>
<td>1.39</td>
<td>14.0</td>
<td>1.37</td>
<td>51.9</td>
</tr>
<tr>
<td>3</td>
<td>BINOL 3</td>
<td>75.8%</td>
<td>12.9</td>
<td>1.42</td>
<td>14.9</td>
<td>1.40</td>
<td>52.5</td>
</tr>
<tr>
<td>4</td>
<td>BINOL 4</td>
<td>72.5%</td>
<td>13.5</td>
<td>1.51</td>
<td>16.0</td>
<td>1.47</td>
<td>46.8</td>
</tr>
<tr>
<td>5</td>
<td>BINOL 5</td>
<td>78.6%</td>
<td>12.1</td>
<td>1.29</td>
<td>14.4</td>
<td>1.29</td>
<td>56.3</td>
</tr>
<tr>
<td>6</td>
<td>BINOL 6</td>
<td>69.7%</td>
<td>11.8</td>
<td>1.36</td>
<td>14.0</td>
<td>1.36</td>
<td>51.6</td>
</tr>
<tr>
<td>7</td>
<td>BINOL 2-OMe</td>
<td>55.9%</td>
<td>29.5</td>
<td>1.65</td>
<td>33.3</td>
<td>1.56</td>
<td>17.5</td>
</tr>
<tr>
<td>8</td>
<td>BINOL 5-OMe</td>
<td>64.2%</td>
<td>42.5</td>
<td>1.70</td>
<td>47.5</td>
<td>1.64</td>
<td>14.0</td>
</tr>
</tbody>
</table>
a Reaction conditions: [MMA]/[EBP]/[BINOL]₀ = 1000:10:1, MMA/DMA (1:1, v/v) at room temperature under purple LEDs irradiation for 5 h. b By ¹H NMR. c Determined by gel permeation chromatography using polystyrene standards. d Determined by gel permeation chromatography using polymethyl methacrylate standards. e Initiator efficiency (I*) calculated according to the equation: I* = (Mₙ,tho)/(Mₙ,GPC) × 100%, Mₙ,tho = [monomer]/[initiator] × Mₙ of monomer × Conv. % + Mₙ of initiator.

Table S3. Supplementary results to Table 2 of photoinduced metal-free ATRP of methyl methacrylate with using BINOL 5 as photocatalyst a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initi.</th>
<th>MMA/Initi./S</th>
<th>Conv. b</th>
<th>Mₙ,c</th>
<th>η Mₙ,d</th>
<th>Mₙ,d</th>
<th>η I*(% )d,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EBP</td>
<td>1000/20/2</td>
<td>80.4%</td>
<td>9.70</td>
<td>1.19</td>
<td>11.7</td>
<td>1.18</td>
</tr>
<tr>
<td>2</td>
<td>EBP</td>
<td>1000/20/1</td>
<td>74.2%</td>
<td>8.80</td>
<td>1.23</td>
<td>10.9</td>
<td>1.22</td>
</tr>
<tr>
<td>3</td>
<td>EBP</td>
<td>1000/20/0.5</td>
<td>73.0%</td>
<td>9.50</td>
<td>1.25</td>
<td>12.0</td>
<td>1.23</td>
</tr>
<tr>
<td>4</td>
<td>EBP</td>
<td>1000/20/0.1</td>
<td>66.8%</td>
<td>10.6</td>
<td>1.32</td>
<td>13.0</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>EBP</td>
<td>1000/15/1</td>
<td>77.9%</td>
<td>10.4</td>
<td>1.25</td>
<td>12.7</td>
<td>1.24</td>
</tr>
<tr>
<td>6</td>
<td>EBP</td>
<td>1000/10/2</td>
<td>72.9%</td>
<td>10.8</td>
<td>1.28</td>
<td>13.1</td>
<td>1.27</td>
</tr>
<tr>
<td>7</td>
<td>EBP</td>
<td>1000/10/1</td>
<td>78.6%</td>
<td>12.1</td>
<td>1.29</td>
<td>14.4</td>
<td>1.29</td>
</tr>
<tr>
<td>8</td>
<td>EBP</td>
<td>1000/10/0.5</td>
<td>69.8%</td>
<td>10.8</td>
<td>1.36</td>
<td>12.8</td>
<td>1.34</td>
</tr>
<tr>
<td>9</td>
<td>EBP</td>
<td>1000/10/0.1</td>
<td>70.1%</td>
<td>12.9</td>
<td>1.47</td>
<td>16.0</td>
<td>1.45</td>
</tr>
<tr>
<td>10</td>
<td>EBP</td>
<td>1000/5/1</td>
<td>74.3%</td>
<td>16.5</td>
<td>1.43</td>
<td>20.0</td>
<td>1.39</td>
</tr>
<tr>
<td>11</td>
<td>EBP</td>
<td>1000/5/0.5</td>
<td>76.4%</td>
<td>16.8</td>
<td>1.50</td>
<td>20.2</td>
<td>1.46</td>
</tr>
<tr>
<td>12</td>
<td>EBP</td>
<td>1000/5/0.1</td>
<td>71.8%</td>
<td>16.5</td>
<td>1.53</td>
<td>19.7</td>
<td>1.48</td>
</tr>
</tbody>
</table>

a Reaction conditions: [MMA]/[EBP]/[BINOL]₀ = 1000:10:1, MMA/DMA (1:1, v/v) at room temperature under purple LEDs irradiation for 5 h. b By ¹H NMR. c Determined by gel permeation chromatography using polystyrene standards. d Determined by gel permeation chromatography using PMMA standards. e Initiator efficiency (I*)
calculated according to the equation: 

\[ I^* = \left( \frac{M_{n,\text{theo}}}{M_{n,\text{GPC}}} \right) \times 100\% \], 

where \( M_{n,\text{theo}} = \frac{[\text{monomer}]/[\text{initiator}]}{} \times M_w \text{ of monomer} \times \text{Conv. \%} + M_w \text{ of initiator}. \]

**GPC traces**
Fig. S7. GPC traces of Table 1: entry 1 (black), entry 2 (blue), entry 3 (green), and entry 4 (purple), entry 5 (red), entry 6 (navy), entry 7 (yellow), entry 8 (orange) and entry 9 (pink).
Fig. S8. GPC traces of Table 2: entry 1 (red), entry 2 (dark cyan), entry 3 (cyan), and entry 4 (light pink).

Fig. S9. GPC traces of Table 2: entry 5 (blue), entry 6 (green), entry 7 (purple), and entry 8 (pink), entry 9 (yellow) and entry 10 (black).
Fig. S10. GPC traces of Table 2: entry 11 (blue), entry 12 (purple), entry 13 (pink), and entry 14 (black).
Fig. S11. GPC traces of Table 2: entry 15 (gray), entry 16 (violet) and entry 17 (atrovirens).

Fig. S12. GPC traces for polymerization kinetic investigation of Figure 2 (C).
Reference

NMR spectra

BINOL 2:

[Chemical structure image]

[1H NMR spectrum with peaks labeled]

[13C NMR spectrum with peaks labeled]
BINOL 3:

\[
\begin{align*}
&\text{OH} \\
&\text{t-Bu} \\
&\text{OH} \\
&\text{t-Bu} \\
&\text{OH} \\
&\text{t-Bu} \\
&\text{OH} \\
&\text{t-Bu}
\end{align*}
\]
BINOL 4:
BINOL 5:
BINOL 6:

\[
\begin{align*}
&-159.09 & -141.14 \\
&153.00 & 153.00 \\
&158.00 & 158.00 \\
&155.00 & 155.00 \\
&77.32 & 77.32 \\
&77.28 & 77.28
\end{align*}
\]

\[
\begin{align*}
&\text{CF}_3 \\
&\text{CF}_3 \\
&\text{CF}_3 \\
&\text{CF}_3
\end{align*}
\]