[Supporting Information]

β-Diketone Boron Difluoride Dye-Functionalized Conjugated Microporous Polymers for Efficient Aerobic Oxidative Photocatalysis

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Section 1. Syntheses

Synthesis of 1,3-Bis(4-bromophenyl)-1,3-propanedione

\[
\begin{align*}
 &\text{Br} \quad \text{O} \\
 &\text{Br} \\
 &\text{H}_2\text{CO} \quad \text{O} \\
 &\text{Br} \\
 &\text{OH} \\
 &\text{Br} \quad \text{Br} \quad \text{Br} \\
 &\text{THF NaH} \\
 &\text{DBH}
\end{align*}
\]

NaH (1.52 g, 63.3 mmol) and dried THF (10 mL) were added to a dried round flask in an ice bath. Then, the corresponding 1-(4-bromophenyl)ethanone (2.5 g, 12.5 mmol) and methyl 4-bromobenzoate (3.00 g, 14 mmol) in THF solution (20 mL) were added in the mixed solution. The mixture was heated to reflux for 16 h. After cooling to room temperature, the reaction mixture was neutralized by 1 M hydrochloric acid. The organic layer was separated and washed two times by brine solution and dried by anhydrous Na\(_2\)SO\(_4\). The organic layer was concentrated under reduced pressure and the residue was recrystallized from ethyl acetate to give a pure product. Yield: 6.82 g (74% yield).

\[\text{^1H NMR} \ (400 \text{ MHz, Chloroform-d}) \ \delta \ 7.86 \text{ (d, } J = 8.6 \text{ Hz, 4H), 7.65 (d, } J = 8.6 \text{ Hz, 4H), 6.79 (s, 1H).}\]

Synthesis of Boron,difluoro[1,3-bis(p-bromophenyl)-1,3-propanionanato]

\[
\begin{align*}
 &\text{BF}_3\cdot \text{Et}_2\text{O} \\
 &\text{DCM} \\
 &\text{DBF}
\end{align*}
\]

Under a nitrogen atmosphere, 1,3-bis(4-bromophenyl)-1,3-propanedione (0.764 g, 2 mmol), BF\(_3\). Et\(_2\)O (1.3 ml, 10 mmol) and anhydrous dichloromethane (30 ml) were added to a dried round flask. Then the mixture was refluxed for 2 h. After cooling to room temperature, the reaction was concentrated and purified by silica gel column chromatography to obtain a pale yellow solid. Yield: 0.782 g (92% yield).

\[\text{^1H NMR} \ (400 \text{ MHz, Chloroform-d}) \ \delta \ 8.04 \text{ (m, 4H), 7.75 (m, 4H), 7.15 (m, 4H).}\]

Synthesis of Model

\[
\begin{align*}
 &\text{Pt(PPh}_3\text{)\text{4 CuI Et}_3\text{N DMF}} \\
 &\text{DBFA}
\end{align*}
\]

The synthesis was carried out by Sonogashira–Hagihara cross-coupling reaction. Under nitrogen protection, in a 25 mL Schlenk tube were added boron complex DBF (0.375 mmol, 160 mg), ethynylbenzene (23 mg, 0.75 mmol), Pd(PPh\(_3\))\(_4\) (0.0259 mmol, 30 mg), CuI (15 mg, 0.078 mmol), dry DMF (2.5 mL), triethylamine (2.5 mL). The reaction mixture was stirred at 100 °C for 3 day. After removal of the solvents at
reduced pressure, the residue was washed three times with water (50 mL) and extracted into CH$_2$Cl$_2$. The organic layer was dried on MgSO$_4$, and the solvent was removed under reduced pressure. The crude mixture was then purified by column chromatography to yield the product as a light yellow solid. Yield: 157 mg (89% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 16.84 (s, 1H), 7.99 (d, $J = 7.9$ Hz, 4H), 7.65 (d, $J = 7.8$ Hz, 4H), 7.56 (s, 4H), 7.38 (s, 6H), 6.88 (d, $J = 2.7$ Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 183.76, 133.79, 130.80, 127.42, 126.13, 121.70, 91.59, 87.77.

**Synthesis of TPB-B-CMP**

DBF (0.75 mmol), TEB (0.5 mmol), Pd(PPh$_3$)$_4$ (60 mg, 0.052 mmol), and CuI (30 mg, 0.16 mmol) were added into a 50 mL flame-dried Schlenk tube with the mixed dry N,N-dimethyl formamide (DMF) (5 mL) and triethylamine (5 mL). The reaction suspension was degassed and then stirred at 100 °C for 3 days under an inert nitrogen atmosphere. After cooling to room temperature, the solid was obtained by filtration and washed with DMF, water, trichloromethane, methanol, and acetone. Further purification was carried out by Soxhlet extraction with methanol and trichloromethane successively for 24h each to give a yellow powder. yield: 0.367 g (95% yield).

**Synthesis of TPA-B-CMP**

The synthesis method is the same as TPB-B-CMP, with the ligand TEB replaced by TEA and give a red powder. yield: 0.327 g (92% yield).

**Synthesis of TPB-NB-CMP**

The synthesis method is the same as TPB-B-CMP, with the dibromide group DBF replaced by DBH and give a pale yellow powder. yield: 0.319 g (90% yield).

**Section 2. TGA Curve**

![Fig. S1. TGA curve of polymer TPB-B-CMP, TPA-B-CMP, and TPB-NB-CMP.](image-url)
Section 3. XRD Pattern

![XRD Pattern](image)

Fig. S2. PXRD of polymer TPB-B-CMP, TPA-B-CMP, and TPB-NB-CMP.

Section 4. SEM Image

![SEM Images](image)

Fig. S3. SEM images of polymer TPB-B-CMP(a), TPA-B-CMP(b), and TPB-NB-CMP (c).

Section 5. Mott-Schottky curve

![Mott-Schottky Curves](image)

Fig. S4. Mott-Schottky curves of TPB-B-CMP (a), TPA-B-CMP (b) and TPB-NB-CMP (c) at different frequencies.
Section 6. Photocatalytic mechanism

![WP-TEC-1020HSL photochemical reaction system.](image)

**Table S1.** Selected catalysts and their catalytic efficiency for amines into imines.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Yield (%)</th>
<th>Substrate (mmol)</th>
<th>Photocatalyst (mg)</th>
<th>T (h)</th>
<th>Light</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPB-B-CMP</td>
<td>97</td>
<td>0.5</td>
<td>3.3</td>
<td>18</td>
<td>10W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>TPA-B-CMP</td>
<td>99</td>
<td>0.5</td>
<td>3</td>
<td>18</td>
<td>10 W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>TPB-NB-CMP</td>
<td>77</td>
<td>0.5</td>
<td>3</td>
<td>18</td>
<td>10 W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>pTCT-2P</td>
<td>98</td>
<td>0.4</td>
<td>2.7</td>
<td>6</td>
<td>26 W white CFL</td>
<td>this work</td>
</tr>
<tr>
<td>CzBDP</td>
<td>75</td>
<td>1</td>
<td>1.95</td>
<td>15</td>
<td>9 W CFL</td>
<td>this work</td>
</tr>
<tr>
<td>C-CMP</td>
<td>94</td>
<td>1.0</td>
<td>20</td>
<td>4</td>
<td>150W Xe lamp</td>
<td>5</td>
</tr>
<tr>
<td>CF-HCP</td>
<td>91</td>
<td>0.2</td>
<td>5.0</td>
<td>6</td>
<td>30 W green LED lamp</td>
<td>6</td>
</tr>
</tbody>
</table>

**Fig. S5** WP-TEC-1020HSL photochemical reaction system.
Table S2. Selected catalysts and their catalytic efficiency for photocatalytic hydroxylation of boric acid.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Yield (%)</th>
<th>Substrate (mmol)</th>
<th>Photocatalyst (mg)</th>
<th>T (h)</th>
<th>Light</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPB-B-CMP</td>
<td>96</td>
<td>0.5</td>
<td>6.6</td>
<td>48</td>
<td>10W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>TPA-B-CMP</td>
<td>99</td>
<td>0.5</td>
<td>6</td>
<td>48</td>
<td>10 W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>TPB-NB-CMP</td>
<td>72</td>
<td>0.5</td>
<td>6</td>
<td>48</td>
<td>10 W blue LED</td>
<td>this work</td>
</tr>
<tr>
<td>PCP-MF</td>
<td>94</td>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>White LED lamp</td>
<td>7</td>
</tr>
<tr>
<td>BBO-COF</td>
<td>99</td>
<td>0.2</td>
<td>21.2</td>
<td>96</td>
<td>18 W white LED</td>
<td>8</td>
</tr>
<tr>
<td>LZU-190</td>
<td>99</td>
<td>0.2</td>
<td>21.2</td>
<td>48</td>
<td>20 W white LEDs</td>
<td>9</td>
</tr>
<tr>
<td>CPOP-29</td>
<td>98</td>
<td>0.5</td>
<td>10</td>
<td>48</td>
<td>23 W white LED lamp</td>
<td>10</td>
</tr>
</tbody>
</table>

EPR measurements of TEMP-\(^1\)O2:

2 mg photocatalyst was dispersed in 0.1 M TEMP (3 ml in CH\(_3\)CN), and the solution was continuously irradiated for 30 min with a blue lamp (\(\lambda=460-465\) nm) before measurement.

UV-Vis measurements of N, N', N'-tetramethyl-p-phenylenediamine (NTPD):

In a typical experimental procedure, two standard solutions of N, N, N', N'-tetramethylp-phenylenedi-amine (NTPD) were prepared separately in acetonitrile. The TPA-B-CMP (2 mg) was added to one of the solutions and both the solutions were stirred for 1h under constant irradiation by visible light (10 W LED). Observe the absorption band in the 450-650 nm range.

Table S3. Quenching experimental data

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Entry</th>
<th>Scavengers</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocatalytic of benzylamine (^a)</td>
<td>1</td>
<td>KI (^c)</td>
<td>7%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>NaN(_3)(^d)</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Benzoquinone(^e)</td>
<td>46%</td>
</tr>
<tr>
<td>Photocatalytic of boric acid (^b)</td>
<td>4</td>
<td>KI (^c)</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>NaN(_3)(^d)</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Benzoquinone(^e)</td>
<td>55%</td>
</tr>
</tbody>
</table>

\(^a\) Benzylamine (0.5 mmol), photocatalyst (2.44mg, 1 mmol%), CH\(_3\)CN(5mL), scavengers (1mmol) 10W blue LED (460-465nm), room temperature (RT), 18 h; conversion was determined by \(^1\)H NMR. \(^b\) Phenylboronic acid (0.5 mmol), photocatalyst (2.44 mg, 1 mmol%), DMF (5 mL), scavengers (1 mmol), air, 10W blue LED (460-465nm), room temperature (RT), 48 h; conversion was determined by \(^1\)H NMR.
NMR. c hole scavenger. d $^1$O$_2$ scavenger. e $O_2^-$ scavenger.

Section 7. Stability and cycling

Fig. S6. Initial infrared spectrum of TPA-B-CMP and spectrum after five cycles.

Section 8. Liquid NMR Spectra of Some Compounds
Fig. S7. $^{13}$C NMR Spectra of DBFA
Section 10. Reference

References: