Electronic Supplementary Information

Electron Donor-free Photoredox Catalysis via Electron Transfer Cascade by Cooperative Organic Photocatalysts

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Photograph of the setup for the sacrificial reagent free and photocatalytic C-C bond formation reactions using cooperative photocatalyst systems

*Products NMR data:*

![Chemical structure](image)

**Diethyl 2-(3-methyl-1H-2,3-benzofuran-2-yl)malonate (table 1, entry 5).** Follow the general procedure, Hexane/CH₂Cl₂ = 1/1 was used as eluent to give the product as a yellow oil (99 mg, 90%). ¹H NMR (300 MHz, DMSO) δ : 7.63 - 7.60 (m, 1 H), 7.56 - 7.54 (m, 1 H), 7.37 - 7.26 (m, 2 H), 5.49 (s, 1 H), 4.26 - 4.14 (m, 4 H), 2.22 (s, 3 H), 1.22 (t, J = 7.4 Hz, 6 H). ¹³C NMR (75 MHz, DMSO) δ : 165.93, 153.47, 144.29, 129.10, 124.67, 122.58, 119.66, 114.25, 110.92, 61.67, 50.00, 13.85, 7.42. Molecular weight C₁₆H₁₈O₅: calculated 290.12, found 290.20.

![Chemical structure](image)

**Diethyl 2-(1,3-dimethyl-1H-indole-2-yl)malonate (table 1, entry 6).** Follow the general procedure, Hexane/CH₂Cl₂ = 2/1 was used as eluent to give the product as a yellow solid (97 mg, 88%). ¹H NMR (300 MHz, CDCl₃) δ : 8.93 (br, 1 H), 7.58 - 7.55 (m, 1 H), 7.39 - 7.36 (m,
1 H), 7.24 - 7.15 (m, 1 H), 7.19 - 7.10 (m, 1 H), 5.00 (s, 1 H), 4.34 - 4.18 (m, 4 H), 2.34 (s, 3 H), 1.31 (t, J = 7.4 Hz, 6 H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 167.38, 135.83, 128.26, 124.53, 122.36, 119.22, 118.78, 111.09, 110.60, 62.29, 49.31, 14.03, 8.51. Molecular weight C$_{16}$H$_{19}$NO$_4$: calculated 289.13, found 289.00.

**Diethyl 2-(1-methyl-1H-indole-2-yl)malonate** (*table 1, entry 7*). Follow the general procedure, Hexane/CH$_2$Cl$_2$ = 1/1 was used as eluent to give the product as a yellow solid (86 mg, 78%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.61 (d, $J$ = 7.81 Hz, 1 H), 7.33 (d, $J$ = 7.72 Hz, 1 H), 7.25 - 7.21 (m, 1 H), 7.13 - 7.08 (m, 1 H), 6.50 (s, 1 H), 4.93 (s, 1 H), 4.34 - 4.20 (m, 4 H), 3.73 (s, 3 H), 1.30 (t, $J$ = 7.4 Hz, 6 H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 166.99, 137.93, 130.90, 127.27, 121.97, 120.79, 119.71, 109.30, 103.01, 62.23, 51.32, 30.31, 14.05. Molecular weight C$_{16}$H$_{19}$NO$_4$: calculated 289.13, found 289.00.

**Diethyl 2-(2-(methoxycarbonyl)-1-methyl-1H-indole-3-yl)malonate** (*table 1, entry 7*). Follow the general procedure, Hexane/CH$_2$Cl$_2$ = 1/2 was used as eluent to give the product as a green-yellow solid (115 mg, 87%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.77 (d, $J$ = 8.21 Hz, 1 H), 7.41 - 7.34 (m, 2 H), 7.21 - 7.15 (m, 1 H), 5.79 (s, 1 H), 4.28 - 4.21 (m, 4 H), 4.03 (s, 3 H), 3.96 (s, 3 H), 1.27 (t, $J$ = 7.4 Hz, 6 H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 168.55, 162.51, 138.68, 138.68, 126.15, 125.65, 125.36, 121.99, 120.77, 114.50, 110.35, 61.69, 51.77, 49.96, 32.28, 14.09. Molecular weight C$_{18}$H$_{21}$NO$_6$: calculated 347.14, found 346.95.
Fig. S1. Reductive potentials of (a) Th-BT-Th, (c) Th-BTz-Th and (e) TA-BT-TA and oxidative potential of (b) Th-BT-Th, (d) Th-BTz-Th and (f) TA-BT-TA determined via cyclic voltammetry (vs. SCE)
Table S1. Redox potentials of the molecular photocatalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalysts</th>
<th>Ground state (V vs. SCE)$^a$</th>
<th>$E_0$,$^b$</th>
<th>Excited state (V vs. SCE)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Th-BT-Th</td>
<td>+1.12</td>
<td>-1.15</td>
<td>2.13</td>
</tr>
<tr>
<td>2</td>
<td>Th-BTz-Th</td>
<td>+0.95</td>
<td>-1.68</td>
<td>2.30</td>
</tr>
<tr>
<td>3</td>
<td>TA-BT-TA</td>
<td>+1.54</td>
<td>-1.20</td>
<td>2.34</td>
</tr>
</tbody>
</table>

$^a$Ground state redox potentials were determined by cyclic voltammetry;

$^b$$E_{0,0}$ was obtained from the maximum emission;

$^c$Excited state redox potential were calculated with the method described in previous report (reference 42 in the manuscript).

For one of the reaction system (Table 1, entry 5), both apparent quantum yield and catalytic turnover number were calculated as below:

Apparent Quantum Yield $\Phi_{AQY}$:

$$\Phi_{AQY} = \frac{\text{moles of product evolved}}{\text{moles of incident photons}} = \frac{N_e}{N_p} \times 100\% = \frac{M \times N_A}{S \times P \times t \times \lambda} \times 100\%$$

$$= \frac{M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

$$= \frac{0.38 \times 10^{-3} \text{mol} \times 0.93 \times 6.023 \times 10^{23} \text{mol}^{-1} \times 6.63 \times 10^{-34} \text{m}^2 \text{kg/s} \times 3 \times 10^9 \text{m/s}}{(3.3 \times 3.14) \text{cm}^2 \times 0.1 \text{w/cm}^2 \times 24 \times 3600 \text{s} \times 460 \text{nm}} \times 100\%$$

$$= 0.04\%$$

Catalytic turnover number $TON$:

$$TON = \frac{\text{the mole of product}}{\text{the mole of photocatalyst}} = \frac{0.38 \text{ mmol} \times 87\%}{0.038 \text{ mmol}} = 8.7$$
Fig. S2. Decay associated spectra (DAS) derived by a global fitting analysis of the TRPL data. (a) Couple 1 and (b) couple 2.
Fig. S3. Fluorescence quenching within the photocatalyst couples in solution by only exciting Th-BT-Th and TA-BT-TA. The ratios of the OSs were 1:1 for both couples. Excitation wavelength: (a) 500 nm, (b) 450 nm.
Fig. S4. Conventional reaction mechanism of the photocatalytic C-C coupling reaction between electron-rich heteroaromates and bromomalonates using a single system photocatalyst. Here, amine is used as sacrificial reagent.
Fig. S5. Fluorescence quenching spectra of (a)Th-BT-Th, (b)TA-BT-TA (c)Th-BTz-Th with diethyl bromomalonate and (d) Stern-Volmer analysis of quenching rate between Th-BTz-Th and diethyl bromomalonate.
Fig. S6. Fluorescence quenching for (a) cooperative catalyst system 1 (Th-BTZ-Th and Th-BT-Th) and (c) cooperative catalyst system 2 (Th-BTZ-Th and TA-BT-TA) with diethyl bromomalonate and Stern-Volmer analysis of (b) cooperative couple 1 and (d) couple 2 with diethyl bromomalonate.
**Fig. S7.** UV/vis absorption and fluorescence spectra of the connected photocatalyst system TA-BT-TA@Th-BTz-Th.

**Fig. S8.** Fluorescence spectra of C6-connected Th-BTz-Th@TA-BT-TA and unconnected photocatalyst couple 2 containing Th-BTz-Th and TA-BT-TA under same molar ratio and concentration.
Fig. S9. Fluorescence quenching of (a) unconnected and (c) connected Th-BTz-Th/TA-BT-TA with diethyl bromomalonate and Stern-Volmer analysis of (b) unconnected and (d) connected Th-BTz-Th/TA-BT-TA with diethyl bromomalonate.
Fig. S10. Reductive potentials of (a) diethyl bromomalonate and (b) ethyl bromoacetate (potentials given vs. SCE)
Fig. S11. C-C coupling between 3-methylbenzofuran and ethyl bromoacetate using couple 2 (Th-BTz-Th/TA-BT-TA) as cocatalyst, Conversion: ~4%.
Fig. S12. C-C coupling between 3-methylbenzofuran and ethyl bromoacetate using Th-BTz-Th as catalyst and 4-methoxytriphenylamine as sacrificial reagent. Reaction conditions: 1 equiv. (0.38 mmol) heteroaromate, 2 equiv. ethyl bromomalonate, 0.1 equiv. photocatalyst in 2.5 mL DMF, white LED, 12 h.