Supplementary Information

Exploring Organic Photosensitizers Based on Hemicyanine Derivatives: A Sustainable Approach for Preparation of Amide Linkages

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Table S1. Comparison of C4 photocatalyst with off shelf photosensitizer for carrying out oxidative amidation of aldehydes.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Solvent</th>
<th>Time</th>
<th>Additive</th>
<th>Reuseability/Recyclability</th>
<th>Yield</th>
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<tr>
<td>C4 (This Work)</td>
<td>DMSO:H$_2$O (1:1)</td>
<td>12h</td>
<td>-</td>
<td>Yes</td>
<td>82%</td>
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<tr>
<td>Phenazine ethosulfate</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>41%</td>
</tr>
<tr>
<td>Ru(bpy)$_3$Cl$_2$</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>37%</td>
</tr>
<tr>
<td>Ru(phen)$_3$Cl$_2$</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>46%</td>
</tr>
<tr>
<td>Ru(phen)$_3$(PF$_6$)$_2$</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>42%</td>
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<tr>
<td>Ir(dtbpy)(ppy)$_2$PF$_6$</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>44%</td>
</tr>
<tr>
<td>Nile red</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>29%</td>
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<tr>
<td>Rhodamine B</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>26%</td>
</tr>
<tr>
<td>Alizarin red S</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>22%</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>MeCN</td>
<td>12h</td>
<td>-</td>
<td>No</td>
<td>16%</td>
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</table>
Fig. S1. Uv-vis spectra of C1, C2, C3 and C4 in DMSO: H₂O (1:1) solvent mixture.

Fig. S2. Fluorescence spectra of C1, C2, C3 and C4 in DMSO:H₂O (1:1) solvent mixture.
Fig. S3 Fluorescence lifetime decay profiles of C1 in H2O: DMSO (1:1, v/v). IRF = instrument response function. λex = 635 nm and emission spectra are recorded at 686 nm with 32 slit width.

Fig. S4 Fluorescence lifetime decay profiles of C2 in H2O: DMSO (1:1, v/v). IRF = instrument response function. λex = 485 nm and emission spectra are recorded at 511 nm with 32 slit width.
Fig. S5 Fluorescence lifetime decay profiles of C3 in H$_2$O: DMSO (1:1, v/v). IRF = instrument response function. $\lambda_{ex} = 485$ nm and emission spectra are recorded at 557 nm with 32 slit width.

Fig. S6 Fluorescence lifetime decay profiles of C4 in H$_2$O: DMSO (1:1, v/v). IRF = instrument response function. $\lambda_{ex} = 485$ nm and emission spectra are recorded at 616 nm with 32 slit width.
Fig. S7 (a) Decrease in absorption maxima of DPBF (50μM) at 418 nm in DMSO under illumination in the presence of 5μM C1 for 50 min after the solution was saturated with air oxygen. (b) Semilogarithmic plots for the absorption decays of DPBF (50μM) (lnA₀/A) versus time at the same experimental conditions. inset: shows semilogarithmic plots for reference dye methylene blue under same conditions.

Fig. S8 (a) Decrease in absorption maxima of DPBF (50μM) at 418 nm in DMSO under illumination in the presence of 5μM C4 for 50 min after the solution was saturated with air oxygen. (b) Semilogarithmic plots for the absorption decays of DPBF (50μM) (lnA₀/A) versus time at the same experimental conditions. inset: shows semilogarithmic plots for reference dye methylene blue under same conditions.
Fig. S9 (A) UV-vis and (B) fluorescence spectra of derivative C1 after irradiation of 36h.

Fig. S10 (A) UV-vis and (B) fluorescence spectra of derivative C2 after irradiation of 36h.
Fig. S11 (A) UV-vis and (B) fluorescence spectra of derivative C3 after irradiation of 36h.

Fig. S12 (A) UV-vis and (B) fluorescence spectra of derivative C1 after irradiation of 36h.
Fig. S13 Absorption spectral changes of derivative C1 (0.02 mM) in presence of MV$^{2+}$ (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 10 min.

Fig. S14 Absorption spectral changes of derivative C2 (0.02 mM) in presence of MV$^{2+}$ (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 12 min.
**Fig. S15** Absorption spectral changes of derivative C3 (0.02 mM) in presence of MV$^{2+}$ (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 12 min.

**Fig. S16** Fluorescence spectra of derivative C4 (5µM) upon addition of pyrrolidine (0.1 mmol) in DMSO:Water (1:1).
Fig. S17 Fluorescence spectra of derivative C1 (5µM) upon addition of pyrrolidine (0.4 mmol) in DMSO:Water (1:1).

Fig. S18 Fluorescence spectra of derivative C2 (5µM) upon addition of pyrrolidine (5 mmol) in DMSO:Water (1:1).
Fig. S19 Fluorescence spectra of derivative C3 (5µM) upon addition of pyrrolidine (4 mmol) in DMSO:Water (1:1).

Fig. S20 Oxidative amidation of nitrobenzaldehyde in presence of solar light using C4 as photosensitizer under optimized conditions.
Fig. S21 Images showing the recovery of photocatalyst C4 by usual work up.

Fig. S22 Reusability of C4 for carrying out oxidative amidation of aromatic aldehydes under visible light irradiation.
**Fig. S23** (a) Whatman filter paper (b) coated with derivative C4 by dip the whatman filter paper into solution of derivative C4 (5 µM).

**Fig. S24** (a) Reaction mixture of pyrrolidine (0.75 mmol) and C4 (1 mol%) after irradiation of 8 h; (b) After addition of mixture KI (1.0 × 10⁻¹ M), aqueous acetic acid (1.0 × 10⁻¹ M) colour of solution changes to brown.

**Pyrrolidine + C4**
(4-nitrophenyl)(pyrrolidin-1-yl)methanone\(^1\), \(5a\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 8.27 (d, \(J = 9\) Hz, 2H, Ar-H), 7.68 (d, \(J = 9\) Hz, 2H, Ar-H), 3.66 (t, \(J = 6\) Hz, 2H, CH\(_2\)), 3.38 (t, \(J = 6\) Hz, 2H, CH\(_2\)), 2.01-1.90 (m, 4H, CH\(_2\)).

(4-methoxyphenyl)(pyrrolidin-1-yl)methanone\(^2\), \(5b\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.51 (d, \(J = 6\) Hz, 2H, Ar-H), 6.92 (d, \(J = 6\) Hz, 2H, Ar-H), 3.83 (s, 3H, OCH\(_3\)), 3.63 (t, \(J = 6\) Hz, 2H, CH\(_2\)), 3.48 (t, \(J = 9\) Hz, 2H, CH\(_2\)), 1.94-1.86 (m, 4H, CH\(_2\)).

Phenyl(pyrrolidin-1-yl)methanone\(^1\), \(5c\)

\[^1\text{H NMR (500 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.51-7.50 (m, 2H, Ar-H), 7.40-7.38 (m, 3H, Ar-H), 3.64 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)), 3.42 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)), 1.98-1.93 (m, 2H, CH\(_2\)), 1.89-1.84 (m, 2H, CH\(_2\)).

(4-cyanophenyl)(pyrrolidin-1-yl)methanone\(^1\), \(5d\)

\[^1\text{H NMR (500 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.68 (d, \(J = 10\) Hz, 2H, Ar-H), 7.59 (d, \(J = 10\) Hz, 2H, Ar-H), 3.62 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)), 3.35 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)), 1.98-1.93 (m, 2H, CH\(_2\)), 1.91-1.86 (m, 2H, CH\(_2\)).

(4-chlorophenyl)(pyrrolidin-1-yl)methanone\(^1\), \(5e\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.43 (d, \(J = 6\) Hz, 2H, Ar-H), 7.33 (d, \(J = 6\) Hz, 2H, Ar-H), 3.59 (t, \(J = 6\) Hz, 2H, CH\(_2\)), 3.37 (t, \(J = 6\) Hz, 2H, CH\(_2\)), 1.94-1.82 (m, 4H, CH\(_2\)).

(4-nitrophenyl)(piperidin-1-yl)methanone\(^3\), \(7a\)

\[^1\text{H NMR (400 MHz, CDCl}_3\]: \(\delta\) (ppm) = 8.27 (d, \(J = 8\) Hz, 2H, Ar-H), 7.55 (d, \(J = 8\) Hz, 2H, Ar-H), 3.73 (bs, 2H, CH\(_2\)), 3.28 (bs, 2H, CH\(_2\)), 1.79-1.52 (m, 6H, CH\(_2\)).

(4-methoxyphenyl)(piperidin-1-yl)methanone\(^2\), \(7b\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.37 (d, \(J = 9\) Hz, 2H, Ar-H), 6.90 (d, \(J = 9\) Hz, 2H, Ar-H), 3.83 (s, 3H, OCH\(_3\)), 3.64 (br, 2H, CH\(_2\)), 3.44 (br, 2H, CH\(_2\)), 1.66-1.58 (m, 6H, CH\(_2\)).

Phenyl(piperidin-1-yl)methanone, \(7c\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.37 (m, 5H, Ar-H), 3.69 (br, 2H, CH\(_2\)), 3.33 (br, 2H, CH\(_2\)), 1.66-1.51 (m, 6H, CH\(_2\)).

(4-cyanophenyl)(piperidin-1-yl)methanone\(^1\), \(7d\)

\[^1\text{H NMR (300 MHz, CDCl}_3\]: \(\delta\) (ppm) = 7.70 (d, \(J = 6\) Hz, 2H, Ar-H), 7.48 (d, \(J = 6\) Hz, 2H, Ar-H), 3.71 (br, 2H, CH\(_2\)), 3.27 (br, 2H, CH\(_2\)), 1.60 (bs, 4H, CH\(_2\)), 1.53 (br, 2H, CH\(_2\)).

(4-chlorophenyl)(piperidin-1-yl)methanone\(^2\), \(7e\)
H NMR (500 MHz, CDCl₃): δ (ppm) = 7.38-7.32 (m, 4H, Ar-H), 3.69 (bs, 2H, CH₂), 3.33 (bs, 2H, CH₂), 1.68-1.51 (m, 6H, CH₂).

**morpholino(4-nitrophenyl)methanone**, 8a

H NMR (400 MHz, CDCl₃): δ (ppm) = 8.27 (d, J = 8 Hz, 2H, Ar-H), 7.57 (d, J = 8 Hz, 2H, Ar-H), 3.79-3.37 (m, 8H, CH₂).

**morpholino(4-methoxyphenyl)methanone**, 8b

H NMR (300 MHz, CDCl₃): δ (ppm) = 7.28 (d, J = 9 Hz, 2H, Ar-H), 6.82 (d, J = 9 Hz, 2H, Ar-H), 3.72 (s, 3H, OCH₃), 3.60 (br, 8H, CH₂).

**Derivative C3.**

H NMR (DMSO-d₆, 400 MHz): δ (ppm) = 10.02 (s, 1H), 8.35 (d, J = 6 Hz, 1H), 8.12 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 2H), 7.62-7.50 (m, 2H), 7.45 (d, J = 16 Hz, 2H), 6.95 (d, J = 8 Hz, 2H), 4.07 (s, 3H), 1.76 (s, 6H), 13C NMR (DMSO-d₆, 125 MHz) δ = 163.69, 154.24, 143.65, 142.33, 134.02, 129.32, 126.46, 123.23, 116.99, 115.11, 109.76, 52.20, 34.97, 26.14; MS (ESI): m/z 278.16 [M]+.

**Derivative C4.**

H NMR (DMSO-d₆, 400 MHz): δ (ppm) = 9.27 (d, J = 16 Hz, 1H), 8.99 (d, J = 8 Hz, 1H), 8.74 (d, J = 8 Hz, 1H), 8.49-8.38 (m, 5H), 8.30 (d, J = 8 Hz, 1H), 8.19-8.14 (m, 1H), 7.98-7.90 (m, 3H), 7.65-7.63 (m, 2H), 4.24 (s, 3H), 1.91 (s, 6H), MS (ESI): m/z 386.48 [M+1]+.

**References**


Fig. S25 $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 5a.
Fig. S26 $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 5b.
Fig. S27 $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 5c.
Fig. S28 $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 5d.
Fig. S29 $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 5e.
Fig. S30 $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7a.
Fig. S31 $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 7b.
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Fig. S40 $^1$H NMR (400 MHz, CDCl$_3$) spectrum of C3.
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Fig. S42 Mass spectrum of C3.
Fig. S43 $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of C4.
Fig. S44 Mass spectrum of C4.