Supplementary information

In-situ Palladium-Doped Conjugated Polymer Network for Visible and Natural Sunlight-Driven Suzuki Type Cross-Coupling Reaction at Room Temperature

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Calculation of Turn Over Number and Turn Over Frequency

For measuring the turnover number, we have performed a C-C cross-coupling reaction to calculate TON. The Pd content in CPN was measured by ICP-AES. The reaction was carried out by 9.2 mg CPN in a reaction mixture of 1 mmol 4-bromo benzonitrile, 1.2 mmol phenylboronic acid, and 2 mmol K$_2$CO$_3$ as a base in 3 ml (ethanol) solvent using 3Watt (0.05white LED. The reaction yield was 92%. The turnover number (TON) and turnover frequency (TOF) of the reaction were calculated as below:

TON = Number of moles of product / Number of moles of catalyst (Pd)
TOF = TON/time of reaction

For C-C cross-coupling reaction

TON = (0.92mmol) / 0.000125mmol (Pd content)
= 7360

TOF = TON/time = 7360/4h = 1840 h$^{-1}$

Synthesis of monomer-

2, 7-Dibromofluorene –

Fluorene (0.831g, 5 mmol), NBS (3.601 g, 20.233 mmol), FeCl$_3$ (0.03232 g, 0.1992 mmol), and 20.328 mL of DMF was added and stirred at 90$^\circ$C temperature for 5 h in dark condition. The mixture was then washed with 3.5% HCl solution, NaHCO$_3$, water, and ethyl acetate. And recrystallized in ethanol then a white solid was obtained. The compound formation is confirmed by NMR (fig S1 $^1$H NMR (500 MHz,) δ 7.64 (s, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 3.84 (s, 2H).
Fig. S1. $^1$H NMR spectra of 2, 7-Dibromofluorene.

2, 7-Dibromofluorenone –

2, 7-Dibromofluorenone ((1.62 g, 5 mmol), $\text{K}_2\text{Cr}_2\text{O}_7$ (1.716 g, 5.832 mmol) was stirred in 15 mL of acetic acid for 6 h at reflux temperature. After cooling to room temperature, the reaction solution was filtered. The filter solid was washed successively with acetic acid, water, and 5% hydrochloric acid to remove impurities. A yellow solid was obtained. The compound formation is confirmed by NMR (fig S2 $^1$H NMR (500 MHz,) $\delta$ 7.76 (s, 2H), 7.69 – 7.55 (m, 2H), 7.40 (t, $J = 21.6$ Hz, 2H).
Fig. S2. $^1$H NMR spectra of 2, 7-Dibromofluorenone.

1, 3, 5-Triazine phenylboronic acid-

In a 250 ml round bottle 4-cyanophenyl boronic acid (1g, 6.8 mmol) and triflic acid (6. 7 ml) and stirred overnight. The reaction mixture was diluted with cold water at vigorous stirring, then filter and wash with water. After washing white colour solid was obtained, and dried at 60$^\circ$C in vacuum oven. The compound formation confirmed by NMR (Fig. S3) $^1$H NMR (600 MHz, DMSO) $\delta$ 8.78 (d, J = 8.0 Hz, 6H), 8.37 (d, J = 27.2 Hz, 6H), 8.04 (dd, J = 94.6, 8.0 Hz, 6H).
Fig. S3 $^1$H NMR spectra of 1, 3, 5-Triazine phenylboronic acid.

Fig. S4 XPS survey spectra of CPN without soxlet extraction (CPNWOSE)
Fig. S5 Cyclic voltammetry of CPN deposited on glassy carbon electrodes. Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile as the supporting electrolyte. The onset of oxidation is mentioned for each CV plot.

Quantum chemical calculations:

To understand the band gap and frontier energy levels, we have performed quantum chemical calculations at the B3LYP/6-31G(d,p) level of theory using the G09 suite of programs. We have also performed geometry optimization and frequency calculations to ensure stationary point geometry.

Fig. S6 Topographical representations of the HOMO and LUMO of CPN (top view)
Fig. S7 Total Mulliken charge of triazine ring and one arm of the monomeric unit in CPN.

Fig. S8 Cyclic voltammetry of 4-bromobenzonitrile in solution (DCM) phase. Glassy carbon electrodes were used as the working electrode, Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in DCM as the supporting electrolyte. The onset of reduction is mentioned in the CV plot.
Table S1 Optimised conditions of C-C cross-coupling reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>Reaction condition*</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, light</td>
<td><img src="image2.png" alt="Structure" /> 25%</td>
</tr>
<tr>
<td>2.</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>Ethanol, light</td>
<td>no reaction</td>
</tr>
<tr>
<td>3.</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, electron quencher (AgNO₃), light</td>
<td>no reaction</td>
</tr>
<tr>
<td>4.</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, hole quencher (TEOA), light</td>
<td><img src="image6.png" alt="Structure" /> 75%</td>
</tr>
<tr>
<td>5.</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, light</td>
<td><img src="image8.png" alt="Structure" /> 11% 15%</td>
</tr>
<tr>
<td>6.</td>
<td><img src="image9.png" alt="Structure" /></td>
<td>Ethanol, light</td>
<td>no reaction</td>
</tr>
<tr>
<td>7.</td>
<td><img src="image10.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, electron quencher (AgNO₃), light</td>
<td><img src="image11.png" alt="Structure" /> 90%</td>
</tr>
<tr>
<td>8.</td>
<td><img src="image12.png" alt="Structure" /></td>
<td>Br₂CO₂Et, Ethanol, hole quencher (TEOA), light</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

*Reaction time 6 hrs, catalyst 5 wt%, reactant 0.5 mol, white LED 3 Watt

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Fig. S9 Cyclic voltammetry of 4-bromobenzonitrile in solution (DCM) phase. Glassy carbon electrodes used as the working electrode, Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in DCM as the supporting electrolyte. The onset of oxidation is mentioned in the CV plot.
Fig. S10 Redox potential of 4-bromo benzonitrile and phenyl boronic acid compared to the HOMO and LUMO energy levels of CPN determined by cyclic voltammetry (vs. NHE).

Table S2. Role of base, light, hole, and electron.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant 1</th>
<th>Reactant 2</th>
<th>Reaction conditiona</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>B(OH)2</td>
<td>Br</td>
<td>Ethanol, K2CO3</td>
<td>no reaction</td>
</tr>
<tr>
<td>2.</td>
<td>B(OH)2</td>
<td>Br</td>
<td>Ethanol, light</td>
<td>no reaction</td>
</tr>
<tr>
<td>3.</td>
<td>B(OH)2</td>
<td>Br</td>
<td>K2CO3, Ethanol, hole quencher (TEOA), light</td>
<td>NC-(\text{Ph-CN}) (48%) (\text{Ph-CN}) (10%)</td>
</tr>
<tr>
<td>4.</td>
<td>B(OH)2</td>
<td>Br</td>
<td>K2CO3, Ethanol, electron quencher (AgNO3), light</td>
<td>(\text{Ph-CN}) (56%) (\text{Ph-CN}) (13%)</td>
</tr>
<tr>
<td>5.</td>
<td>B(OH)2</td>
<td>CN</td>
<td>K2CO3, Ethanol, hole quencher (TEOA) and electron quencher(AgNO3), light</td>
<td>no reaction</td>
</tr>
<tr>
<td>6.</td>
<td>B(OH)2</td>
<td>Br</td>
<td>K2CO3, Ethanol, radical quencher (benzoquinone), light</td>
<td>(\text{Ph-CN}) (9.3%)</td>
</tr>
</tbody>
</table>

aReaction time 6 hrs, catalyst 5 wt% phenylboronic acid 0.55 mmol, 4-bromobenzonitrile (0.5 mmol), solvent 3ml

NMR data analysis data of the coupled products are listed in Fig.
Biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.59 (d, \(J = 7.8\) Hz, 1H), 7.44 (t, \(J = 7.6\) Hz, 1H), 7.34 (t, \(J = 7.4\) Hz, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 140.19, 127.70, 126.20, 126.12.

4-Methyl-1,1-biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50 (t, \(J = 9.4\) Hz, 1H), 7.41 (t, \(J = 7.6\) Hz, 1H), 7.35 (t, \(J = 7.3\) Hz, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 140.12, 137.32, 135.96, 128.44, 127.66, 126.20, 126.12, 125.93, 28.69.

4-phenylbenzonitrile-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.64 (t, \(J = 9.4\) Hz, 1H), 7.61 (d, \(J = 7.7\) Hz, 1H), 7.51 (d, \(J = 7.6\) Hz, 1H), 7.41 (t, \(J = 7.4\) Hz, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 145.70, 139.24, 132.62, 129.13, 128.67, 127.76, 127.25, 118.96, 110.92.

4-phenyl benzaldehyde-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 10.06 (s, 1H), 7.96 (t, \(J = 9.4\) Hz, 2H), 7.75 (d, \(J = 8.1\) Hz, 2H), 7.64 (d, \(J = 7.5\) Hz, 2H), 7.48 (t, \(J = 7.7\) Hz, 2H), 7.42 (t, \(J = 6.5\) Hz, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 192.12, 147.17, 139.86, 135.37, 130.18, 129.04, 128.56, 127.64, 127.19, 118.65, 115.64, 61.68.

2-amino-1,1-biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.73 – 7.57 (m, 1H), 7.47 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 7.25 (dt, \(J = 13.8, 4.0\) Hz, 1H), 7.05 (dt, \(J = 16.0, 9.6\) Hz, 2H), 6.72 (t, \(J = 6.6\) Hz, 1H), 6.65 (dd, \(J = 8.0, 0.7\) Hz, 1H), 3.78 – 3.46 (m, 2H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 167.71, 143.57, 139.59, 132.29, 131.00, 130.48, 129.13, 128.90, 128.84, 128.53, 127.64, 127.19, 118.65, 115.64, 61.68.

4-acetyl biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 8.04 (d, \(J = 7.1\) Hz, 1H), 7.77 – 7.58 (m, 2H), 7.48 – 7.36 (m, 1H), 2.64 (s, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 139.96, 135.50, 129.32, 128.46, 127.13, 26.99.

4-nitro biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 8.30 (d, \(J = 8.8\) Hz, 2H), 7.74 (d, \(J = 8.8\) Hz, 2H), 7.62 (t, \(J = 7.9\) Hz, 2H), 7.50 (t, \(J = 7.6\) Hz, 2H), 7.48 – 7.41 (m, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 147.66, 147.11, 138.79, 129.17, 128.93, 127.82, 127.40, 124.12.

4-methoxybiphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.54 (dd, \(J = 12.4, 8.1\) Hz, 1H), 7.48 – 7.35 (m, 1H), 7.30 (t, \(J = 7.3\) Hz, 1H), 6.97 (t, \(J = 10.8\) Hz, 1H), 3.85 (s, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 158.93, 140.85, 133.80, 128.74, 128.18, 126.76, 126.68, 114.22, 55.36.

2-carboxylc acid-1,1-biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 8.19 (d, \(J = 8.3\) Hz, 1H), 7.71 (d, \(J = 8.3\) Hz, 1H), 7.65 (d, \(J = 7.3\) Hz, 1H), 7.49 (dd, \(J = 18.6, 11.2\) Hz, 1H), 7.41 (t, \(J = 7.4\) Hz, 1H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 171.12, 146.56, 139.91, 130.76, 128.93, 128.38, 127.86, 127.34, 29.64.

4-chloro, 2-amino-1,1-biphenyl-\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.37 – 7.28 (m, 4H), 7.09 (td, \(J = 7.9, 1.5\) Hz, 1H), 7.01 (dd, \(J = 7.6, 1.4\) Hz, 1H), 6.75 (td, \(J = 7.5, 0.9\) Hz, 1H), 6.69 (d, \(J = 8.0\) Hz, 1H), 4.10 – 3.20 (m, 2H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 143.42, 137.94, 133.13, 130.49, 130.36, 129.01, 128.85, 126.35, 118.82, 115.77.
4-cyano, 4-methyl-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.66 – 7.55 (m, 4H), 7.45 – 7.35 (m, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 145.63, 138.77, 136.16, 132.58, 129.74, 127.48, 127.12, 119.06, 110.55, 21.19.

4-cyano, 4-carbaldehyde 1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 10.02 (s, 1H), 7.93 (d, $J = 7.7$ Hz, 2H), 7.83 – 7.50 (m, 7H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 191.64, 144.93, 144.16, 136.15, 132.81, 130.45, 128.06, 127.94, 125.45, 119.03, 119.01, 118.90, 118.86, 116.13, 116.10, 110.82.

4-cyano, 2-amino-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.72 (t, $J = 10.5$ Hz, 2H), 7.60 (d, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 3.80 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 144.61, 144.57, 143.38, 143.28, 132.92, 132.64, 130.25, 129.84, 129.65, 129.63, 127.98, 125.45, 119.03, 119.01, 118.90, 118.86, 116.13, 116.10, 110.82.

4-cyano, 4-nitro-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 8.35 (d, $J = 8.7$ Hz, 2H), 7.79 (dd, $J = 16.7$, 6.0 Hz, 2H), 7.78 – 7.70 (m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.94, 145.40, 143.15, 132.93, 128.17, 128.11, 124.39, 118.36, 112.70.

4, 4-dicyano-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.4$ Hz, 4H), 7.62 (d, $J = 8.4$ Hz, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 142.52, 131.88, 126.93, 117.40, 111.44.

4-methoxy, 4-methyl biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.51 – 7.29 (m, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 7.4$ Hz, 1H), 3.75 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.95, 137.99, 136.37, 133.77, 133.51, 129.46, 127.97, 127.76, 126.60, 114.18, 55.36, 21.07.

4-methoxy, 4-cyano biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.59 (dd, $J = 30.3$, 7.8 Hz, 1H), 7.46 (d, $J = 7.7$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 3.79 (s, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.94, 137.98, 136.37, 133.77, 133.51, 129.46, 127.97, 127.76, 126.60, 114.17, 55.18.

4-methoxy, 4-nitro-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 8.27 (d, $J = 7.9$ Hz, 2H), 7.69 (d, $J = 7.9$ Hz, 2H), 7.58 (d, $J = 7.6$ Hz, 2H), 6.99 (dd, $J = 39.0$, 7.6 Hz, 2H), 3.88 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.78, 143.59, 131.79, 130.53, 130.23, 128.23, 127.51, 118.78, 116.10, 115.65, 114.84, 114.26, 55.35, 55.35.

4, 4-dimethoxy-1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 157.42, 132.26, 126.71, 113.14, 54.15.

4, 4-carbaldehyde 1, 1-biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 10.09 (s, 1H), 8.00 (d, $J = 7.7$ Hz, 2H), 7.81 (d, $J = 7.7$ Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 191.96, 146.11, 135.96, 130.65, 127.99.
4'-acetyl-[1,1'-biphenyl]-4-carbonitrile- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ = 8.3 Hz, 1H), 7.77 (d, $J$ = 8.3 Hz, 1H), 7.73 (d, $J$ = 8.3 Hz, 1H), 7.69 (d, $J$ = 8.3 Hz, 1H), 2.66 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 197.51, 144.33, 143.55, 136.92, 132.76, 129.14, 127.95, 127.47, 118.65, 111.92, 26.73.

3-chlorobiphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.61 – 7.50 (m, 1H), 7.47 – 7.37 (m, 1H), 7.37 – 7.23 (m, 1H).

3-chloro, 4-nitro-1,1’biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J$ = 7.6 Hz, 1H), 7.72 (d, $J$ = 7.6 Hz, 1H), 7.62 (d, $J$ = 17.9 Hz, 1H), 7.57 – 7.46 (m, 1H), 7.46 – 7.36 (m, 1H).

3-chloro, 4-methyl biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.51 (dd, $J$ = 33.7, 16.3 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.29 (dd, $J$ = 17.8, 10.1 Hz, 2H), 7.26 – 7.17 (m, 2H), 2.36 (s, 3H).

3-chloro, 4-carbonitrile biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J$ = 7.8 Hz, 1H), 7.53 (d, $J$ = 7.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.35 (d, $J$ = 7.2 Hz, 1H), 7.33 – 7.25 (m, 1H).

3-chloro, 4-acetyl-1,1’biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 7.6 Hz, 1H), 7.58 (d, $J$ = 7.6 Hz, 1H), 7.53 (s, 1H), 7.46 – 7.37 (m, 1H), 7.37 – 7.24 (m, 1H), 2.57 (s, 2H).

3-chloro, 4-carboxaldehyde-1,1’biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.07 (s, 1H), 7.96 (d, $J$ = 7.7 Hz, 2H), 7.73 (d, $J$ = 7.7 Hz, 2H), 7.62 (s, 1H), 7.57 – 7.47 (m, 1H), 7.47 – 7.34 (m, 2H).

4-Acetyl, 4-methylbiphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J$ = 8.0 Hz, 1H), 7.66 (t, $J$ = 9.1 Hz, 1H), 7.53 (d, $J$ = 7.7 Hz, 1H), 7.38 – 7.13 (m, 1H), 2.63 (s, 1H), 2.41 (s, 1H).

4-Acetyl, 4-nitro biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.34 (d, $J$ = 7.8 Hz, 1H), 8.09 (d, $J$ = 7.7 Hz, 1H), 7.75 (dd, $J$ = 33.9, 7.7 Hz, 2H), 2.66 (s, 2H).

4, 4-diacetyl-1,1’biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.41 – 8.21 (m, 1H), 8.20 – 8.01 (m, 1H), 2.74 – 2.67 (m, 1H).

4, 4-diacyl-1,1’biphenyl- $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.41 – 8.21 (m, 1H), 8.20 – 8.01 (m, 1H).
Napthyl-1-phenyl- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.84 (dd, $J = 18.2, 17.3$ Hz, 3H), 7.63 – 7.30 (m, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 140.88, 140.38, 133.92, 131.74, 130.19, 128.38, 127.75, 127.35, 127.05, 126.14, 125.88, 125.50.

Napthyl-1-Benzocarbonitrile- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.82 (dd, $J = 17.8, 8.5$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.53 – 7.46 (m, 1H), 7.43 (dd, $J = 15.9, 7.9$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 11.6$ Hz, 1H).

Napthyl-1-(4-nitrobenzene) – $^1$H NMR (600 MHz, CDCl$_3$) δ 8.36 (d, $J = 7.5$ Hz, 1H), 7.98 – 7.89 (m, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.60 – 7.51 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.70, 147.21, 137.80, 133.80, 130.95, 128.99, 128.59, 127.11, 126.76, 126.25, 125.34, 125.15, 123.61.

Napthyl-1-Benzaldehyde- $^1$H NMR (600 MHz, CDCl$_3$) δ 10.05 (s, 1H), 7.94 (d, $J = 7.5$ Hz, 2H), 7.84 (dd, $J = 20.7, 10.6$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.55 – 7.43 (m, 2H), 7.38 (dd, $J = 16.7, 7.6$ Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 192.05, 147.28, 138.83, 135.34, 133.83, 131.13, 130.80, 129.77, 128.58, 128.51, 127.04, 126.53, 126.11, 125.48, 125.37.

Napthyl-1-(2-aminobenzene)- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.87 (dd, $J = 17.2, 8.2$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.52 (dd, $J = 8.1, 7.0$ Hz, 1H), 7.47 (tt, $J = 5.7, 2.8$ Hz, 1H), 7.45 – 7.36 (m, 2H), 7.24 (qd, $J = 7.8, 3.4$ Hz, 1H), 7.15 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.87 (td, $J = 7.4, 1.7$ Hz, 1H), 6.80 (dd, $J = 8.0, 0.8$ Hz, 1H), 3.75 – 2.99 (m, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 143.19, 135.89, 132.77, 130.62, 130.15, 127.72, 127.27, 126.93, 126.54, 126.51, 125.22, 124.97, 124.90, 124.77, 117.34, 114.33.

2, 7-diphenyl-9H-fluorene- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, $J = 7.7$ Hz, 2H), 7.79 (s, 2H), 7.65 (dd, $J = 19.5, 7.6$ Hz, 6H), 7.46 (t, $J = 7.1$ Hz, 4H), 7.36 (t, $J = 7.1$ Hz, 2H), 4.03 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 144.16, 141.48, 140.63, 139.92, 128.80, 127.20, 126.12, 123.84, 120.22, 37.09.

3-phenyl thiophene- $^1$H NMR (600 MHz, CDCl$_3$) δ 7.53 (dd, $J = 9.5, 8.0$ Hz, 2H), 7.37 (dd, $J = 9.7, 5.7$ Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.21 (dd, $J = 14.2, 6.8$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 127.78, 127.73, 126.23, 126.15, 125.44, 125.33, 125.17, 125.05, 119.24, 118.75.
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Fig. S84. $^{13}$C NMR spectra of 2, 7-diphenyl-9H-fluorene.
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Fig. S86. $^{13}$C NMR spectra of 3-phenyl thiophene.
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<th>Reaction condition</th>
<th>Light source</th>
<th>Substrate Scope</th>
<th>TON / TOF (h^-1)/conversion</th>
<th>Reference</th>
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</thead>
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<tr>
<td>Pd-Azo-POP</td>
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<td>EtOH/H₂O, CsCO₃</td>
<td>350 Watt Xenon lamp or Sunlight</td>
<td>19</td>
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<tr>
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<td>8</td>
<td>Conversion 98%</td>
<td>S2</td>
</tr>
<tr>
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<td>5 wt% Pd loaded ex-situ</td>
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<td>12</td>
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<td>S3</td>
</tr>
<tr>
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<td>8</td>
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<tr>
<td>Alloy-1 photocatalysts (Au/Pd, 1:1.62)</td>
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<td>13</td>
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<td>S5</td>
</tr>
<tr>
<td>Pd–BiVO₄</td>
<td>0.002 equivalent, Pd loaded ex-situ modification</td>
<td>EtOH/H₂O (3:1), K₂CO₃</td>
<td>18Watt Blue LED,</td>
<td>40</td>
<td>TON: 31200 TOF: 207</td>
<td>S6</td>
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<tr>
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<td>0.5mol%, Pd loaded ex-situ</td>
<td>H₂O, K₃PO₄</td>
<td>Blue LED</td>
<td>31</td>
<td>TOF: 193</td>
<td>S7</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂@TiO₂@Schiff base@Pd-(0)</td>
<td>0.159 wt%, Pd loaded ex-situ modification</td>
<td>K₂CO₃, PEG-400</td>
<td>Blue LED (20 W)</td>
<td>23</td>
<td>TOF: 5444 min⁻¹</td>
<td>S8</td>
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<tr>
<td>m-CNR-Pd</td>
<td>3 wt%, Pd loaded ex-situ</td>
<td>EtOH/H₂O, K₂CO₃</td>
<td>150 w Xenon lamp</td>
<td>16</td>
<td>Conversion 99%</td>
<td>S9</td>
</tr>
<tr>
<td>CPN</td>
<td>0.013 mol%</td>
<td>EtOH, K₂CO₃</td>
<td>3 Watt white LED light or sunlight</td>
<td>50</td>
<td>TON: 7360 TOF: 1840</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table-S3: Comparison table of the CPN performance with previously reported catalyst towards C-C cross-coupling reaction.
Table S4. C-C cross-coupling reaction, maintaining at 25°C, white LED.

![Diagram of C-C cross-coupling reaction](image1)

**Substrate Scope -**

- ![Substrate 1](image2) >90%, 4h
- ![Substrate 2](image3) >90%, 4h
- ![Substrate 3](image4) >90%, 6h
- ![Substrate 4](image5) >90%, 6h

*Reaction condition- Catalyst (5 wt%) arylboronic acid 0.55 mmol, arylhalide (0.5 mmol), base (1 mmol) solvent 3ml*

Table S5 C-C cross-coupling reaction using CPN in sunlight

![Diagram of C-C cross-coupling reaction](image6)

**Substrate Scope -**

- ![Substrate 5](image7) >90%, 4h
- ![Substrate 6](image8) >90%, 4h
- ![Substrate 7](image9)

*Reaction condition- Catalyst (5 wt%) arylboronic acid 0.55 mmol, arylhalide (0.5 mmol), base (1 mmol) solvent 3ml, time-4h*

Yield Conversion- >90%

![Image of synthesis](image10)

**Fig. S87.** Synthesis of 1, 1-biphenyl, 4-carbonitrile in sunlight.
Fig. S88. Gram scale synthesis of 4-chloro, 2-amino biphenyl in visible light.

Fig. S89. Recyclability of catalyst, conversion obtained at 4 h reaction time in repeated runs of the C-C cross-coupling reaction of 4-bromobenzonitrile and phenylboronic acid using the same reaction condition.
Fig. S90 TGA curve of Pd doped CPN

Fig. S91. Comparison of FTIR spectra of Pd doped CPN before and after reaction.
Fig. S92 Comparison of XPS Survey spectra of Pd doped CPN before and after the reaction.

Fig. S93 (a & c) High resolution C1S spectra of Pd doped CPN, (a) before reaction (c) after reaction. (b &d) High resolution N1S spectra of Pd doped CPN, (b) before reaction and (d) after reaction.
Fig. S94. TEM images of Pd doped CPN after use in reaction.

Reference:


6 H. R. Choe, S. S. Han, Y. Kim, C. Hong, E. J. Cho and K. M. Nam, , DOI:10.1021/acsami.0c15488.

