Supporting Information

Conducting 1D Nanostructures from Light Stimulated Copper Metalated Porphyrin – Dibenzothiophene

Yelukala Rama Krishna, a Madarapu Naresh, a,b Botta Bhavani, a,b Seelam Prasanthkumar* a,b

a Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, T.S., India.
b Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

Email of corresponding (*) E-mail: prasanth@iict.res.in (ORCID: 0000-0001-6287-1977)
Supporting information

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1. Synthesis of P$_{Fb}$-DBT, P$_{Cu}$-DBT and P$_{Zn}$-DBT

1.1. Synthesis of P$_{Fb}$-DBT:

Scheme S1. Reagent and Conditions: (i) Pd(PPh$_3$)$_2$Cl$_2$, Na$_2$CO$_3$, THF, Toluene, 90 °C, 12 h, N$_2$ atmosphere, yield: 60%.

**Synthetic Procedure for P$_{Fb}$-DBT:** To a 5 mL THF solution of dibromoporphyrin (500 mg, 0.537 mmol), dibenzo[b,d]thiophen-2-ylboronic acid (1) (1160 mg, 2.296 mmol) in 20 mL toluene, 1M Na$_2$CO$_3$ and bis(triphenylphosphine)palladium(II) dichloride Pd(PPh$_3$)$_2$Cl$_2$ (catalytic amount) were added and refluxed for 12 h at 70 °C under N$_2$ atmosphere. Subsequently, the reaction mixture was washed with ethyl acetate/water and organic layer was separated and dried over sodium sulphate. The crude product was purified by column chromatography (silica gel 100 – 200 mesh, DCM/hexane to give purple solid P$_{Fb}$-DBT (yield: 60%).

$^1$H NMR (400 MHz, CDCl$_3$) δ: 8.69 – 8.39 (m, 9H), 8.30 – 8.06 (m, 4H), 7.76 (s, 2H), 7.55 – 7.33 (m, 6H), 6.81 (s, 3H), 4.00 (s, 1H), 3.74 (d, $J$ = 31.5 Hz, 8H), 1.51 (s, 1H), 1.28 (d, $J$ = 15.5 Hz, 2H), 1.17 (s, 8H), 0.94 – 0.67 (m, 17H), 0.59 – 0.39 (m, 33H), -2.61 (d, $J$ = 53.9 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 160.13, 145.64, 140.98, 137.81, 135.64, 135.05, 132.67, 130.99, 130.50, 129.95, 126.70, 124.43, 123.72, 122.86, 122.15, 121.13, 120.40, 116.01, 113.01, 105.07, 68.65, 67.90, 38.75, 31.55, 30.40, 29.66, 29.34, 29.05, 25.38, 23.78, 23.10, 22.82, 22.33, 14.21, 13.95, 11.04. MALDI-TOF-MS (m/z) = 1339.67 (calculated mass = 1339.763).
1.2. Synthesis of \( \text{P}_{\text{Cu}}\text{-DBT} \):

\[
\text{P}_{\text{Cu}}\text{-DBT} \quad \text{P}_{\text{Cu}}\text{-DBT}
\]

\textbf{Scheme S2}. Reagent and Conditions: (ii) \( \text{Cu(OAc)}_2 \), DCM/MeOH (1:3 v/v), 3 h, 25 °C, \( \text{N}_2 \) atmosphere, yield: 70%.

\textbf{Synthetic Procedure for \( \text{P}_{\text{Cu}}\text{-DBT} \)}: A mixture of \( \text{P}_{\text{Pb}}\text{-DBT} \) (200 mg, 0.00142 mmol) and \( \text{Cu(OAc)}_2 \) (261 mg, 0.0023 mmol) in DCM/CH\(_3\)OH (1:3 v/v) were refluxed for 3 h under \( \text{N}_2 \) atmosphere at 25 °C. The progress of the reaction monitored by thin layer chromatography (TLC) and excess solvent was removed under reduced pressure. The extraction performed with hexane/DCM. The organic layer was washed with water and dried over \( \text{Na}_2\text{SO}_4 \). The solid residue was subjected to column chromatography (silica gel: 100–200 mesh, DCM/ hexane) to give pink coloured solid (yield: 70%); (MALDI-TOF-MS (m/z) = 1399.67 (calculated mass = 1399.62).

1.3. Synthesis of \( \text{P}_{\text{Zn}}\text{-DBT} \):

\[
\text{P}_{\text{Zn}}\text{-DBT} \quad \text{P}_{\text{Zn}}\text{-DBT}
\]

\textbf{Scheme S2}. Reagent and Conditions: (iii) \( \text{Zn(OAc)}_2 \), DCM/MeOH (1:3 v/v), 3 h, 25 °C, \( \text{N}_2 \) atmosphere, yield: 70%.

\textbf{Synthetic Procedure for \( \text{P}_{\text{Zn}}\text{-DBT} \)}: The synthetic strategy followed the \( \text{P}_{\text{Cu}}\text{-DBT} \) procedure by simple modification of \( \text{Cu(OAc)}_2 \) with \( \text{Zn(OAc)}_2 \).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.70 (dd, $J = 23.3$, 10.5 Hz, 6H), 8.42 (d, $J = 7.8$ Hz, 1H), 8.27 – 8.11 (m, 3H), 7.76 (dd, $J = 11.8$, 7.3 Hz, 2H), 7.49 (t, $J = 8.2$ Hz, 2H), 7.35 (dd, $J = 19.3$, 7.6 Hz, 3H), 7.25 – 7.15 (m, 2H), 6.83 (d, $J = 8.3$ Hz, 3H), 6.39 (t, $J = 8.1$ Hz, 1H), 3.91 – 3.60 (m, 8H), 1.78 – 1.48 (m, 2H), 1.28 (d, $J = 1.8$ Hz, 3H), 1.17 (t, $J = 3.8$ Hz, 12H), 0.95 – 0.74 (m, 12H), 0.54 – 0.31 (m, 33H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 158.93, 150.83, 150.00, 149.74, 148.07, 145.85, 144.58, 141.67, 139.74, 137.38, 135.09, 134.52, 134.07, 133.74, 131.42, 130.56, 129.86, 129.39, 128.65, 125.45, 123.63, 123.44, 123.44, 123.06, 122.46, 121.62, 120.98, 120.49, 119.64, 117.82, 115.83, 114.83, 112.51, 105.13, 104.07, 103.19, 68.32, 68.13, 66.76, 37.59, 34.80, 33.20, 30.65, 30.33, 29.25, 28.90, 28.16, 27.51, 24.95, 24.19, 22.62, 21.78, 21.15, 13.07, 12.76, 9.88. (MALDI-TOF-MS (m/z) = 1401.67 (calculated mass = 1401.62).

2. $^1$H NMR Spectra
2.1. $^1$H NMR of P$_{Fb}$-DBT:

![Figure S1. $^1$H NMR Spectrum of P$_{Fb}$-DBT.](image)
2.2. $^1$H NMR of $\text{P}_{\text{Zn}}$-DBT:

![Figure S2. $^1$H NMR Spectrum of $\text{P}_{\text{Zn}}$-DBT.]

3. $^{13}$C NMR Spectra

3.1. $^{13}$C NMR of $\text{P}_{\text{Fl}}$-DBT:

![Figure S3. $^{13}$C NMR Spectrum of $\text{P}_{\text{Fl}}$-DBT.]

S6
3.2. $^{13}$C NMR of P$_{Zn}$-DBT:

![Figure S4. $^{13}$C NMR Spectrum of P$_{Zn}$-DBT.]

4. MALDI-TOF-MS Spectra

4.1. MALDI-TOF-MS of P$_{Fb}$-DBT:

MALDI-TOF-MS (m/z) = 1339.67 (calculated mass = 1339.763).

![Figure S5. MALDI-TOF-MS Spectrum of P$_{Fb}$-DBT.]

S7
4.2. MALDI-TOF-MS of $P_{Zn}$-DBT:

(MALDI-TOF-MS (m/z) = 1401.67 (calculated mass = 1401.62).

![MALDI-TOF-MS Spectrum of $P_{Zn}$-DBT](image)

**Figure S6.** MALDI-TOF-MS Spectrum of $P_{Zn}$-DBT.

4.3. MALDI-TOF-MS of $P_{Cu}$-DBT:

(MALDI-TOF-MS (m/z) = 1399.67 (calculated mass = 1399.62).

![MALDI-TOF-MS Spectrum of $P_{Cu}$-DBT](image)

**Figure S7.** MALDI-TOF-MS Spectrum of $P_{Cu}$-DBT.
5. Theoretical calculations of P-DBT derivatives:

Figure S8. Theoretical calculations of P$_{\text{Fb}}$-DBT, P$_{\text{Cu}}$-DBT and P$_{\text{Zn}}$-DBT and their HOMO and LUMO energy levels.

6. Photophysical data of freebase and metalated P-DBT derivatives:

Figure S9. UV-vis optical absorption spectra of a) P$_{\text{Fb}}$-DBT, b) P$_{\text{Cu}}$-DBT and c) P$_{\text{Zn}}$-DBT in various solvents such as tetrahydrofuran (THF), chloroform (CHCl$_3$), dichloromethane (CH$_2$Cl$_2$) and toluene at a concentration of 1 × 10$^{-4}$ M at 25 °C.
Figure S10. UV-vis optical absorption spectra of $P_{Fb}$-DBT, $P_{Cu}$-DBT and $P_{Zn}$-DBT in tetrahydrofuran (THF) and acetonitrile (ACN) at a concentration of $1 \times 10^{-4}$ M at 25 °C.

Figure S11. a) UV-vis optical absorption spectra of $P_{Fb}$-DBT in chloroform with different interval of time from 0 to 60 min at 25 °C. b) The corresponding emission spectra of $P_{Fb}$-DBT at an excitation wavelength of 420 nm.

Figure S12. UV-vis optical absorption spectra of $P_{Zn}$-DBT in chloroform with different interval of time from 0 to 120 min at 25 °C.
Table S1. Photophysical and electrochemical data of P-DBT derivatives

<table>
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<tr>
<th>S.No.</th>
<th>Samples</th>
<th>Absorption λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Emission λ&lt;sub&gt;ems&lt;/sub&gt; (nm)</th>
<th>Lifetime τ (ns) Before</th>
<th>After light</th>
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<th>E&lt;sub&gt;Red&lt;/sub&gt;</th>
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<td>After light</td>
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Figure S13. UV-vis optical absorption spectra of a) P<sub>Fb</sub>-DBT, b) P<sub>Cu</sub>-DBT and c) P<sub>Zn</sub>-DBT in tetrahydrofuran and recorded their spectral changes whilst addition of acid and base.

7. MALDI-TOF-MS of light stimulated P-DBT derivatives:

Figure S14. MALDI-TOF-MS spectra of light stimulated samples: a) [H<sub>2</sub>P<sub>Fb</sub>-DBT]<sup>+</sup>[Cl<sup>-</sup>], b) H<sup>+</sup>[P<sub>Cu</sub>-DBT(Cl)]<sup>+</sup> and c) P<sub>Fb</sub>-DBT.
8. Spectroelectrochemistry of P<sub>Fb</sub>-DBT:

![Spectroelectrochemical UV-vis optical absorption spectra of P<sub>Fb</sub>-DBT in chloroform: a) oxidation potential (1.30 V) and b) reduction potential (-1.01 V).](image)

**Figure S15.** Spectroelectrochemical UV-vis optical absorption spectra of P<sub>Fb</sub>-DBT in chloroform: a) oxidation potential (1.30 V) and b) reduction potential (-1.01 V).

9. Electron microscopic images of P<sub>Fb</sub>-DBT:

![Electron microscopic images of P<sub>Fb</sub>-DBT](image)

**Figure S16.** (a,b) Scanning electron microscopic and transmission electron microscopic images of P<sub>Fb</sub>-DBT and [H<sub>2</sub>P<sub>Fb</sub>-DBT]<sup>+</sup>Cl<sup>-</sup> aggregates were drop-casted from methanol solution at 25 °C.

![Electron microscopic images of light illuminated P<sub>Fb</sub>-DBT aggregates](image)

**Figure S17.** (a-d) Scanning electron microscopic images of light illuminated P<sub>Fb</sub>-DBT aggregates were drop-casted from methanol solution at different time intervals of light illumination in chloroform.
10. Electrochemical Impedance analysis of $P_{Fb}$-DBT and $P_{Cu}$-DBT at before and light illuminations conditions:

10.1. Electrochemical Impedance analysis of before and after light illuminated $P_{Fb}$-DBT:

**Figure S18.** Electrochemical impedance spectral data of $P_{Fb}$-DBT. (a,d) Temperature dependent Nquist plot of before and after light illuminated $P_{Fb}$-DBT from 25 °C to 75 °C (b,e) Corresponding temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c,f) Plot represents the temperature in Kelvin against bulk resistance at both conditions to determine the electronic and ionic conduction mechanism.
10.2. Electrochemical Impedance analysis of $P_{\text{Cu-DBT}}$: 

Figure S19. Electrochemical impedance spectral data of $P_{\text{Cu-DBT}}$: (a) Nyquist plot with variable temperature from 25 °C to 75 °C. (b) Corresponding temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Plot represents the bulk resistance against temperature.

10.3. Electrochemical Impedance analysis of light illuminated $P_{\text{Cu-DBT}}$: 

Figure S20. a) Temperature-dependent changes of logarithmic frequency vs Imaginary impedance. b) plot of bulk resistance against the increase in temperature from 25 °C to 75 °C (298 – 348 K) of light-illuminated $P_{\text{Cu-DBT}}$. 
10.4. Summary of electrochemical impedance data of PFb-DBT and PCu-DBT:

Table S2. Electrochemical impedance spectroscopy data of PFb-DBT and PCu-DBT; where, $R_b =$ bulk resistance; $f_b =$ bulk frequency, $\sigma =$ specific conductivity, $C_b =$ bulk capacitance and $\tau_b =$ the bulk relaxation time and estimated for the samples at variable temperatures. (* represents light illuminated condition)

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<th>T (K)</th>
<th>$R_b$ (GΩ)</th>
<th>$f_b$ (MHz)</th>
<th>$\sigma \times 10^{-3}$ (S/cm)</th>
<th>$C_b$ (fF)</th>
<th>$\tau_b$ (µs)</th>
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