Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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

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Supporting information

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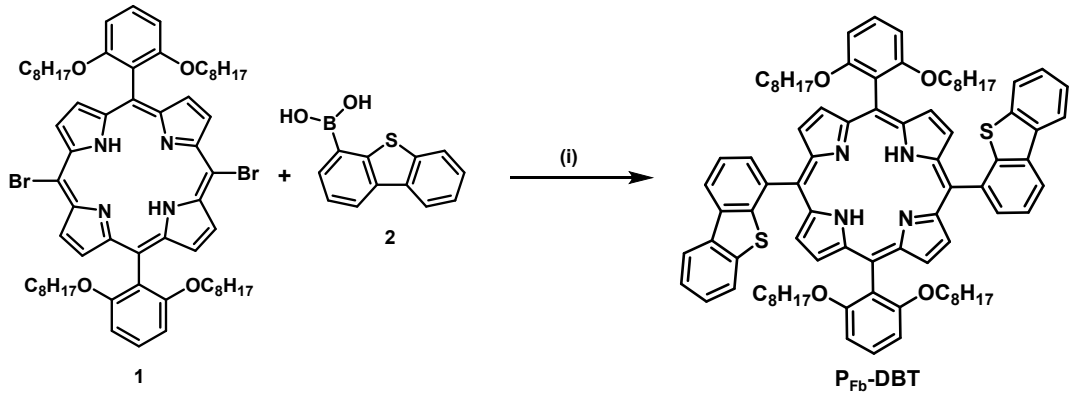
1. Synthesis of P_{Fb}-DBT, P_{Cu}-DBT and P_{Zn}-DBT

1.1. Synthesis of P_{Fb}-DBT:

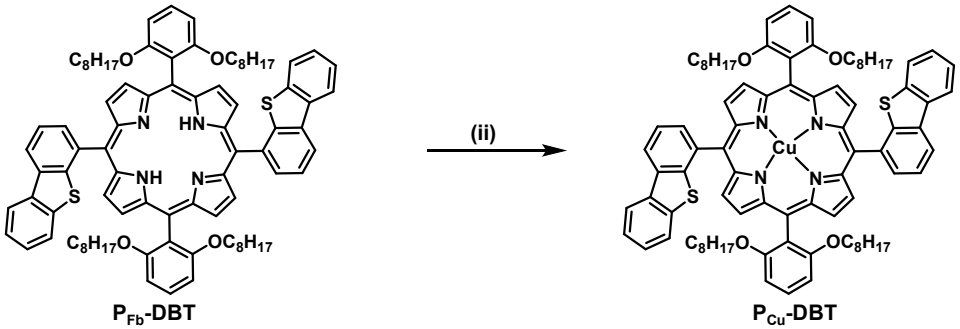


Scheme S1. Reagent and Conditions: (i) $Pd(PPh_3)_2Cl_2$, Na_2CO_3, THF, Toluene, 90 ^oC, 12 h, N_2 atmosphere, yield: 60%.

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_2CO_3 and bis(triphenylphosphine)palladium(II) dichloride $Pd(PPh_3)_2Cl_2$ (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 suphate. 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).

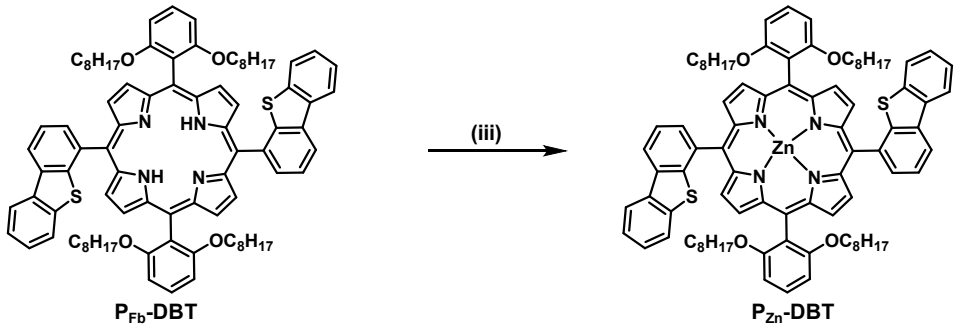
1.2. Synthesis of P_{Cu}-DBT:



Scheme S2. Reagent and Conditions: (ii) $Cu(OAc)_2$, DCM/MeOH (1:3 v/v), 3 h, 25 °C, N_2 atmosphere, yield: 70%.

Synthetic Procedure for P_{Cu}-DBT: A mixture of **P_{Fb}-DBT** (200 mg, 0.00142 mmol) and $Cu(OAc)_2$ (261 mg, 0.0023 mmol) in DCM/CH_3OH (1:3 v/v) were refluxed for 3 h under 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 Na_2SO_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 P_{Zn}-DBT:



Scheme S2. Reagent and Conditions: (iii) $Zn(OAc)_2$, DCM/MeOH (1:3 v/v), 3 h, 25 °C, N_2 atmosphere, yield: 70%.

Synthetic Procedure for P_{Zn}-DBT: The synthetic strategy followed the P_{Cu}-DBT procedure by simple modification of $Cu(OAc)_2$ with $Zn(OAc)_2$.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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:

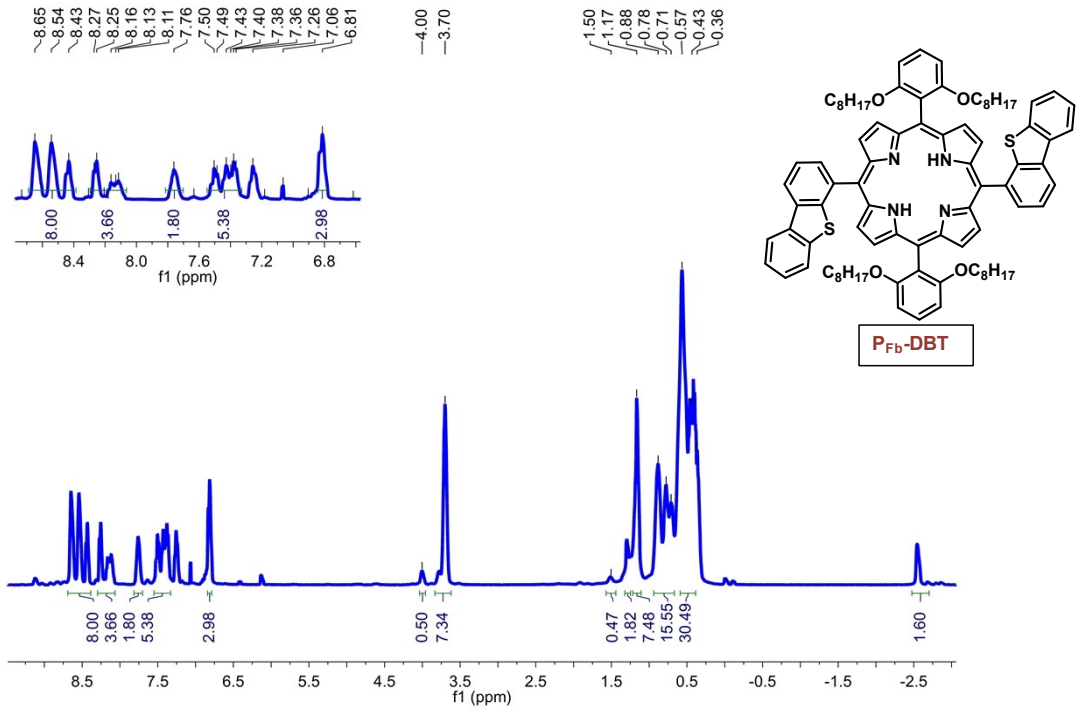


Figure S1. ^{1}H NMR Spectrum of P_{Fb}-DBT.

2.2. ^{1}H NMR of P_{Zn}-DBT:

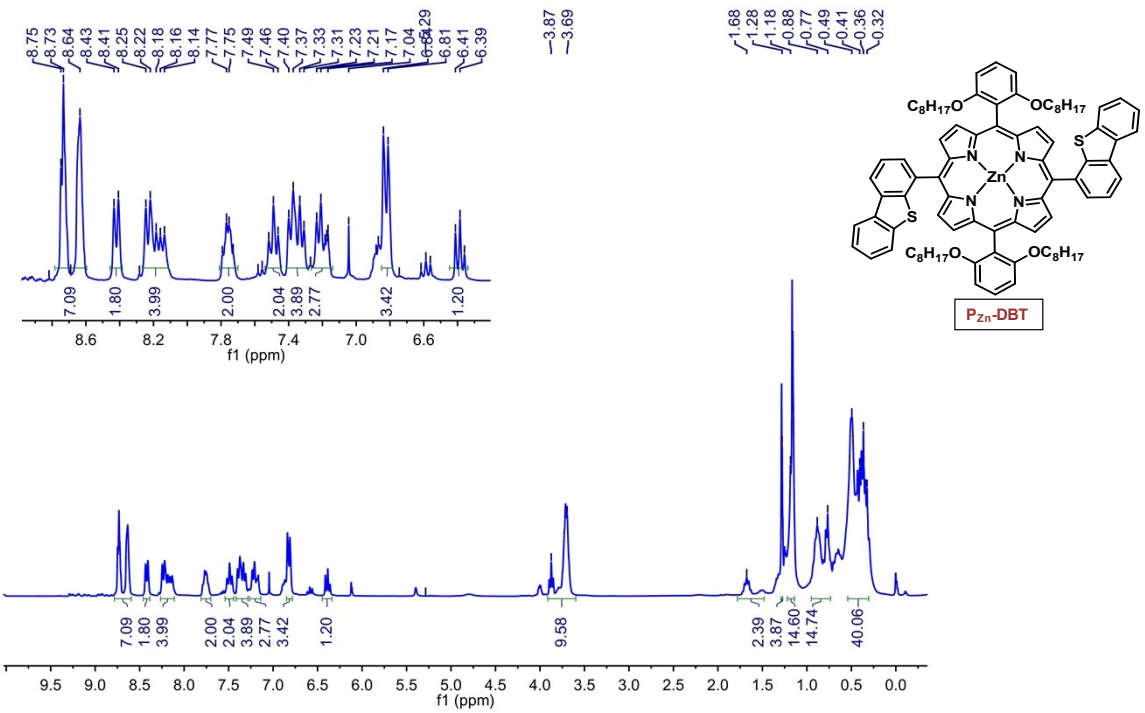


Figure S2. ^{1}H NMR Spectrum of P_{Zn}-DBT.

3. ^{13}C NMR Spectra

3.1. ^{13}C NMR of P_{Fb}-DBT:

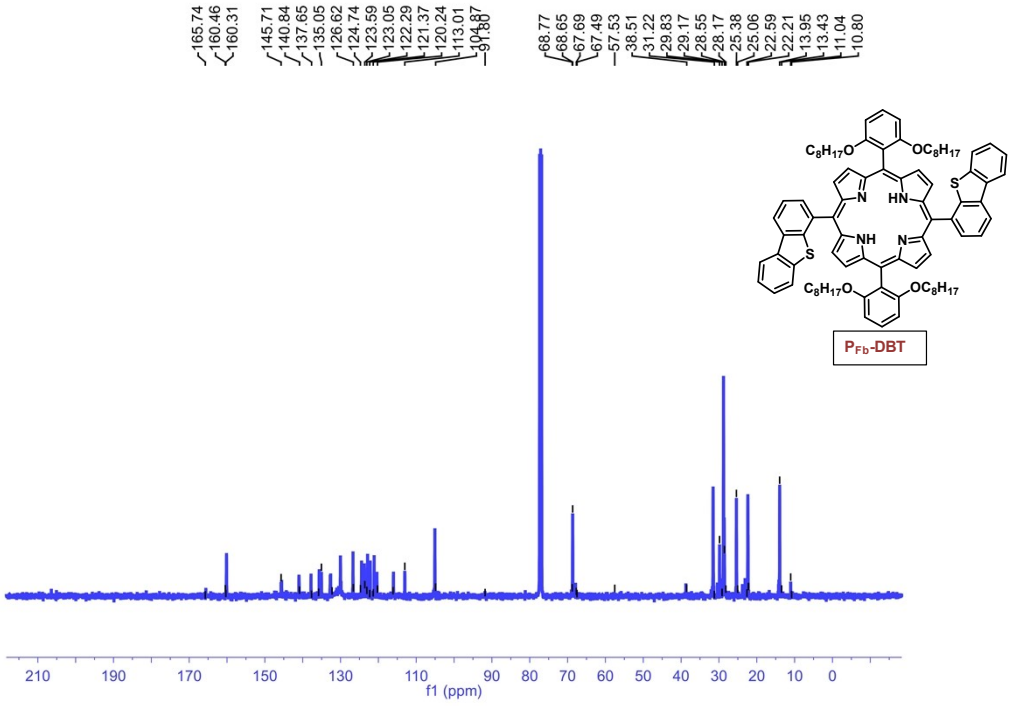


Figure S3. ^{13}C NMR Spectrum of P_{Fb}-DBT.

3.2. ^{13}C NMR of P_{Zn}-DBT:

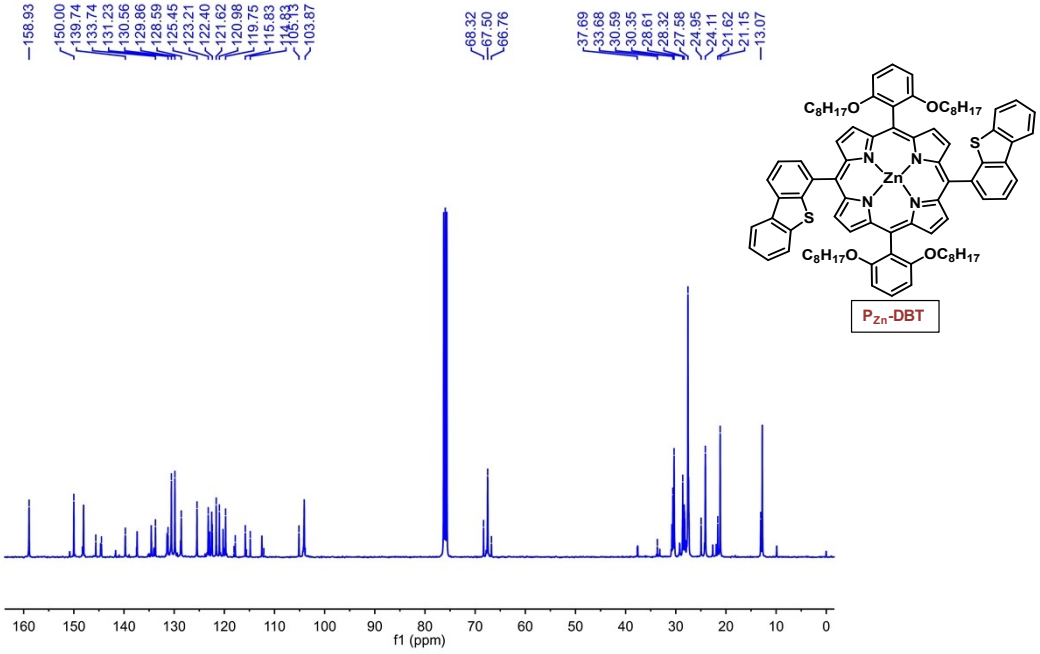


Figure S4. ^{13}C NMR Spectrum of P_{Zn}-DBT.

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).

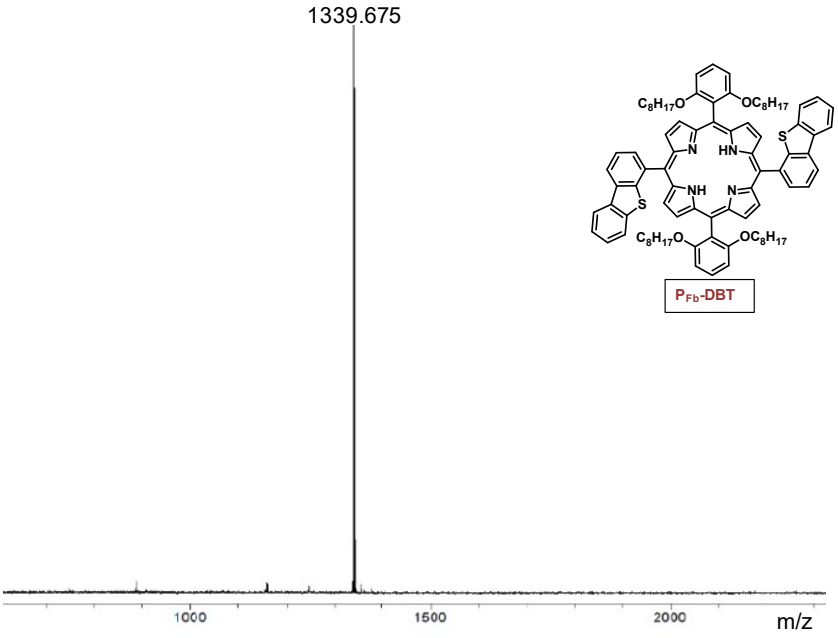


Figure S5. MALDI-TOF-MS Spectrum of P_{Fb}-DBT.

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

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

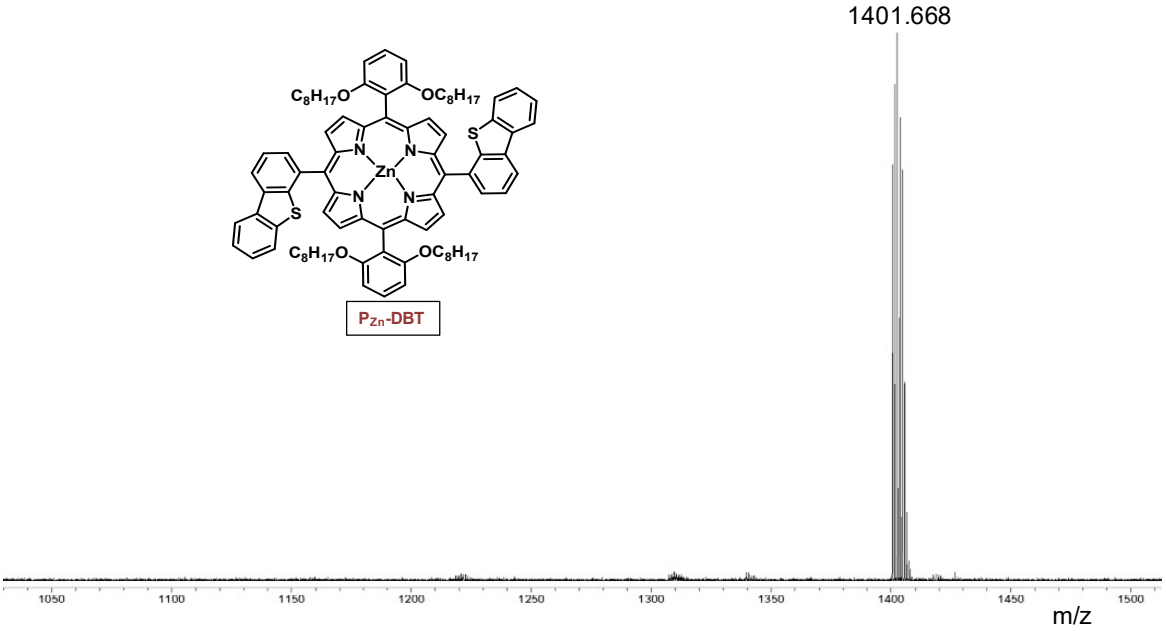


Figure S6. MALDI-TOF-MS Spectrum of P_{Zn}-DBT.

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

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

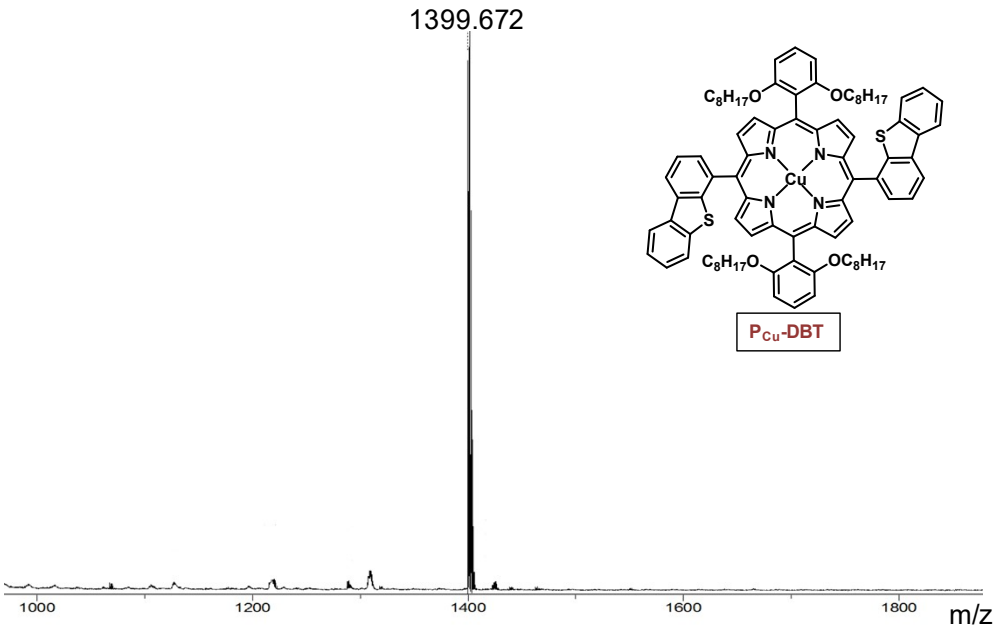


Figure S7. MALDI-TOF-MS Spectrum of P_{Cu}-DBT.

5. Theoretical calculations of P-DBT derivatives:

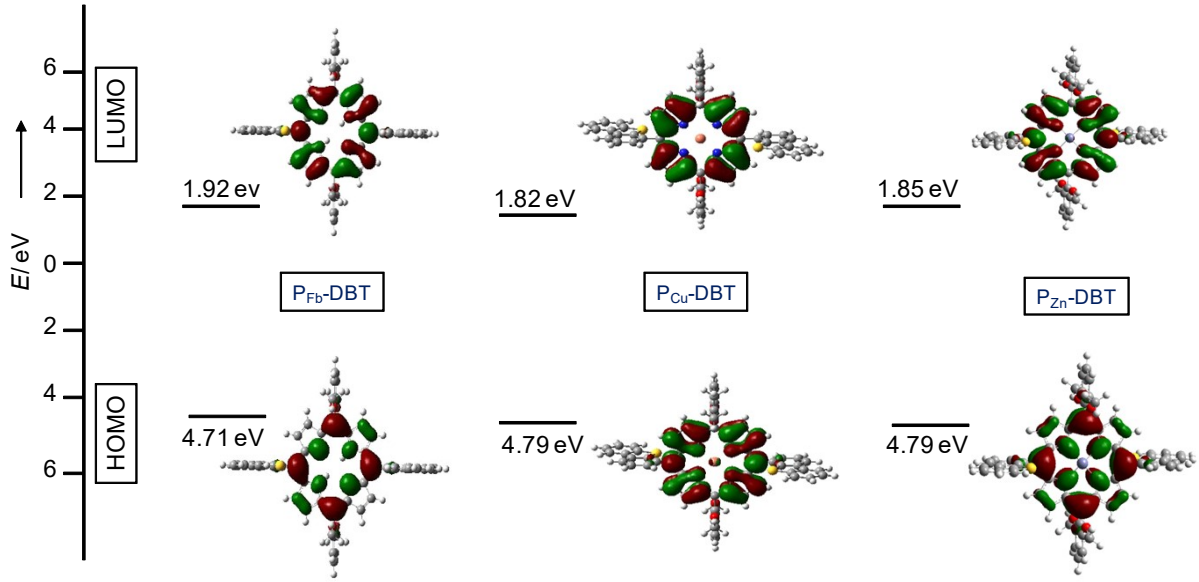


Figure S8. Theoretiecal calculations of **P_{Fb}-DBT, P_{Cu}-DBT** and **P_{Zn}-DBT** and their HOMO and LUMO energy levels.

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

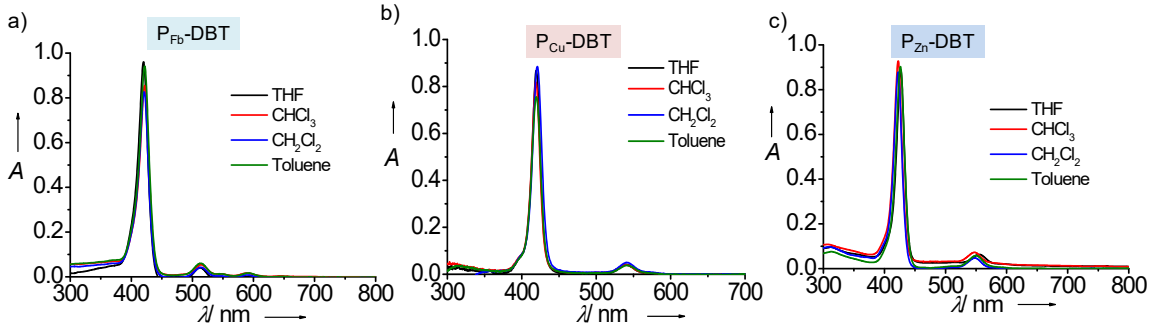


Figure S9. UV-vis optical absorption spectra of a) **P_{Fb}-DBT,** b) **P_{Cu}-DBT** and c) **P_{Zn}-DBT** in various solvents such as tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and toluene at a concentration of 1×10^{-4} M at 25 °C.

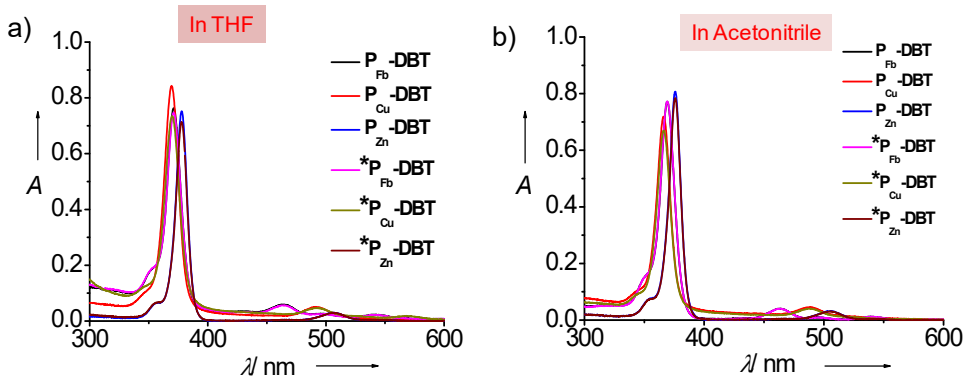


Figure S10. UV-vis optical absorption spectra of **P_{Fb}-DBT, P_{Cu}-DBT** and **P_{Zn}-DBT** in tetrhydrofuran (THF) and acetonitrile (ACN) at a concentration of 1×10^{-4} M at 25 °C.

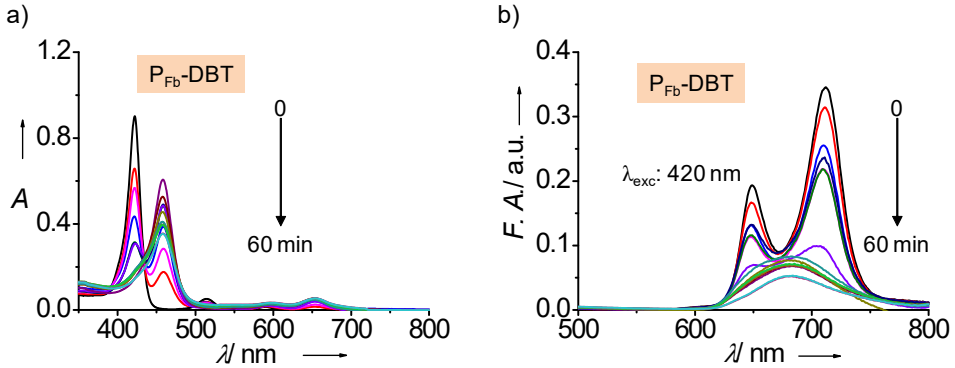


Figure S11. a) UV-vis optical absorption spectra of **P_{Fb}-DBT** in chloroform with different interval of time from 0 to 60 min at 25 °C. b) The corresponding emission spectra of **P_{Fb}-DBT** at an excitation wavelength of 420 nm.

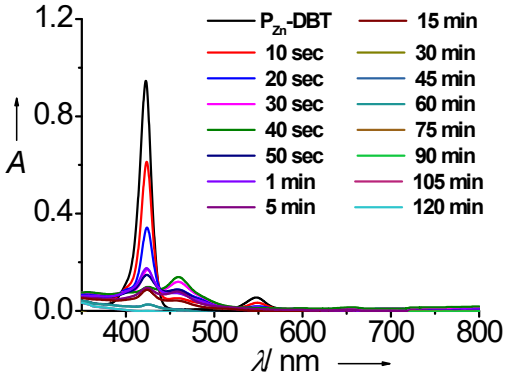


Figure S12. UV-vis optical absorption spectra of **P_{Zn}-DBT** in chloroform with different interval of time from 0 to 120 min at 25 °C.

Table S1. Photophysical and electrochemical data of **P-DBT** derivatives

S.No.	Samples	Absorption λ_{max} (nm)		Emission λ_{ems} (nm)	Lifetime τ (ns)		E_{Ox}	E_{Red}
		Before	After light		Before	After light		
1	**P_{Fb}-DBT**	421	457	728	8.41	4.48	1.302	-0.995
		514	597			8.70		
		589	652					
2	**P_{Cu}-DBT**	419	425	-	-	-	0.84	-0.983
		540					1.36	
3	**P_{Zn}-DBT**	422	423	668	2.89	0.64	0.66	-1.01
		547	460			3.48	1.22	

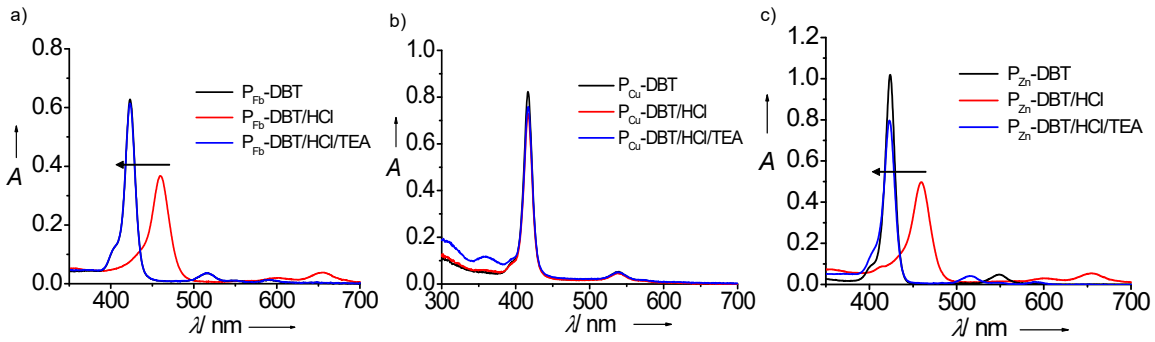


Figure S13. UV-vis optical absorption spectra of a) **P_{Fb}-DBT,** b) **P_{Cu}-DBT** and c) **P_{Zn}-DBT** in tetrahydrofuran and recorded their spectral changes whilst addition of acid and base.

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

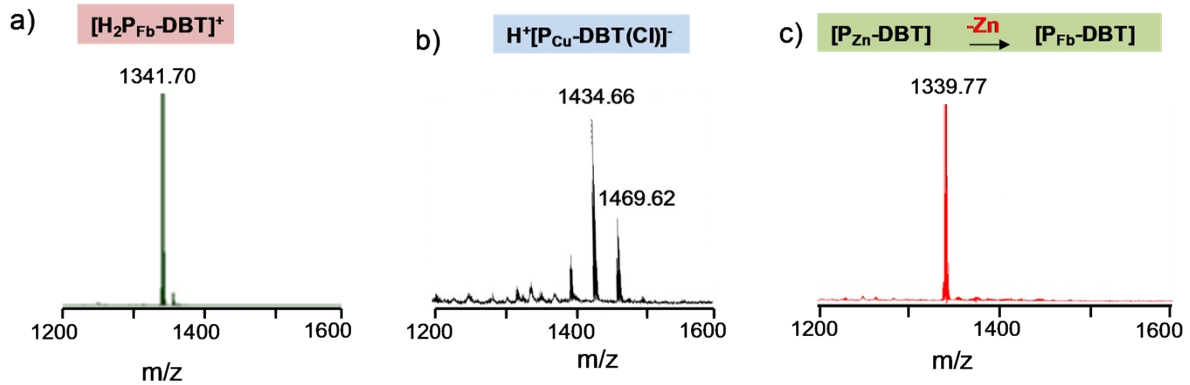


Figure S14. MALDI-TOF-MS spectra of light stimulated samples: a) **$[H_2P_{Fb}\text{-DBT}]^+Cl^-$,** b) **$H^+[P_{Cu}\text{-DBT(Cl)}]^-$** and c) P_{Fb}-DBT.

8 . Spectroelectrochemistry of P_{Fb}-DBT:

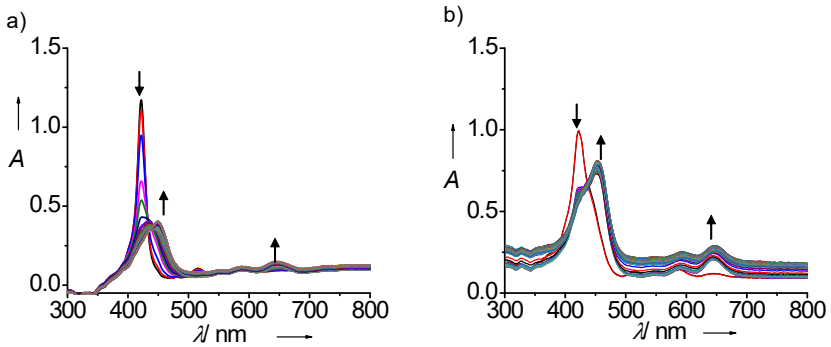


Figure S15. Spectroelectrochemical UV-vis optical absorption spectra of **P_{Fb}-DBT** in chloroform: a) oxidation potential (1.30 V) and b) reduction potential (-1.01 V).

9. Electron microscopic images of P_{Fb}-DBT :

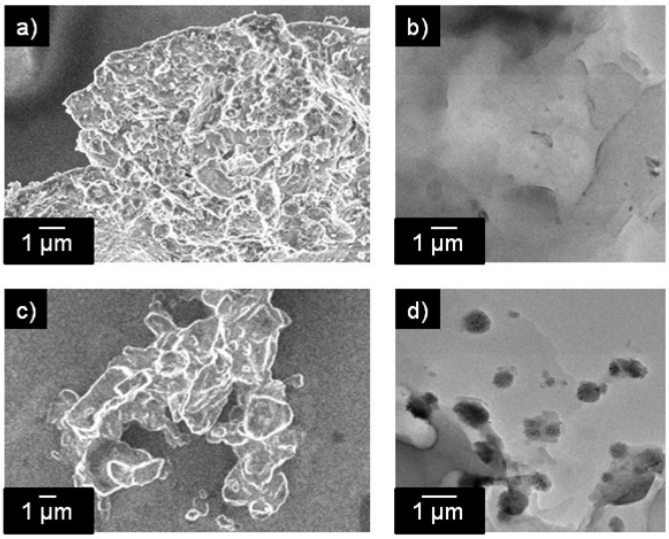


Figure S16. (a,b) Scanning electron microscopic and transmission electron microscopic images of **P_{Fb}-DBT** and **$[H_2P_{Fb}\text{-DBT}]^+Cl^-$** aggregates were drop-casted from methanol solution at 25 °C.

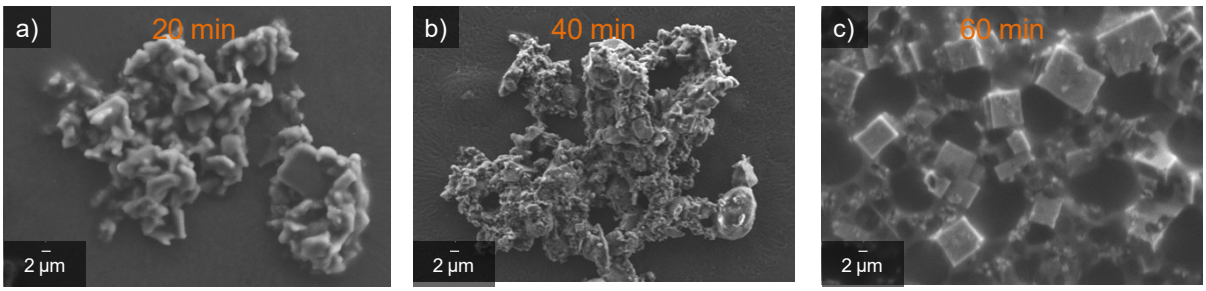


Figure S17. (a-d) Scanning electron microscopic images of light illuminated **P_{Fb}-DBT** aggregates were drop-casted from methanol solution at different time intervals of light illumination in chloroform.

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:

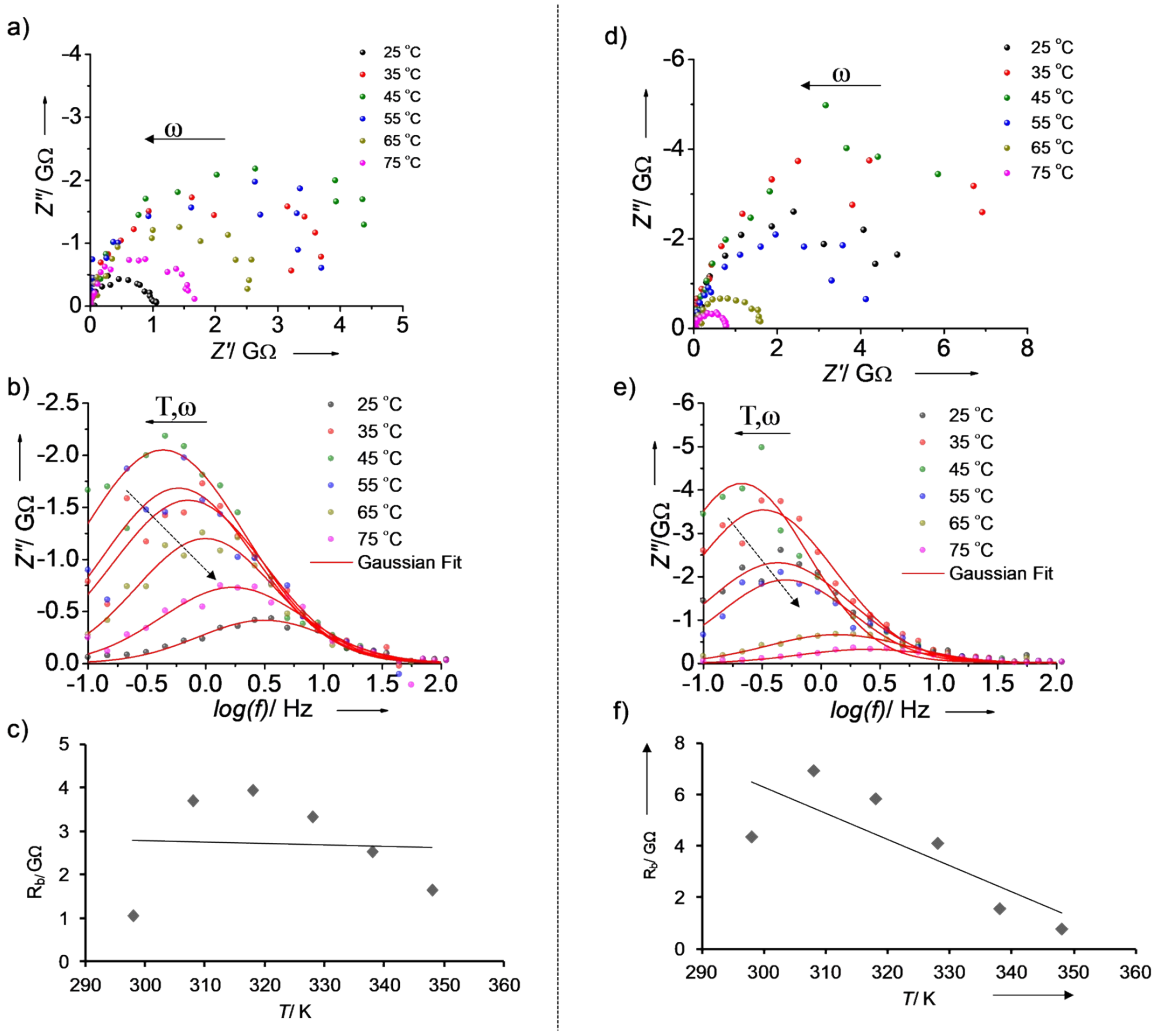


Figure S18. Electrochemical impedance spectral data of **P_{Fb}-DBT**. (a,d) Temperature dependent Nquist plot of before and after light illuminated **P_{Fb}-DBT** from 25 °C to 75 °C (b,e) Corresponding temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c,f) Plot represents 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_{Cu}-DBT:

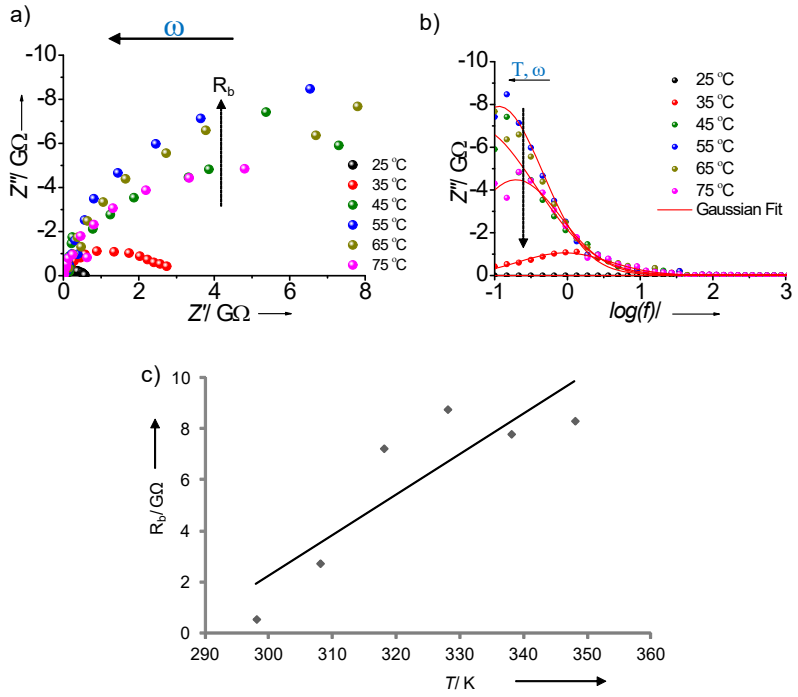


Figure S19. Electrochemical impedance spectral data of **P_{Cu}-DBT:** (a) Nquist plot with variable temperature from 25 °C to 75 °C. (b) Corresponding temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Plot represents the bulk resistance against temperature.

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

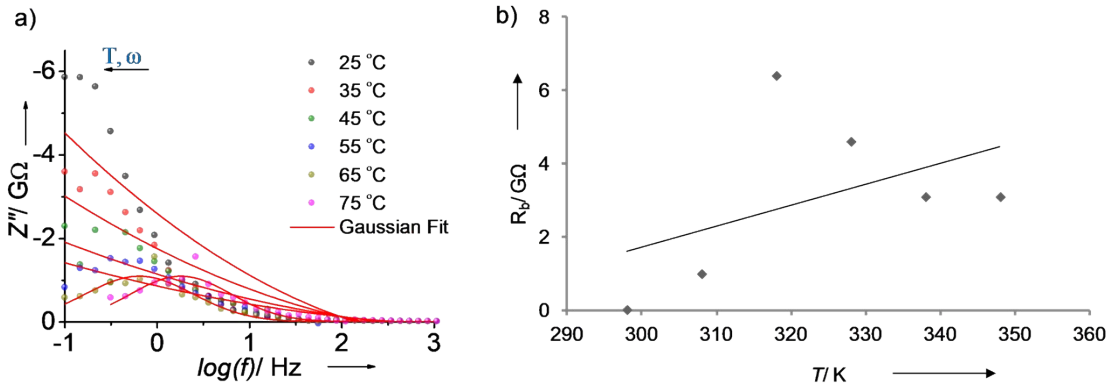


Figure S20. a) Temperature-dependent changes of logarithmic frequency vs Imaginary impedance. b) plot of bulk resistance against the increase in temperature from 25 °C to 75 °C (298 – 348 K) of light-illuminated **P_{Cu}-DBT**.

10.4. Summary of electrochemical impedance data of P_{Fb}-DBT and P_{Cu}-DBT:

Table S2. Electrochemical impedance spectroscopy data of **P_{Fb}-DBT** and **P_{Cu}-DBT**; where, R_b = bulk resistance; f_b = bulk frequency, σ = specific conductivity, C_b = bulk capacitance and τ_b = the bulk relaxation time and estimated for the samples at variable temperatures.(* represents light illuminated condition)

Samples	T (K)	R_b (GΩ)	f_b (MHz)	σx10^{-3} (S/cm)	C_b (fF)	τ_b (μs)
P_{Fb}-DBT						
	298	1.1	1.04	0.09	1.0	1.529
	308	3.7	2.54	0.03	0.2	0.626
	318	3.9	4.03	0.02	0.1	0.394
	328	3.3	3.20	0.03	0.2	0.497
	338	2.5	2.57	0.04	0.3	0.618
	348	1.6	2.03	0.06	0.5	0.782
P_{Fb}-DBT*						
	298	4.8	4.01	0.02	0.08	0.396
	308	6.9	4.48	0.01	0.05	0.355
	318	5.8	5.04	0.02	0.05	0.316
	328	4.1	4.01	0.03	0.10	0.396
	338	1.5	1.79	0.06	0.60	0.885
	348	7.6	1.61	0.01	1.0	0.989
P_{Cu}-DBT						
	298	0.5	7.97	0.17	0.40	0.199
	308	2.7	1.20	0.03	0.50	1.325
	318	7.2	2.20	0.013	0.09	0.721
	328	8.7	7.96	0.01	0.02	0.200
	338	7.8	7.94	0.012	0.03	0.201
	348	8.3	6.35	0.01	0.03	0.250
P_{Cu}-DBT*						
	298	0.0002	2.53	38.0	252.0	0.628
	308	0.1	1.62	0.09	1.0	0.980
	318	6.4	7.73	0.01	0.03	0.205
	328	4.6	0.64	0.02	0.05	0.249
	338	3.0	0.64	0.03	0.08	0.249
	348	3.1	5.03	0.03	0.10	0.316