Solvent/Metal-Free Benzimidazolium-Based Carboxyl Functionalized

Porphyrin Photocatalyst for Room-Temperature Alkylation of Amines

under Irradiation of Visible Light

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Fig.S1.¹H NMR Spectrum of compound 4B



Fig.S2.¹³C NMR Spectrum of compound 4B



Fig.S3 FT-IR Spectrum of compound 4B



Fig.S4 GCMS Spectrum of compound 4B



Fig.S5¹H NMR Spectrum of compound 4C



Fig. S6¹³CNMR Spectrum of compound 4C



Fig.S7. FT-IR Spectrum of Compound 4C



Fig.S8 GCMS Spectrum of compound 4C



Fig.S9 ¹H NMR Spectrum of Compound 4D



Fig.S10¹³ CNMR Spectrum of compound 4D



Fig.S11. ¹H NMR spectrum of compound 4E



Fig.S12. ¹³ CNMR spectrum of compound 4E







Fig.S14. ¹H NMR spectrum of compound 4F



Fig.S15. ¹³CNMR spectrum of compound 4F



Fig.S16. FT-IR spectrum of compound 4F



Fig.S17.¹H NMR spectrum of Photocatalyst (MFBBCFPc)





Fig.S19¹H NMR spectrum of N-ethyl aniline (**D1**)



Fig.S20 GCMS spectrum of N-ethyl aniline (D1)



Fig.S21. ¹H NMR spectrum of N-ethyl-4-nitroaniline (**D2**)



Fig.S22 ¹H NMR spectrum of N¹, N⁴-dimethylbenzene-1, 4-diamine (D3)



Fig.S23 GCMS spectrum of N¹, N⁴-dimethylbenzene-1, 4-diamine (D3)



Fig.S24 ¹H NMR spectrum of N¹, N⁴-diethylbenzene-1,4-diamine (**D4**)



Fig.S25 ¹H NMR spectrum of N^1 , N^4 -dipropylbenzene-1, 4-diamine (**D5**)



Fig.S26 GCMS Spectrum of N1,N4-Dipropylbenzene-1,4-diamine (D5)



FigS.27 ¹H NMR spectrum of 4-chloro-N, N-dimethyl aniline (**D6**)



Fig. S28¹³ CNMR spectrum of 4-chloro-N, N-dimethyl aniline (D6)



Fig.S29 GCMS spectrum of 4-chloro-N, N-dimethyl aniline (D6)



Fig. S30 ¹H NMR spectrum of 4-chloro-N,N-diethylaniline (**D7**)



Fig. S31¹³ CNMR spectrum of 4-chloro-N,N-diethylaniline (**D7**)



Fig. S32 GCMS spectrum of 4-chloro-N,N-diethylaniline (D7)



Fig. S33 ¹H NMR spectrum of 4-chloro-N,N-dipropylaniline (**D8**)



Fig. S34 ¹³C NMR spectrum of 4-chloro-N,N-dipropylaniline (D8)



Fig. S35 ¹H NMR spectrum of 4-chloro-N, N-dibutylaniline (**D9**)



Fig. S36 ¹H NMR spectrum of 4-bromo-N,N-dimethylaniline (D10)



Fig.S37 ¹H NMR spectrum of 4-bromo-N,N-diethylaniline (**D11**)



Fig. S38 GCMS spectrum of 4-bromo-N,N-diethylaniline (D11)



Fig.S39¹H NMR 4-bromo-N, N-dipropylaniline (D12)



Fig. S40 ¹H NMR spectrum of 4-bromo-N, N-dibutylaniline (**D13**)



Fig. S41 ¹H NMR spectrum of 4-bromo-N, N-dipentylaniline (**D14**)



Fig. S42 ¹H NMR spectrum of 1-methyl-1H-pyrrole (**D15**)



Fig. S43 GCMS spectrum of 1-methyl-1H-pyrrole (D15)



Fig. S44 ¹H NMR spectrum of 1-ethyl-1H-pyrrole (**D16**)



Fig. S45 GCMS spectrum of 1-ethyl-1H-pyrrole (D16)



Fig. S46 ¹HNMR spectrum of 1-Propyl l-1H-pyrrole (**D17**)



Fig. S47 GCMS spectrum of 1-Propyl l-1H-pyrrole (D17)



Fig. S48 ¹H NMR spectrum of 1-Butyl l-1H-pyrrole (D18)



Fig. S49 GCMS spectrum of 1-Butyl l-1H-pyrrole (D18)



Fig.S50 ¹H NMR spectrum of 1-pentyl-1H-pyrrole (D19)



Fig.S51 ¹H NMR spectrum of 1-hexyl-1H-pyrrole (**D20**)



Fig.S52¹³ CNMR spectrum of 1-hexyl-1H-pyrrole (D20)



Fig.S53 ¹³ GCMS spectrum of 1-hexyl-1H-pyrrole (**D20**)



Fig.S54 ¹H NMR spectrum of 4-methylmorpholine (**D21**)



Fig.S55 ¹H NMR spectrum of 4-Ethyl morpholine (**D22**)



Fig.S56 ¹H NMR spectrum of 4-Propyl morpholine (**D23**)



Fig.S57¹³ CNMR spectrum of 4-propylmorpholine (**D23**)



Fig. S58 ¹H NMR spectrum of 4-butylmorpholine (D24)



Fig. S59 ¹H NMR spectrum of 4-pentylmorpholine (**D25**)



Fig. S60 ¹³C NMR spectrum of 4-pentylmorpholine (**D25**)



Fig. S61 ¹H NMR spectrum of 4-hexylmorpholine (**D26**)



Fig. S62 ¹³C NMR spectrum of 4-hexylmorpholine (**D26**)



Fig. S63 ¹H NMR spectrum of 4-octylmorpholine (**D27**)



Fig. S64 ¹³C NMR spectrum of 4-octylmorpholine (**D27**)



Fig. S65 ¹H NMR spectrum of N¹, N⁴-dibenzylbenzene-1,4-diamine (**D28**)



Fig. S66 ¹H NMR spectrum of N¹,N⁴-bis(furan-2-ylmethyl)benzene-1,4-diamine(**D29**)



Fig. S67 ¹H NMR spectrum of N-benzylaniline (D30)



Fig. S68 ¹H NMR spectrum of N-(furan-2-ylmethyl) aniline (**D31**)



Fig. S69 ¹GCMS spectrum of N-(furan-2-ylmethyl) aniline (D31)



Fig. S70 Leaching test of photocatalyst under optimized conditions



Fig. S71 Home-made Photocatalytic Reactor



Fig. S72. Atomic absorption spectroscopy of Zn

Sr.no	Porphyrin	Range of	References
	catalyst	energies in XPS	
1.	Zn-TESP	Zn 2p _{3/2} B.E range 1020- 1025 eV	Killian, M. S., Gnichwitz, J. F., Hirsch, A., Schmuki, P., & Kunze, J. (2010). ToF-SIMS and XPS studies of the adsorption characteristics of a Zn-porphyrin on TiO ₂ . <i>Langmuir</i> , <i>26</i> (5), 3531-3538.
2.	Platinum complex/Zn- porphyrin	Pt 4f _{7/2} B.E range 70-73 eV	Polzonetti, G., Ferri, A., Russo, M. V., Iucci, G., Licoccia, S., & Paolesse, R. (1999). Platinum complex/Zn-porphyrin macrosystem assemblies: Electronic structure and conformational investigation by x-ray photoelectron spectroscopy. <i>Journal of Vacuum Science & Technology A:</i> <i>Vacuum, Surfaces, and Films, 17</i> (3), 832-839.
3.	Porphyrin- based porous polyimide polymer/Pd nanoparticle	Pd 3d _{5/2} B.E range 335-345 eV	Zhu, W., Wang, X., Li, T., Shen, R., Hao, S. J., Li, Y., & Gu, Z. G. (2018). Porphyrin-based porous polyimide polymer/Pd nanoparticle composites as efficient catalysts for Suzuki–Miyaura coupling reactions. Polymer Chemistry, 9(12), 1430-1438.
4.	Fe (III) Porphyrin surface anchored TiO ₂	Fe 2p _{3/2} B.E 710 eV	ArunaKumari, M. L., & Devi, L. G. (2015). New insights into the origin of the visible light photocatalytic activity of Fe (III) porphyrin surface anchored TiO ₂ . Environmental Science: Water Research & Technology, 1(2), 177-187.
5.	MFBBCFPc	No evidence of metal B.E with respect to Zn/ Pt/ Pd/ Fe observed in MFBBCFPc photocatalyst	Present work (Fig.6 (a) XPS survey of MFBBCFPc, (b) High resolution of O1s of MFBBCFPc, (c) High resolution of N1s of MFBBCFPc, (d) High resolution of C1s of MFBBCFPc, (e) High resolution of Br3d of MFBBCFPc)

Table S1. Comparison of binding energies of different metals in XPS

Table S2. Elemental ID and Quantification obtained from XPS data

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
C1s	285.53	1.75	895404.71	67.88	1
O1s	532.95	3.27	318090.56	9.98	1
N1s	400.95	3.49	171619.32	8.39	1
Br3d	68.83	2.97	43531.69	1.06	1
Si2p ???	102.96	4.01	11327.96	0.86	1
S2p ???	169.59	2.00	10906.55	0.41	1
Br3d	67.91	2.02	5675.21	0.14	1
C1s	284.87	1.73	116234.76	8.81	1
N1s	400.44	2.99	22530.84	1.10	1
O1s	532.49	2.72	43977.98	1.38	1

Sample	Conc mg/L	Mean Abs
ID		
Std 1	5	0.8688
Std 2	10	1.0359
Std 3	15	1.294
SR-158	Х	0.1461

Table S3. Atomic absorption spectroscopy of Zn

 $X=0.812\ mg/L$

Table S4. ICP-OES of CN-35 and MFBBCFPC

SOPHISTICATED ANALYTICAL INSTRUMENT FACILITY IIT MADRAS, CHENNAI-36 PERKIN ELMER OPTIMA 5300 DV ICP-OES Sample code Element symbol and Concn.in ppm Wavelength (nm) ug/ml (or) mg/litre

Sample code	Wavelength (nm)	Concn.in ppm μg/ml (or) mg/litre
CN-35	Fe 238.204	0.070 mg/L
	Pd 340.458	BDL
	Ru 240.272	0.002 mg/L
	Zn 206.200	0.020 mg/L
MFBBCFPC	Fe 238.204	0.912 mg/L
	Pd 340.458	BDL
	Ru 240.272	0.013 mg/L
	Zn 206.200	0.678 mg/L