Electronic Supporting Information

Ruthenium(III)-bis(phenolato)bipyridine/TiO_2 hybrids : unprecedented photocatalytic hydrogen evolution

Binitendra Naath Mongal,*[†] Amritanjali Tiwari,[‡,§] Malapaka Chandrasekharam,[†,§] and Ujjwal Pal*[‡,§]

[†]Polymer & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, India

[‡]Centre for Environmental Engineering and Fossil Fuels, CSIR-Indian Institute of Chemical Technology, Hyderabad, India

[§]Academy of Scientific and Innovative Research (AcSIR), New Delhi, India

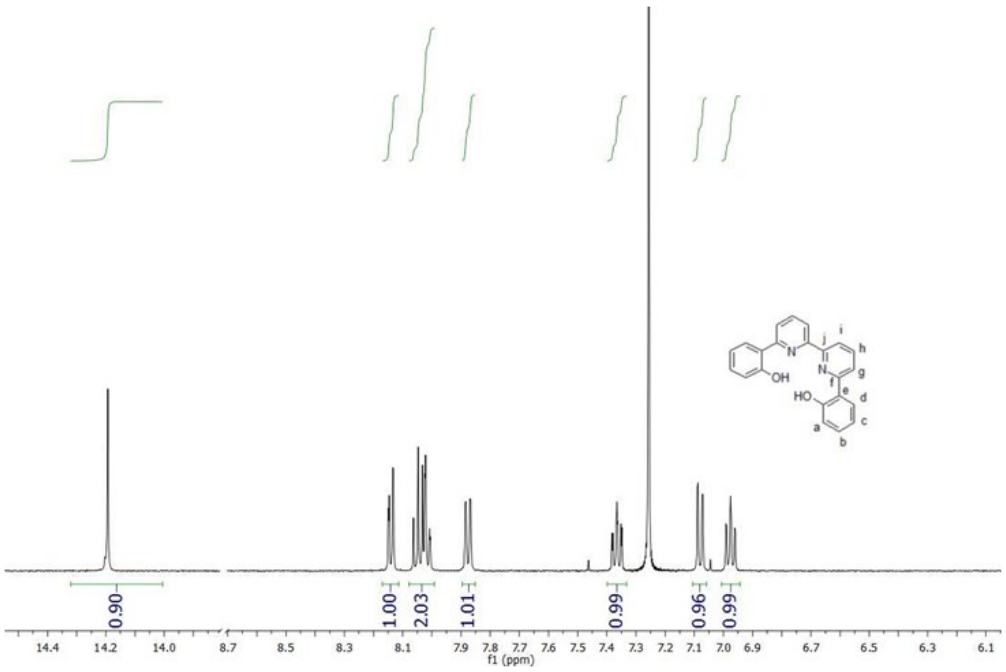

Figure S1. NMR spectra of the ligand H_2L.

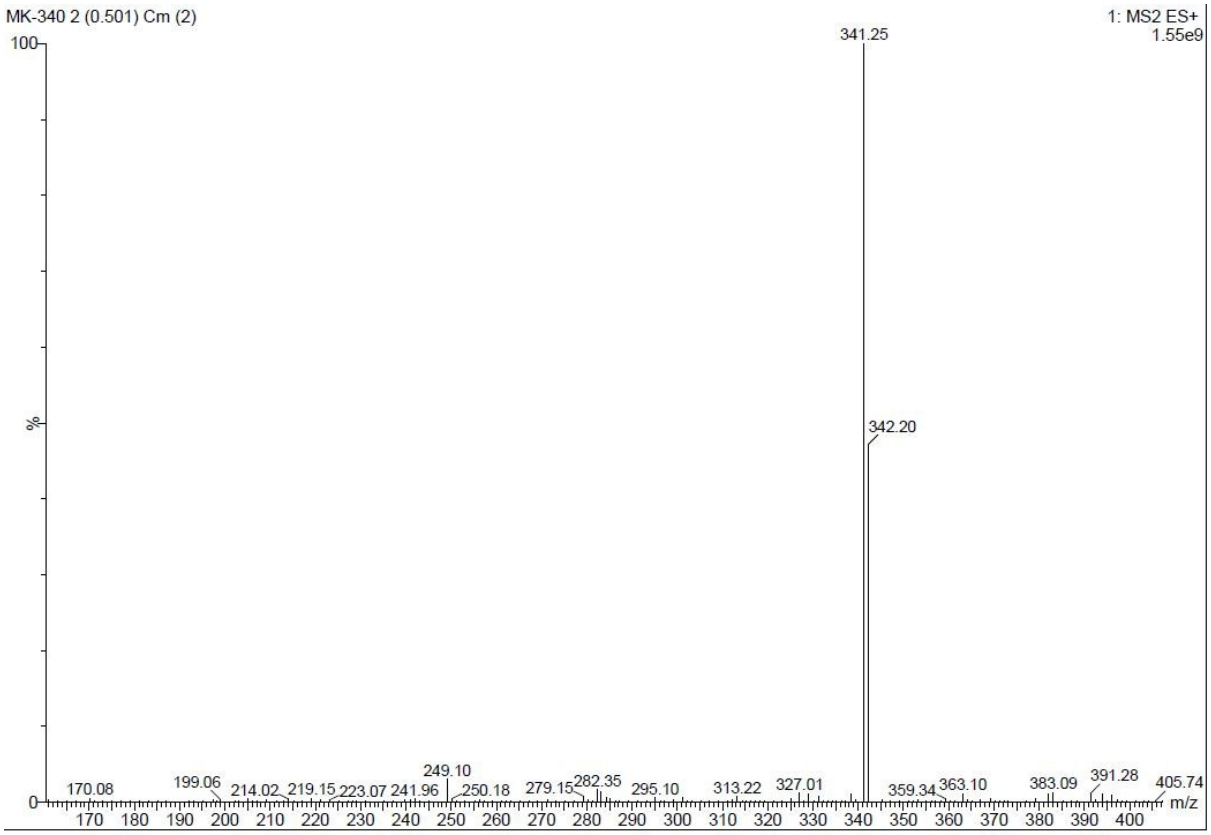

Figure S2. ESI Mass Spectrum of the ligand H_2L.

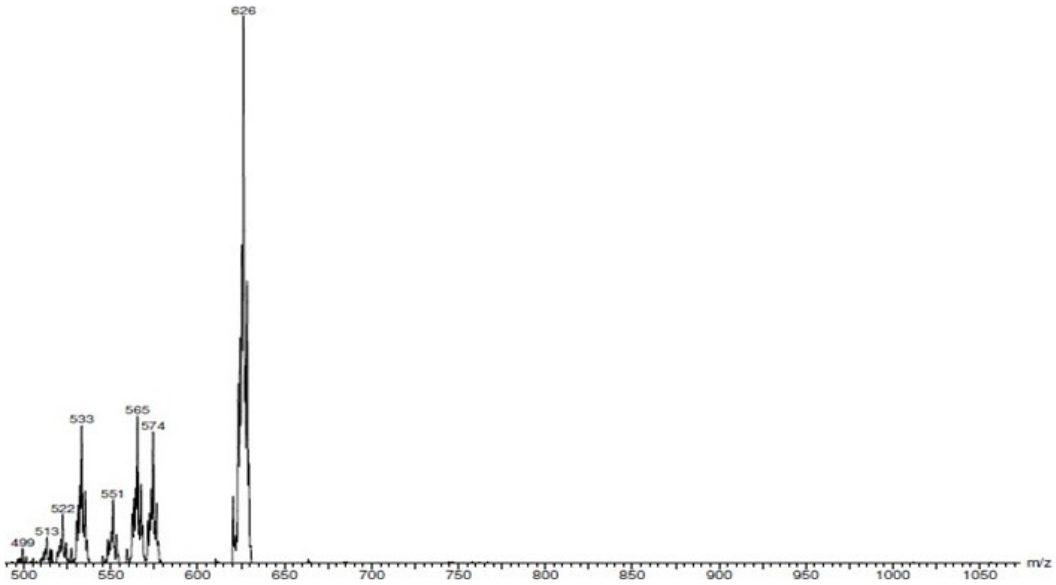

Figure S3. ESI Mass Spectrum of MCS-B4M

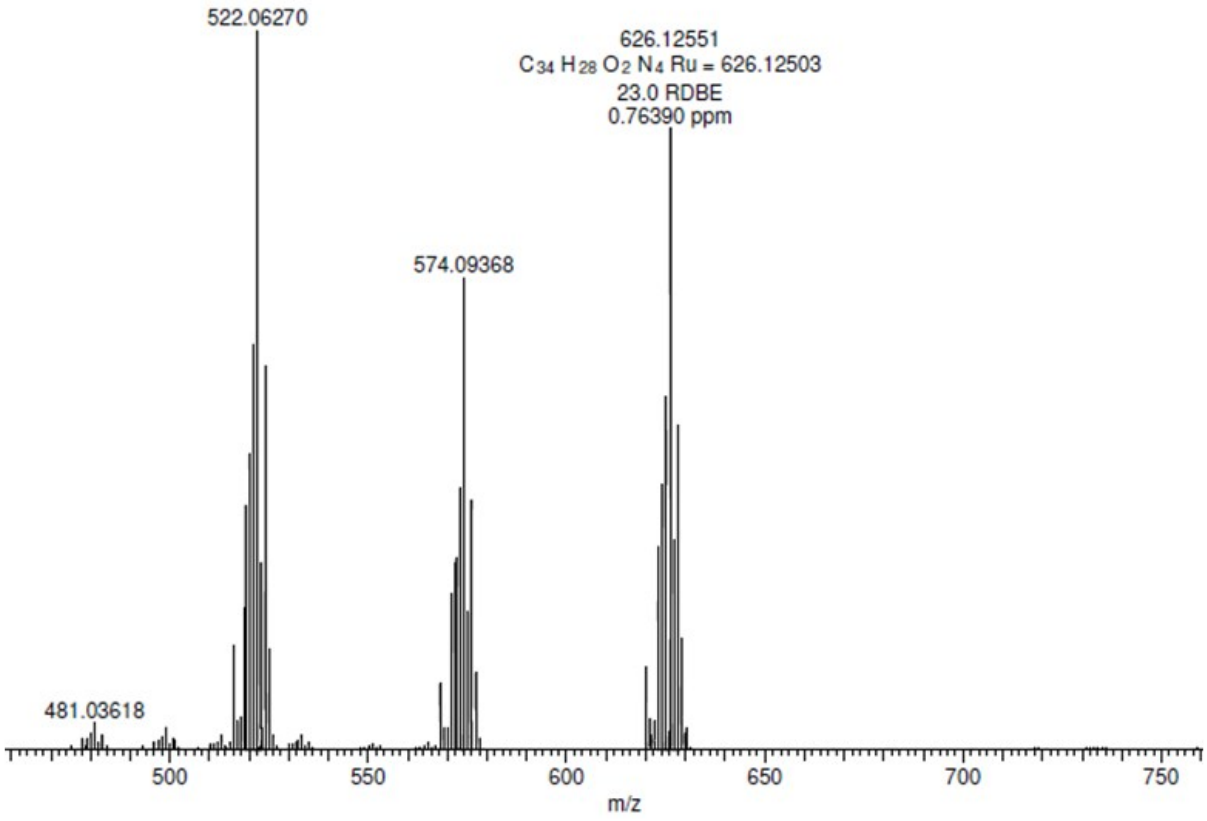

Figure S4. High resolution Mass spectrum of MCS-B4M

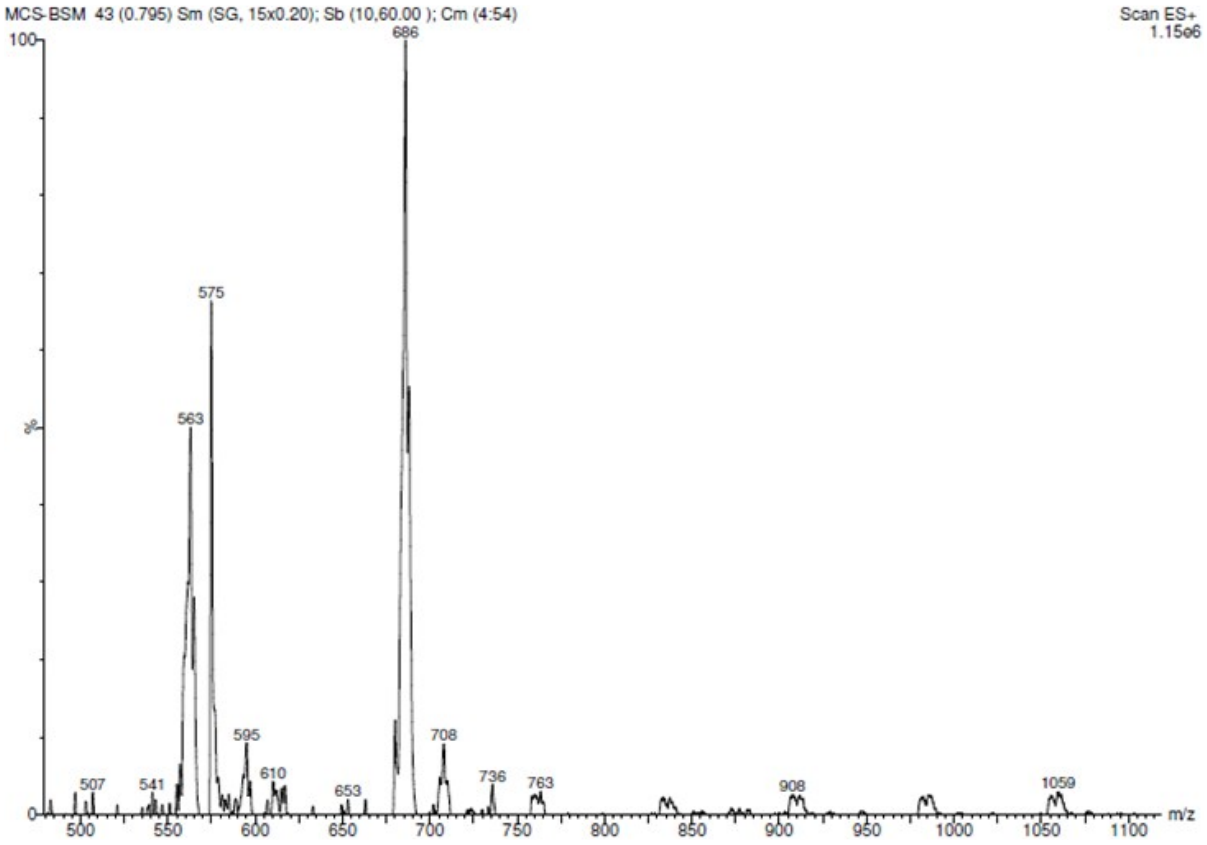

Figure S5. ESI Mass spectrum of MCS-B5M

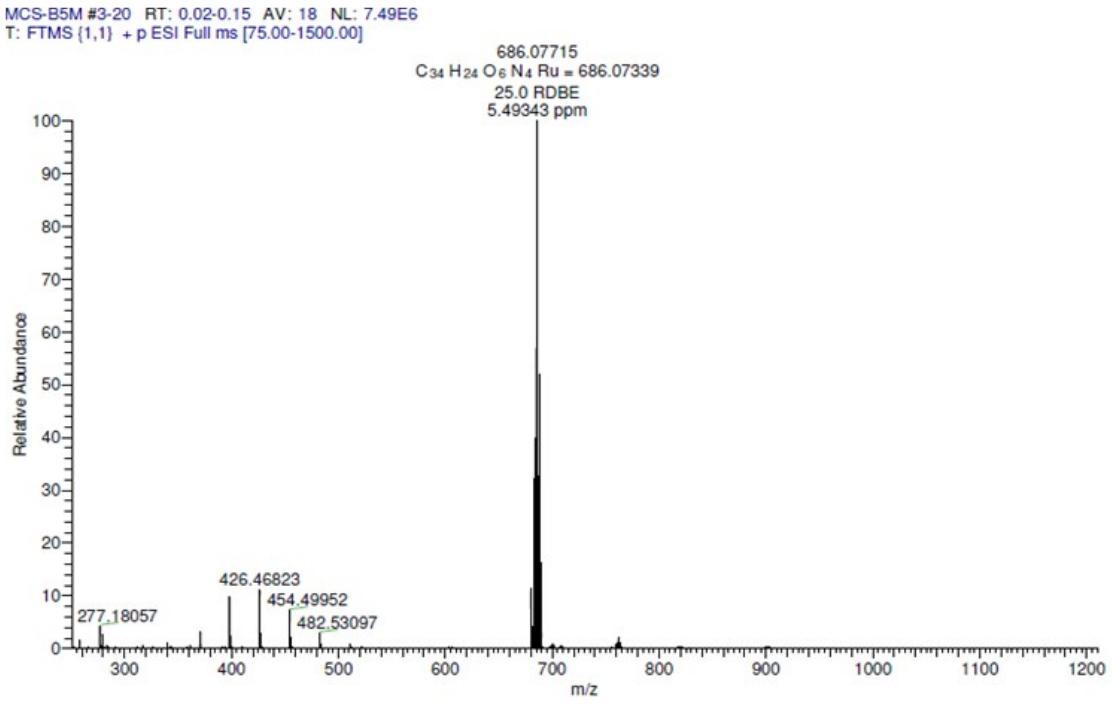

Figure S6. High resolution Mass Spectrum of MCS-B5M

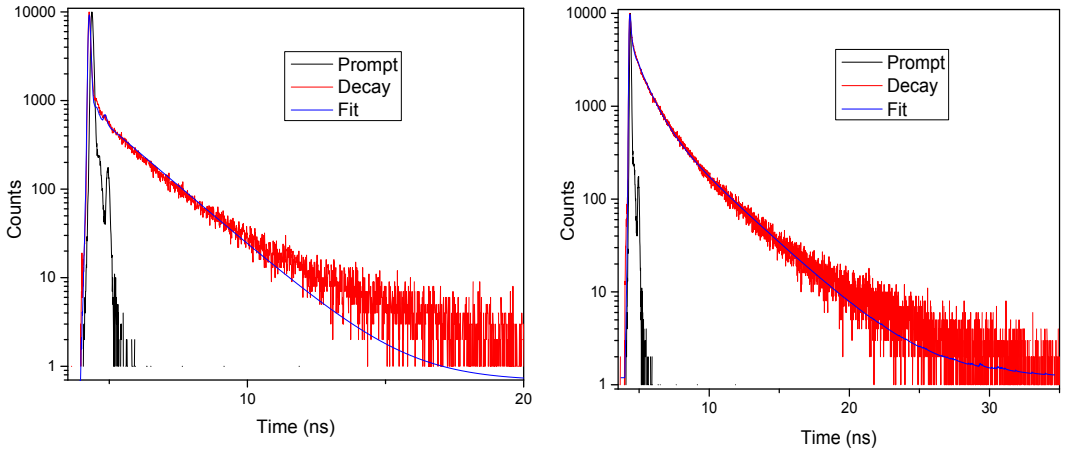

Figure S7. Excited state lifetime decay profile of MCS-B4M (left) and MCS-B5M (right).

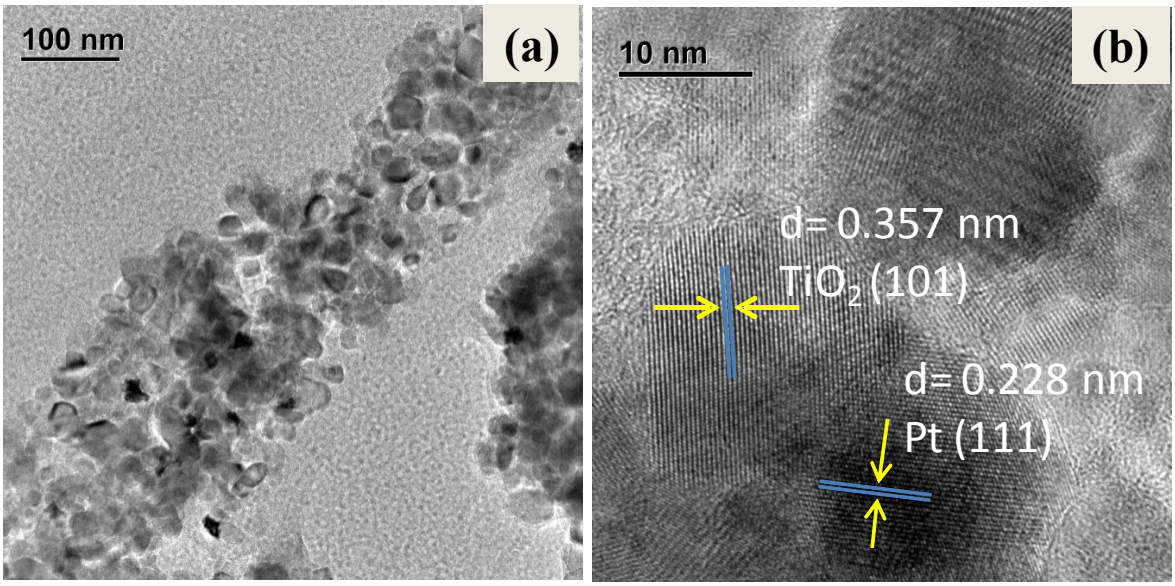

Figure S8. TEM images Pt-TiO_2 (a) low and (b) high magnification

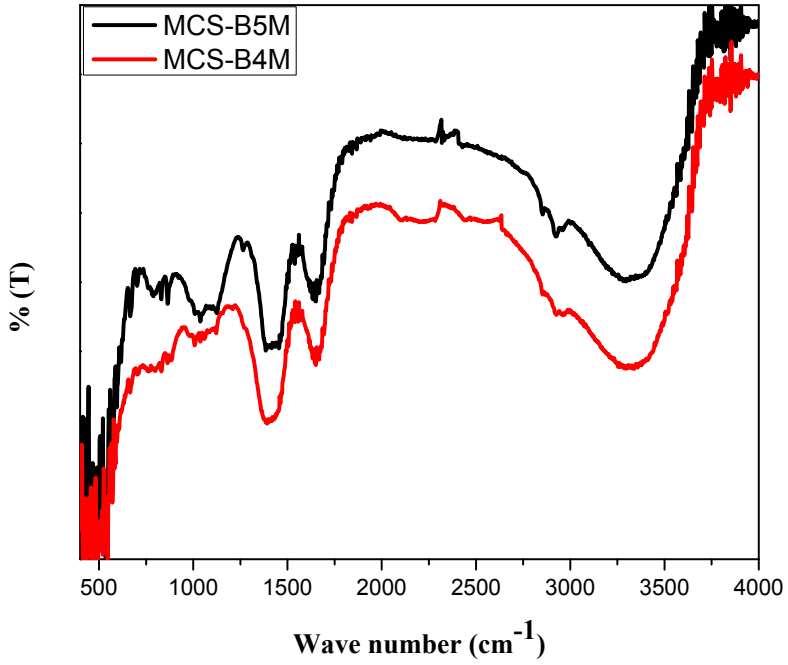

Figure S9. FT-IR spectra of MCS-B4M (red) and MCS-B5M (black).

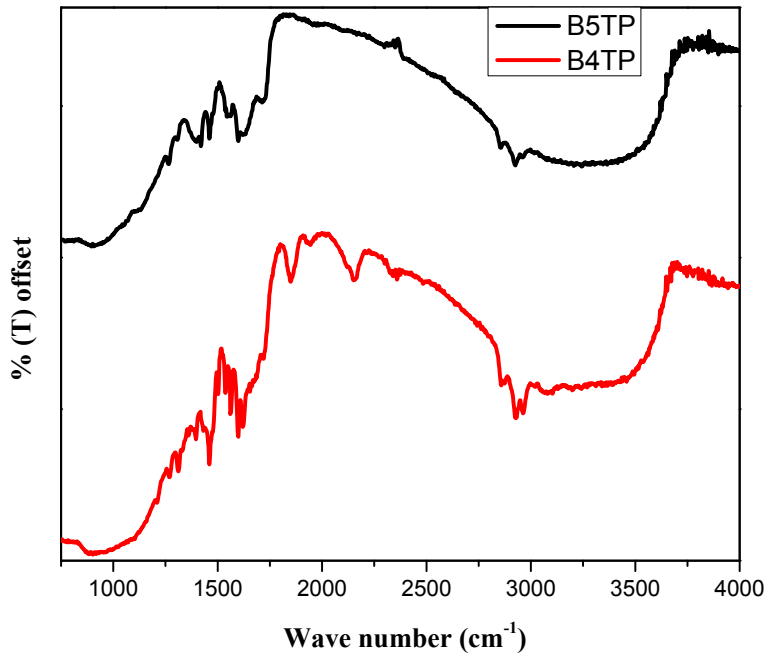

Figure S10. FT-IR spectra of B4TP (red) and B5TP (black).

Table S1. Photocatalytic activity and average TON of prepared photocatalyst

Photocatalyst	H_2O + TEOA solution	H_2 Yield (µmol)	TON	TON (average)
B5TP	9:1	21239	84,956	84,600
		21149	84,596	
		21062	84,250	
B4TP	9:1	15467	61,868	61,482
		15363	61,452	
		15282	61,128	
N719TP	9:1	5336	21,344	21,152
		5276	21,104	
		5252	21,010	

Apparent quantum efficiency:[1,2]

The apparent quantum efficiency was measured by the following equation:

$$\eta_{photons} = \frac{P\lambda}{hc} \times t$$

Where,

Ηphotons	=	No. of photons
P	=	Power of light
λ	=	Wavelength
t	=	Time
h	=	Planck's constant
c	=	Velocity of light

In the study, we use 300 W Xe lamp with ≥ 420 nm band-pass filter and the incident photon number is determined by optical power/energy meter (Newport, model: 842-PE). The average incident irradiation is determined to be 0.16 W/cm^2 by Newport (Oriel instrument solar simulator, USA model) and area was 7.4 cm^2 for a photo reacted solution mixture. The amount of hydrogen gas produced in 5 h for B4TP, B5TP and N719TP was 15467, 21239 and 5336 μmol, respectively. Here, we calculate the quantum efficiency at λ ≥ 420 for B4TP, B5TP and N719TP and the calculations are given below.

Number of incident photons (η) in 5 h over 7.4 cm^2 area of irradiated zone in the photoreactor:

$$= \frac{0.16\ J.s^{-1}.cm^{-2} \times 7.4\ cm^2 \times 5 \times 3600\ s \times 420 \times 10^{-9}\ m}{6.626 \times 10^{-34}\ J.s \times 3 \times 10^{8}\ m.s^{-1}} = 4.5 \times 10^{22}$$

Therefore, incident photon = 4.5×10^{22}

$$QE = 2 \times \frac{\text{Number of evolved } H_2 \text{ molecule}}{\text{Number of incident photon}} \times 100\%$$

$$QE_{B4TP} = 2 \times \frac{15467 \times 10^{-6} \times 6.023 \times 10^{23}}{4.5 \times 10^{22}} \times 100\% = 41.4\ \%$$

$$QE_{B5TP} = 2 \times \frac{21239 \times 10^{-6} \times 6.023 \times 10^{23}}{4.5 \times 10^{22}} \times 100\% = 57.2\ \%$$

$$QE_{N719TP} = 2 \times \frac{5336 \times 10^{-6} \times 6.023 \times 10^{23}}{4.5 \times 10^{22}} \times 100\% = 14.2\ \%$$

DFT Optimised parameters for MCS-B4M

Ru	-0.00790260	0.07225629	-0.17695070
C	2.64777829	0.36780466	1.16230703
C	0.69763792	0.62610969	2.49643466
C	3.41209843	0.79328911	2.27020793
C	1.44048316	0.97853592	3.61897944
C	2.82124353	1.08641441	3.48801419
H	4.48771048	0.91496986	2.16169971
H	0.95039312	1.19226590	4.56814541
H	3.43462063	1.40878549	4.33214367
C	-0.77341300	0.53627612	2.49692356
C	-2.67968219	0.04790585	1.16319963
C	-1.55204939	0.79257006	3.62124005
C	-3.48826334	0.37445894	2.27346566
C	-2.93582915	0.73233580	3.49186566
H	-1.09034634	1.06061299	4.57085325
H	-4.57087436	0.36550949	2.16723361
H	-3.58284107	0.97444449	4.33771598
N	1.29054011	0.35650233	1.29739188
N	-1.33071957	0.19936514	1.29750759
O	-1.40279977	-0.17900460	-1.62652575
O	1.40755409	-0.00771906	-1.62716790
C	3.30605682	-0.03846464	-0.08987470
C	2.66657732	-0.14523054	-1.37987088
C	4.69315034	-0.33614952	-0.02763006

C	3.50069991	-0.43010352	-2.50440225
C	5.46138227	-0.65021072	-1.12901342
H	5.18411620	-0.35340987	0.94648167
C	4.84890187	-0.67473300	-2.39383287
H	2.99312721	-0.46559509	-3.47097042
H	6.52135255	-0.88436849	-1.01227930
H	5.43583777	-0.90535544	-3.28757394
C	-3.28604077	-0.42927657	-0.09020592
C	-2.63746839	-0.46179592	-1.37962865
C	-4.62967340	-0.88493131	-0.02958985
C	-3.43186385	-0.84231968	-2.50471615
C	-5.35583188	-1.28501847	-1.13146080
H	-5.11640451	-0.95904330	0.94383255
C	-4.74320946	-1.23995428	-2.39555723
H	-2.92253540	-0.81980343	-3.47074285
H	-6.38200621	-1.63926948	-1.01554888
H	-5.29860200	-1.53717300	-3.28978877
C	-0.14441466	2.45041831	-1.88475425
C	-0.20588997	3.08295857	0.32637883
C	-0.22625470	3.77150448	-2.29920323
H	-0.08680070	1.62067247	-2.59019073
C	-0.28938203	4.42565197	-0.01525493
H	-0.20034148	2.77961371	1.37514535
C	-0.29915223	4.80609765	-1.36053512
H	-0.23491730	3.98857010	-3.36991612

H	-0.34955348	5.17391533	0.77837568
C	0.15563980	-2.66486820	-1.21400828
C	0.17856475	-2.67614158	1.08858578
C	0.24572511	-4.04838837	-1.25488042
H	0.10376836	-2.05367789	-2.11660057
C	0.26949899	-4.05967471	1.12267590
H	0.14819427	-2.09472820	2.01252773
C	0.30786473	-4.78928175	-0.07035419
H	0.26483346	-4.54752266	-2.22641972
H	0.30837631	-4.56669463	2.08951870
N	-0.13258232	2.10289611	-0.58498501
N	0.12261964	-1.97991893	-0.05702286
C	-0.35923786	6.24372871	-1.77730006
H	-0.76101733	6.88140396	-0.97740629
H	0.64870085	6.61684132	-2.02462004
H	-0.98258142	6.37548998	-2.67383593
C	0.43667358	-6.28169871	-0.08058194
H	1.49391330	-6.57727976	-0.18790249
H	0.06323229	-6.72689849	0.85246089
H	-0.11260375	-6.72658770	-0.92293809

1 18 1.0 19 1.0 20 1.0 21 1.0 60 1.0 61 1.0

2 4 1.5 18 1.5 22 1.0

3 5 1.5 10 1.0 18 1.5

4 6 1.5 7 1.0

5 6 1.5 8 1.0

6 9 1.0

7

8

9

10 12 1.5 19 1.5

11 13 1.5 19 1.5 32 1.0

12 14 1.5 15 1.0

13 14 1.5 16 1.0

14 17 1.0

15

16

17

18

19

20 33 1.0

21 23 1.0

22 23 1.5 24 1.5

23 25 1.5

24 26 1.5 27 1.0

25 28 1.5 29 1.0

26 28 1.5 30 1.0

27

28 31 1.0

29

30

31

32 33 1.5 34 1.5

33 35 1.5

34 36 1.5 37 1.0

35 38 1.5 39 1.0

36 38 1.5 40 1.0

37

38 41 1.0

39

40

41

42 44 1.5 45 1.0 60 1.5

43 46 1.5 47 1.0 60 1.5

44 48 1.5 49 1.0

45

46 48 1.5 50 1.0

47

48 62 1.0

49

50

51 53 1.5 54 1.0 61 1.5

52 55 1.5 56 1.0 61 1.5

53 57 1.5 58 1.0

54

55 57 1.5 59 1.0

56

57 66 1.0

58

59

60

61

62 63 1.0 64 1.0 65 1.0

63

64

65

66 67 1.0 68 1.0 69 1.0

67

68

69

DFT Optimised parameters for MCS-B5M

Ru	-0.08361200	-0.00001000	-0.08387300
C	-0.10329400	2.66987200	1.26501000
C	-0.35873500	0.73723300	2.62614000
C	-0.37663700	3.45762900	2.40537700
C	-0.56002200	1.49802600	3.77284800
C	-0.59257400	2.88348400	3.64588300
H	-0.43978700	4.53897600	2.30641700
H	-0.71501000	1.02171300	4.74010700

H	-0.79624100	3.51414900	4.51383700
C	-0.35891500	-0.73751400	2.62604300
C	-0.10350800	-2.66998800	1.26470900
C	-0.56079200	-1.49846500	3.77255500
C	-0.37749100	-3.45789600	2.40480600
C	-0.59373200	-2.88389100	3.64533400
H	-0.71600000	-1.02229000	4.73984900
H	-0.44088500	-4.53921000	2.30557100
H	-0.79794900	-3.51463600	4.51310200
N	-0.16256000	1.31558800	1.40635300
N	-0.16258200	-1.31572400	1.40622900
O	-0.04111100	-1.40569800	-1.53999000
O	-0.04131700	1.40575500	-1.53984800
C	0.22538100	3.30288300	-0.02195600
C	0.18817900	2.65711600	-1.31161200
C	0.59960300	4.67298600	0.00520200
C	0.42416800	3.46947700	-2.46191600
C	0.86041700	5.41943500	-1.12393900
H	0.72502700	5.16585900	0.96997300
C	0.74809700	4.80301700	-2.38185100
H	0.35234800	2.95805900	-3.42433000
H	1.15866600	6.46579100	-1.03499000
H	0.93491300	5.37399400	-3.29572300
C	0.22577700	-3.30282800	-0.02216500
C	0.18880400	-2.65699800	-1.31178200

C	0.60042700	-4.67279800	0.00513600
C	0.42577800	-3.46917200	-2.46200500
C	0.86201300	-5.41909800	-1.12393300
H	0.72558300	-5.16561300	0.96998100
C	0.75014400	-4.80261000	-2.38184800
H	0.35428000	-2.95773200	-3.42443200
H	1.16055700	-6.46536400	-1.03491900
H	0.93764500	-5.37345500	-3.29566300
C	-2.58335500	-0.00034700	-1.58488000
C	-3.03391600	0.00005100	0.68333000
C	-3.93674000	-0.00038900	-1.89232300
H	-1.81012100	-0.00050800	-2.35340600
C	-4.40080300	0.00002200	0.45971000
H	-2.63842300	0.00022600	1.70025400
C	-4.87130500	-0.00019100	-0.85515300
H	-4.25859600	-0.00057700	-2.93399300
H	-5.10849000	0.00017000	1.29010700
C	2.54117600	0.00034200	-1.34904700
C	2.75242900	-0.00007000	0.95653300
C	3.91862100	0.00037200	-1.51351100
H	1.84926900	0.00051900	-2.19257400
C	4.13410500	-0.00003300	0.87513400
H	2.24777200	-0.00025000	1.92424600
C	4.73959200	0.00018000	-0.38412200
H	4.34756700	0.00054400	-2.51576500

H	4.75198100	-0.00017900	1.77434600
N	-2.13418100	-0.00013100	-0.31546900
N	1.96189100	0.00012100	-0.13282500
C	-6.34108200	-0.00022800	-1.08599400
O	-7.16358600	-0.00009900	-0.20570100
O	-6.66337200	-0.00054600	-2.38413700
H	-7.63155600	-0.00054400	-2.42866300
C	6.22469900	0.00026500	-0.46119100
O	6.95214900	0.00007200	0.49928300
O	6.67997200	0.00073600	-1.71927800
H	7.64746000	0.00081600	-1.66271600

1 18 1.0 19 1.0 61 1.0

2 4 1.5 18 1.5 22 1.0

3 5 1.5 10 1.0 18 1.5

4 6 2.0 7 1.0

5 6 1.5 8 1.0

6 9 1.0

7

8

9

10 12 1.5 19 1.5

11 13 1.5 19 1.5 32 1.0

12 14 1.5 15 1.0

13 14 2.0 16 1.0

14 17 1.0

15

16

17

18

19

20 33 1.5

21 23 1.5

22 23 1.5 24 1.5

23 25 1.5

24 26 2.0 27 1.0

25 28 2.0 29 1.0

26 28 1.5 30 1.0

27

28 31 1.0

29

30

31

32 33 1.5 34 1.5

33 35 1.5

34 36 2.0 37 1.0

35 38 2.0 39 1.0

36 38 1.5 40 1.0

37

38 41 1.0

39

40

41

42 44 1.5 45 1.0 60 1.5

43 46 2.0 47 1.0 60 1.5

44 48 1.5 49 1.0

45

46 48 1.5 50 1.0

47

48 62 1.0

49

50

51 53 1.5 54 1.0 61 1.5

52 55 2.0 56 1.0 61 1.5

53 57 1.5 58 1.0

54

55 57 1.5 59 1.0

56

57 66 1.0

58

59

60

61

62 63 2.0 64 1.5

63

64 65 1.0

65

66 67 2.0 68 1.5

67

68 69 1.0

69

References

1. A. Tiwari, N. V. Krishna, L. Giribabu, and U. Pal, *J. Phys. Chem. C*, 2018, 122, 1, 495-502.
2. F. Raziq, Y. Qu, X. Zhang, M. Humayun, J. Wu, A. Zada, H. Yu, X. Sun and L. Jing, *J. Phys. Chem. C*, 2016, 120, 1, 98-107.