Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Materials (ESI)

Fluorene Functionalized Porphyrins as Broadband Absorbers for TiO_2 Nanocrystalline Solar Cells

Wenhui Li[a], Liping Si[b,c], Zonghao Liu[a], Zhixin Zhao*[a], Hongshan He*[b,c], Kai Zhu[d], Brian Moore[e] and Yi-Bing Cheng[a,f],

[a]Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics Department, School of Optical and Electronic Information, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, P. R. China; [b]Department of Chemistry, Eastern Illinois University, Charleston, IL, 61920, USA; [c]Center for Advanced Photovoltaics, South Dakota State University, Brookings, SD 57007, USA; [d]Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, CO 84041, USA; [e]University Networking Research & Services, South Dakota State University, Brookings, SD 57007, USA; [f]Department of Materials Engineering,Monash University, Melbourne,Victoria, 3800, Australia.

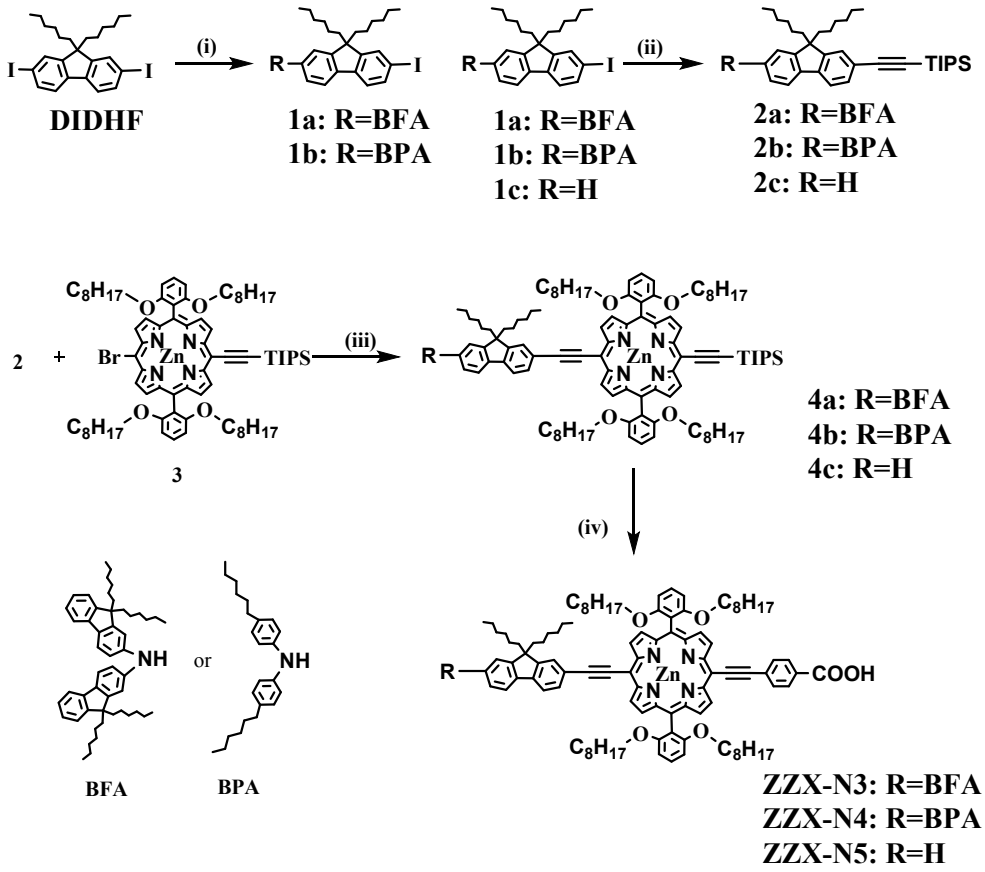
EXPERIMENTAL

General

All chemicals were obtained from commercial sources and used directly without further purification. Solvents used for reactions were dried by standard procedures. All reactions were carried out under N_2 atmosphere. The synthesis procedure of bis(9,9-dihexyl-9H-fluoren-7-yl)amine(**BFA**) has been reported elsewhere. 2,7-diiodo-9,9-dihexyl-9H-fluorene (**DIDF**), bis(4-hexylphenyl)amine (**BPA**) and [5-

Bromo-15-(triisopropylsilyl)ethynyl-10,20-bis(2,6-di-octoxyphenyl)porphyrinato] zinc(II)(**3**) were prepared according to literature methods[1,2] and confirmed by ^{1}H NMR. 2-Iodo-9,9-dihexyl-9H-fluorene (**1c**) was purchased from Sigma-Aldrich. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 spectrometer.

Synthesis of ZZX-Nx (x=3,4,5)



Scheme 1 Synthesis of fluorene-based porpyrin dyes. Reaction conditions: (i) copper bronze, K_2CO_3, 18-crown-6, 1,2-dichlorobenzene, reflux, (ii) ethynyltriisopropylsilane, $Pd(PPh_3)_2Cl_2$, CuI, THF, TEA, (iii) (a) TBAF, THF; (b) $Pd(PPh_3)_2Cl_2$, CuI, THF, TEA, (iv) (a) TBAF, THF; (b) $Pd_2(dba)_3$, $AsPh_3$, 4-iodobenzoic acid, THF, TEA.

Synthesis

The synthesis of 1a~1b. Diarylamines (1.5 mmol) and **DIDF** (1.8 mmol) were

dissolved in 8 ml 1,2-dichlorobenzene at room temperature under N_2. To this mixture were added K_2CO_3 (2 g, 14.40 mmol), 18-crown-6 (0.135 g, 0.50 mmol) and copper bronze (0.563 g, 8.86 mmol). The reaction mixture was heated at 180ºC for overnight. Upon completion, the brown mixture was filtered through a short silica gel plug and the yellow solution was concentrated, resulting in a yellow–brown oil. 1,2-Dichlorobenzene was removed under reduced pressure. Purification was accomplished by column chromatography using hexane as eluent.

1a. Yellow oil (0.64 g, 37.4%). ^{1}H NMR ($(CD_3)_2CO$, 400MHz) δ 7.83 (s, 1H), 7.71 (d, J=8.32Hz, 6H), 7.54 (d, J=8.00Hz, 1H), 7.43 (d, J=7.36Hz, 2H), 7.30-7.36 (m, 7H), 7.05-7.09 (m, 3H), 1.90-2.04 (m, 12H), 1.10-1.20 (m, 36H), 0.64-0.84 (m, 30H). MS (m/z, APCI) calcd for $C_{75}H_{98}IN$ 1140.5, found 1141.0 $[M]^+$.

1b. Colorless oil (0.49 g, 40.7%). ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.30 (d, J=1.40Hz, 1H), 7.61 (s, 1H), 7.49 (d, J=8.16Hz, 1H), 7.34 (d, J=7.68Hz, 1H), 7.04-7.08 (m, 10H), 2.59 (s, 4H), 1.83 (t, J=8.28Hz, 4H), 1.60-1.67 (m, 4H), 1.34-1.35 (m, 12H), 1.07-1.19 (m, 12H), 0.92 (t, J=6.74Hz, 6H), 0.84 (t, J=7.16Hz, 6H), 0.66-0.68 (m, 4H). MS (m/z, APCI) calcd for $C_{49}H_{66}IN$ 796.0, found 796.4 $[M]^+$.

The synthesis of 2a~2c. Compound **1** (0.61 mmol) was dissolved in a mixture of dry THF (22 ml) and dry TEA (4 ml) under N_2. (Triisopropylsilyl)acetltene (1.53 mmol), $Pd(PPh_3)Cl_2$ (0.12 mmol) and CuI (0.18 mmol) were added. The reaction mixture was stirred at room temperature under dark for 4.5h. The solvent was removed under reduced pressure and the residue was subjected to column chromatography using hexane as eluent.

2a. Yellow solid (0.70 g, 96.0%). ^{1}H NMR ($(CD_3)_2CO$, 400MHz) δ 7.72 (t, J=6.14Hz, 6H), 7.57 (s, 1H), 7.49 (d, J=7.84Hz, 1H), 7.44 (d, J=6.76Hz, 2H), 7.30-7.34 (m, 7H), 7.06-7.09 (m, 3H), 1.91-2.04 (m, 12H), 1.11-1.19 (m, 57H), 0.64-0.84 (m, 30H). MS (m/z, APCI) calcd for $C_{86}H_{119}NSi$ 1195.0, found 1195.5 $[M]^+$.

2b. Yellow solid (0.49 g, 94.4%). ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.51 (d, J=8.08Hz, 2H), 7.80 (d, J=7.80Hz, 1H), 7.37 (s, 1H), 7.03-7.09 (m, 10H), 2.59 (s, 4H), 1.81-1.90 (m, 4H), 1.60-1.68 (m, 4H), 1.19 (s, 21H), 1.09-1.12 (m, 12H), 0.92 (t, J=6.64Hz, 6H), 0.83 (t, J=7.14Hz, 6H), 0.67-0.69 (m, 4H). MS (m/z, APCI) calcd for $C_{60}H_{87}NSi$ 850.4, found 851.1 $[M+1]^+$.

2c. Yellow oil (0.29 g, 91.8%). ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.69 (d, J=7.64Hz, 1H), 7.62 (d, J=7.80Hz, 1H), 7.47 (d, J=7.80Hz, 1H), 7.43 (s, 1H), 7.34-7.35 (m, 3H), 1.97 (t, J=4.15Hz, 4H), 1.20 (s, 21H), 1.07-1.06 (m, 12H), 0.79 (t, J=7.06Hz, 6H), 0.61-0.66 (m, 4H). MS (m/z, APCI) calcd for $C_{36}H_{54}Si$ 514.9, found 515.3 $[M]^+$.

The synthesis of 4a~4c. To a solution of Compound **2** (0.82 mmol) in dry THF (100 ml) was added TBAF (4.91 ml, 1M in THF) under N_2. The reaction mixture was stirred at room temperature for 0.5h and then quenched by water. The mixture was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent of organic layer was removed under reduced pressure. The residue was dissolved in a mixture of dry THF (80 ml) and dry TEA (16 ml) and degassed with nitrogen for 30 minutes. Then $Pd(PPh_3)Cl_2$ (0.077 mmol), CuI (0.077 mmol), and brominated porphyrin **3** (0.39 mmol) were added. The solution was refluxed under N_2 for 4h. Then the solvent was removed under reduced pressure and residue was subjected to column chromatography (silica gel) using CH_2Cl_2/hexane=1/3(v:v) as eluent. The product was recrystallized from CH_2Cl_2/MeOH.

4a. Green solid (230 mg, 25.8%). ^{1}H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ 9.66 (d, J=4.52Hz, 2H), 9.57 (d, J=4.52Hz, 2H), 8.83 (d, J= 4.08Hz, 2H), 8.80 (d, J=4.52Hz, 2H), 7.94 (d, J=7.24Hz, 1H), 7.88 (s, 1H), 7.58-7.76 (m, 9H), 7.32-7.34 (m, 8H), 7.07 (d, J=5.24Hz, 3H), 7.01 (d, J=8.48Hz, 4H), 3.86 (t, J=3.33Hz, 8H), 1.1.85-1.99 (m, 12H), 1.41 -1.42 (m, 21H), 1.10-1.22 (m, 36H), 0.93-0.83 (m, 40H), 0.69-0.74 (m, 14H), 0.59-0.47 (m, 36H). MS (m/z, TOF) calcd for $C_{152}H_{201}N_5O_4SiZn$ 2255.7, found 2255.3 $[M]^+$.

4b. Green solid (120 mg, 16.3%). ^{1}H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ 9.65 (d, J=4.48Hz, 2H), 9.56 (d, J=4.52Hz, 2H), 8.82 (d, J=4.48Hz, 2H), 8.79 (d, J=4.52Hz, 2H), 7.91 (d, J=7.64Hz, 1H), 7.85 (s, 1H), 7.67-7.74 (m, 3H), 7.60 (d, J=7.80Hz, 1H), 7.15 (d, J=1.96Hz, 1H), 7.00-7.08 (m, 13H), 3.85 (t, J=6.60Hz, 8H), 2.60 (t, J=7.78Hz, 4H), 1.85-1.88 (m, 4H), 1.61-1.66 (m, 4H), 1.41-1.42 (m, 21H), 1.34-1.37 (m, 12H), 1.13-1.19 (m, 12H), 0.89-0.94 (m, 20H), 0.70-0.84 (m, 20H), 0.45-0.61 (m, 36H). MS (m/z, TOF) calcd for $C_{126}H_{169}N_5O_4SiZn$ 1911.2, found 1912.9 $[M+1]^+$.

4c. Purple solid (80 mg, 20.4%). ^{1}H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ 9.66 (d, J=4.48Hz, 2H), 9.57 (d, J=4.48Hz, 2H), 8.84 (d, J=4.48Hz, 2H), 8.80 (d, J=4.52Hz, 2H), 7.97 (d, J=1.12Hz, 1H), 7.90 (s, 1H), 7.84 (d, J=7.80Hz, 1H), 7.78 (d, J=6.32Hz, 1H), 7.70 (t, J=8.40Hz, 2H), 7.34-7.42 (m, 3H), 7.01 (d, J=8.48Hz, 4H), 3.86 (t, J=6.62Hz, 8H), 2.08-2.13 (m, 4H), 1.41-1.42 (m, 21H),1.06-1.18 (m, 12H), 0.87-0.98 (m, 14H), 0.68-0.80 (m, 20H), 0.49-0.61 (m, 30H). MS (m/z, TOF) calcd for $C_{102}H_{136}N_4O_4SiZn$ 1575.7, found 1576.4 $[M]^+$.

The synthesis of ZZX-N3~N5. To a solution of Compound **4** (0.07 mmol) in dry THF (25 ml) was added TBAF (385 ml, 1M in THF) under N_2. The reaction mixture was stirred at room temperature for 0.5h and then quenched by water. The mixture was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. the solvent of organic layer was removed under reduced pressure. The residue was dissolved in a mixture of dry THF (18 ml) and dry TEA (4 ml) and degassed with nitrogen for 30 minutes. Then $Pd_2(dba)_3$ (0.017 mmol), $AsPh_3$ (0.136 mmol), and 4-iodobenzoic acid (0.136 mmol) were added. The solution was refluxed under N_2 for 4h. Then the solvent was removed under reduced pressure and residue was subjected to column chromatography (silica gel) using CH_2Cl_2/MeOH=20/1(v:v) as eluent. Recrystallization from CH_2Cl_2/MeOH gave the final porphyrin dyes.

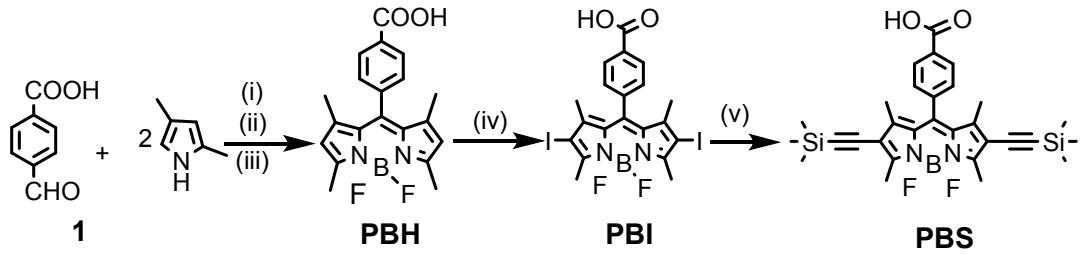
ZZX-N3. Green solid (130 mg, 85.6%). ^{1}H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ

9.66 (d, J=4.48Hz, 2H), 9.59 (d, J=4.52Hz, 2H), 8.83 (d, J=4.52Hz, 4H), 8.29 (d, J=8.24Hz, 2H), 8.03 (d, J=8.16Hz, 2H), 7.94 (d, J=8.52Hz, 1H), 7.88 (s, 1H), 7.58-7.77 (m, 9H), 7.32-7.34 (m, 8H), 7.07-7.10 (m, 3H), 7.02 (d, J=8.52Hz, 4H), 3.87 (t, J=6.52Hz, 8H), 1.85-2.00 (m, 12H), 1.10-1.27 (m, 36H), 0.93-0.83 (m, 40H), 0.76-0.85 (m, 14H), 0.60-0.46 (m, 36H). MS (m/z, TOF) calcd for $C_{150}H_{185}N_5O_6Zn$ 2219.5, found 2220.1$[M]^+$.

ZZX-N4. Green solid (70 mg, 63.5%). ^1H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ 9.66 (d, J=4.48Hz, 2H), 9.59 (d, J=4.48Hz, 2H), 8.83 (d, J=4.48Hz, 4H), 8.29 (d, J=8.24Hz, 2H), 8.03 ((d, J=8.20Hz, 2H),) 7.92 (d, J=6.96Hz, 2H), 7.86 (s, 1H), 7.69-7.75 (m, 3H), 7.60 (d, J=8.16Hz, 1H), 7.15 (d, J=1.84Hz, 1H), 7.02-7.08 (m, 13H), 3.87 (t, J=6.52Hz, 8H), 2.60 (t, J=7.78Hz, 4H), 1.86-1.88 (m, 4H), 1.61-1.66 (m, 4H), 1.34-1.37 (m, 12H), 1.17-1.22 (m, 12H), 0.91-0.97 (m, 20H), 0.72-0.84 (m, 20H), 0.46-0.62 (m, 36H). MS (m/z, TOF) calcd for $C_{124}H_{153}N_5O_6Zn$ 1875.0, found 1575.1$[M]^+$.

ZZX-N5. Green solid (85 mg, 78.9%). ^1H NMR ($CDCl_3$/d_5-pyridine, 400MHz) δ 9.66 (d, J=4.48Hz, 2H), 9.60 (d, J=4.50Hz, 2H), 8.84 (q, J=2.27Hz, 4H), 8.29 (d, J=8.28Hz, 2H), 8.03 (d, J=8.16Hz, 2H), 7.96 (d, J=7.76Hz, 1H), 7.91 (s, 1H), 7.85 (d, J=7.80Hz, 1H), 7.72 (t, J=8.46Hz, 2H), 7.32-7.43 (m, 3H), 7.03 (d, J=8.48Hz, 4H), 3.88 (t, J=6.54Hz, 8H), 1.85-1.83 (m, 4H), 1.11-1.27 (m, 26H), 0.73-0.97 (m, 20H), 0.46-0.62 (m, 36H). MS (m/z, TOF) calcd for $C_{100}H_{120}N_4O_6Zn$ 1539.4, found 1540.0 $[M]^+$.

Synthesis of complementary Dye



Scheme 3 Synthesis of complementary dye PBS Reaction conditions: (i) TFA, CH_2Cl_2, overnight, N_2, (ii) DDQ, 10 minutes, (iii) TEA, BF_3•OEt_2, (iv) I_2, HIO_3, EtOH, 60°C , 1h, (v)

ethynyltriisopropylsilane, $Pd(PPh_3)_2Cl_2$, CuI, THF, TEA.

Synthesis of PBH. To a flask was added pyrrole (0.92 mL, 8.97 mmol), formybenzoic acid (0.6 g, 4.0 mmol) absolute CH_2Cl_2 (200 mL) under nitrogen atmosphere. One drop of trifluoroacetic acid was added to initiate the reaction. The resulting mixture was stirred for 12h at room temperature. Then dichlorodicyanobenzoquinone (0.9 g, 4 mmol) in CH_2Cl_2 (100 ml) was added. The color of the solution became purple. After continued stirring for 10 min, triethylamine(8 mL) and $BF_3 \cdot OEt_2$ (8 mL) were added consecutively. Then the solution was stirring for another 6 h. And then the black and majority of redish impurities were first removed by a flash chromatograph. Orange color powder (0.3 g, 40%). ^{1}H NMR ($CDCl_3$, 400MHz): 8.25(d, 2H); 7.45(d, 2H); 5.95(s, 2H); 2.50(s, 6H); 1.45(s, 6H). MS (m/z, ESI) calcd for $C_{20}H_{19}BF_2N_2O_2$, 368.2, found 367.0 $[M-1]^-$.

Synthesis of PBI. To 0.30 g (0.815 mmol) of PBH in 40 mL of ethanol, 0.52 g (2.04 mmol) of I_2 was added and stirred magnetically till it was dissolved. Then, 0.286 g (1.63 mmol) of HIO_3 was dissolved in water (1mL), and added dropwise by a syringe during 30 minutes at room temperature. After the addition was complete, the solution was heated to 60°C and refluxed for 1 h. The fluorescence was quenched and color of the solution became purple. The progress of the reaction was followed by TLC until completion. Ethanol and water were removed by evaporator under vacuum. The solid was dissolved in chloroform and purified by column chromatography with a silica gel solid phase and chloroform/methanol as the eluting solvent. The product PBI was collected as the first fraction. Purple color powder (0.25 g, 50%).^{1}H NMR ($CDCl_3$, 400MHz): 8.35 (d, 2H); 7.20 (d, 2H); 2.65 (s, 6H); 1.45 (s, 6H). MS (M-1/z, ESI) calcd for $C_{20}H_{17}BF_2I_2N_2O_2$, 619.9, found 618.7$[M-1]^-$.

Synthesis of PBS. To a round bottom flask was added PBI (300 mg), $Pd(PPh_2)Cl_2$ (10 mol%), PPh_3 (10 mol%), CuI (20 mol%) under N_2. Then dye THF (10 mL), Et_3N (5 mL), and trimethylsilylacetylene (4 times of PBI) were added to the flask and the

reaction was carried out at 60°C for 12 h. The typical fluorescence should be recovered after the reaction. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. The crude product directly purified by silica gel chromatography using dichloromethane or chloroform. Orange color powder (0.12 g, 45%).^{1}H NMR ($CDCl_3$, 400MHz): 8.15 (d, 2H); 7.30 (d, 2H); 2.50 (s, 6H); 1.30 (s, 6H); 0.10 (s, 18H). MS (m/z, ESI) calcd for $C_{30}H_{35}BF_2I_2N_2O_2Si_2$ 560.2, found 559.0 $[M-1]^-$.

Table S1. Photovoltaic parameters of ZZX-N3, ZZX-N4 and ZZX-N5 sensitized solar cells*

	Cell	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	η (%)
ZZX-N3	a	9.99	656	0.588	3.85
	b	9.87	662	0.584	3.81
	Average	9.93 ± 0.06	659 ± 3	0.586 ± 0.02	3.83 ± 0.02
ZZX-N4	a	9.92	664	0.639	4.21
	b	10.03	660	0.635	4.20
	Average	9.97 ± 0.05	662 ± 2	0.637 ± 0.02	4.20 ± 0.01
ZZX-N5	a	8.70	650	0.653	3.69
	b	8.88	648	0.644	3.70
	Average	8.79 ± 0.09	649 ± 1	0.649 ± 0.05	3.70 ± 0.01
ZZX-N3/PBS	a	7.67	635	0.661	3.22
	b	7.78	633	0.665	3.27
	Average	7.73 ± 0.05	632 ± 1	0.662 ± 0.03	3.24 ± 0.03
ZZX-N4/PBS	a	8.94	646	0.661	3.81
	b	8.82	640	0.655	3.70
	Average	8.88 ± 0.06	643 ± 3	0.658 ± 0.03	3.75 ± 0.05
ZZX-N5/PBS	a	6.36	651	0.672	2.78
	b	6.28	655	0.666	2.73
	Average	6.32 ± 0.04	653 ± 2	0.669 ± 0.03	2.76 ± 0.02

Reference

1. S. H. Lee, T. Nakamura and T. Tsutsui. *Org. Lett.*, 2001, **3**, 2005-2007.
2. A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629-634.

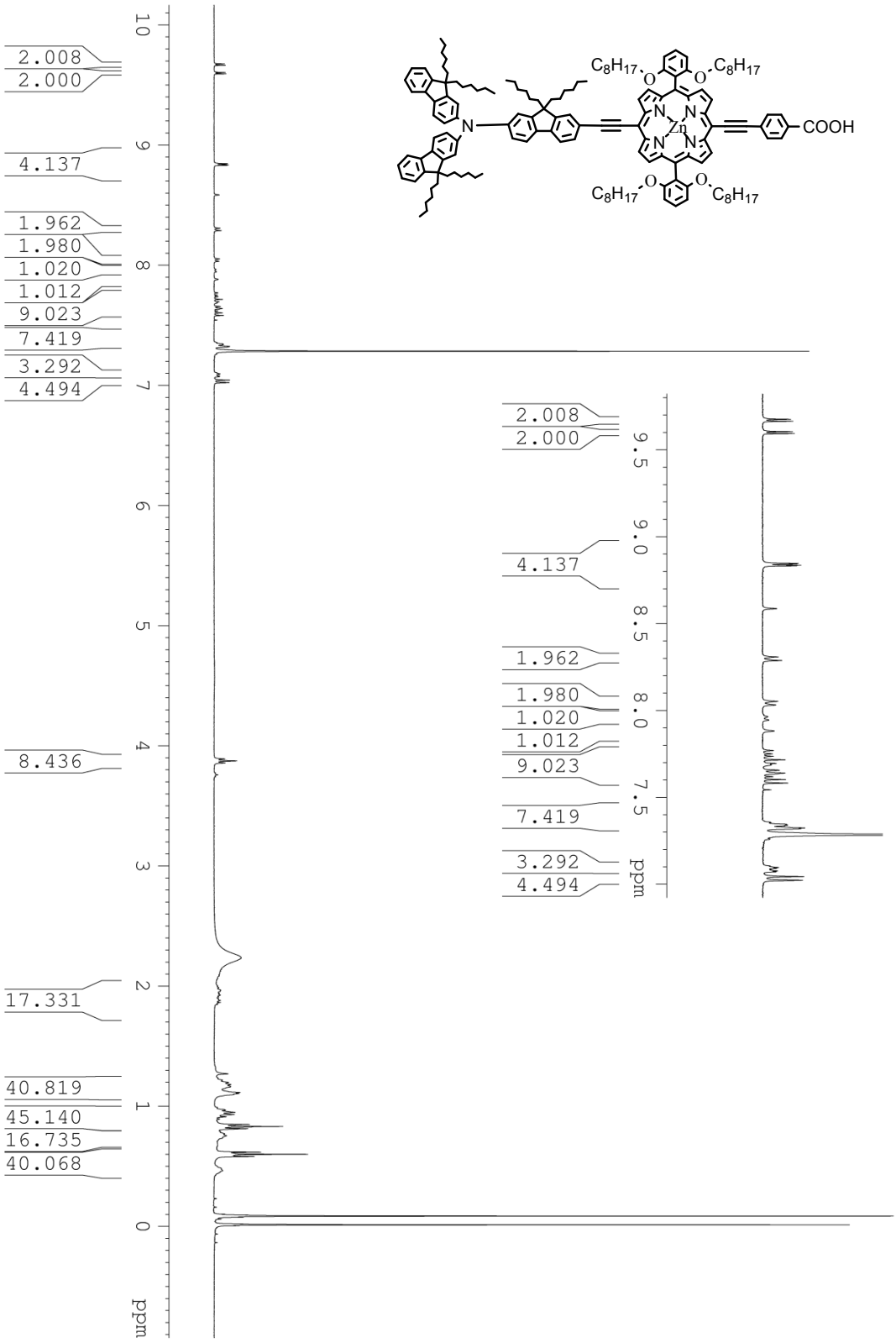


Figure S1 ^{1}H NMR of ZZX-N3 ($CDCl_3$/d_5-pyridine)

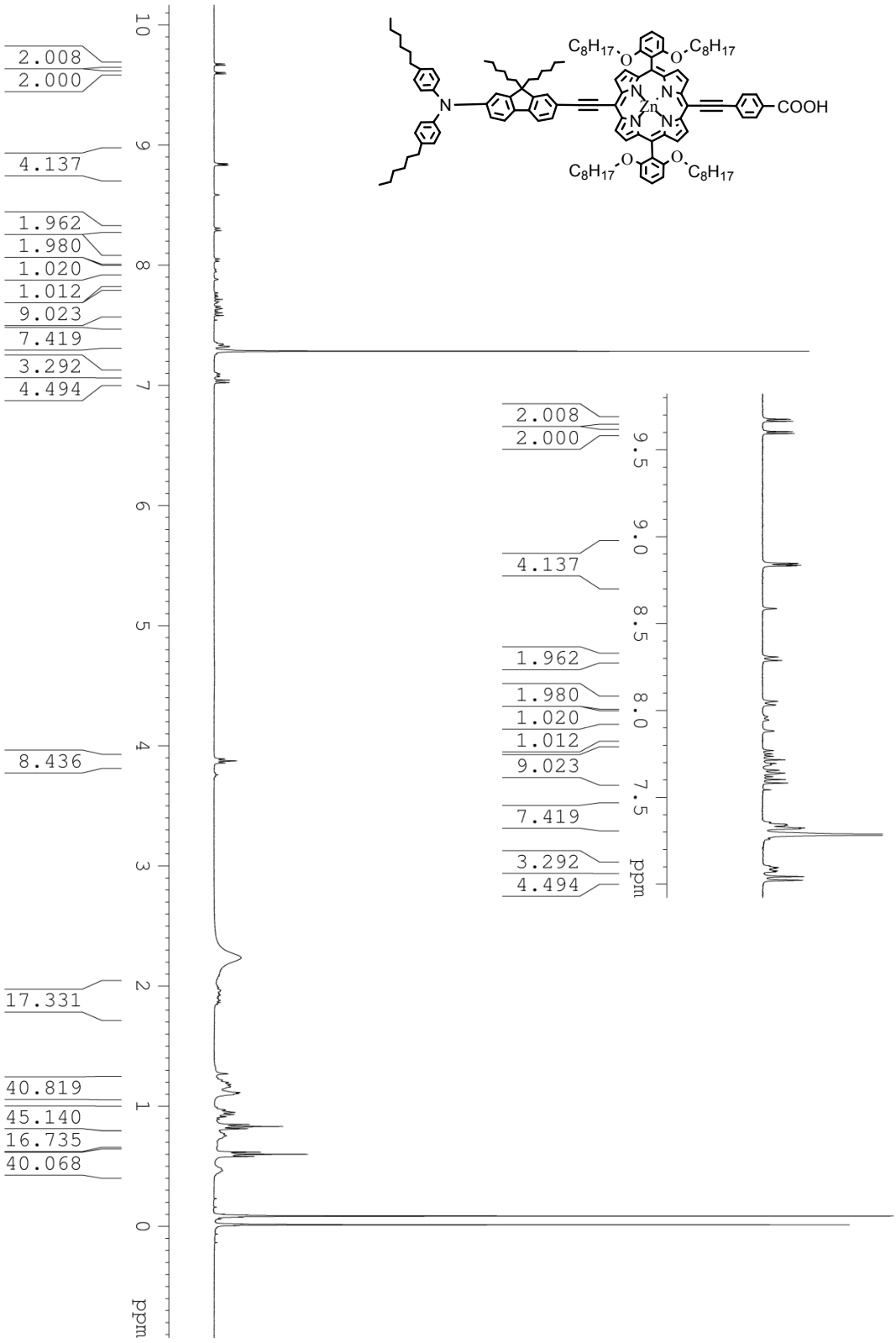


Figure S2 ^{1}H NMR of ZZX-N4 ($CDCl_3$/d_5-pyridine)

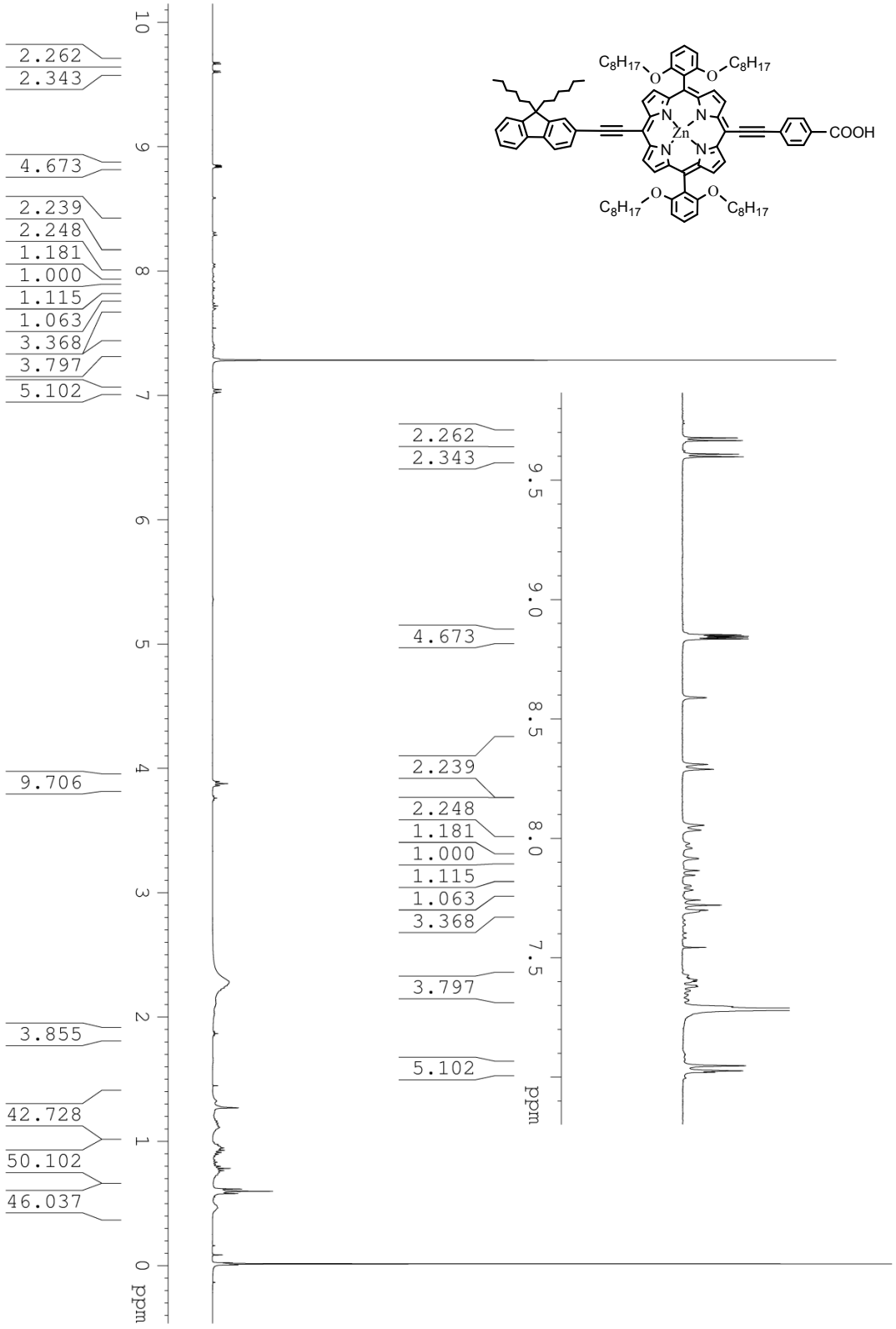


Figure S3 ^{1}H NMR of ZZX-N5 ($CDCl_3$/d_5-pyridine)