Supporting Information

Novel Donor-Acceptor Structured Ionic Organic Framework/Porous Carbon Nitride for Efficient Photocatalysis Imine Synthesis

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Section S1. Supplementary Figures and Tables

Section S1.1 SEM of other proportion catalysts

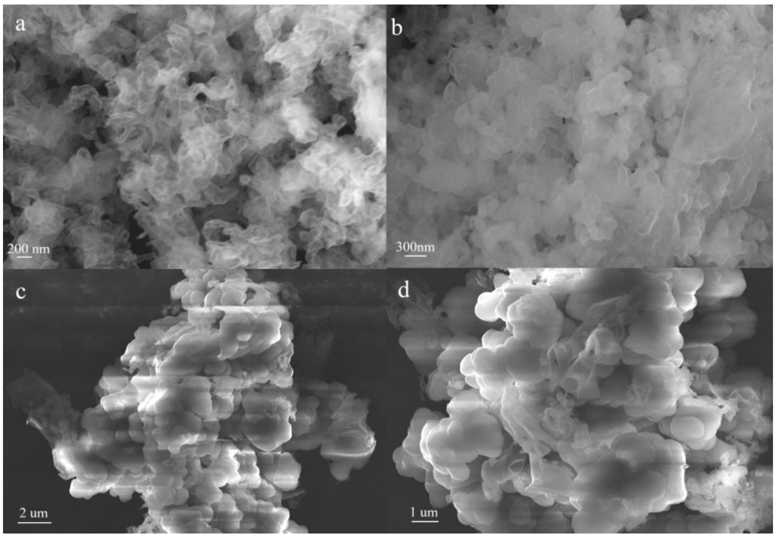


Figure S1 SEM images of IO5$_1$/PCN$_9$ (a), IO5$_3$/PCN$_7$ (b), IO5$_7$/PCN$_3$ (c) and IOF$_9$/PCN$_1$ (d).

Section S1.2 N_2 adsorption isotherms and pore size distribution

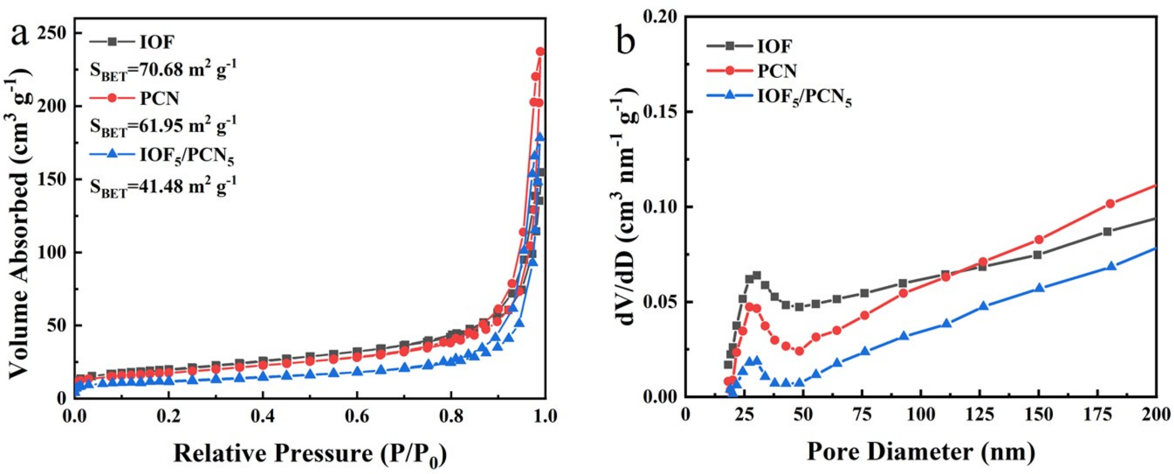


Figure S2 N_2 sorption isotherms(a) of IOF, PCN and IOF$_5$/PCN$_5$, and pore diameter distribution map (b) of IOF, PCN, IOF$_5$/PCN$_5$

Section S1.3 XPS survey spectra of IOF, PCN and IOF_5/PCN_5

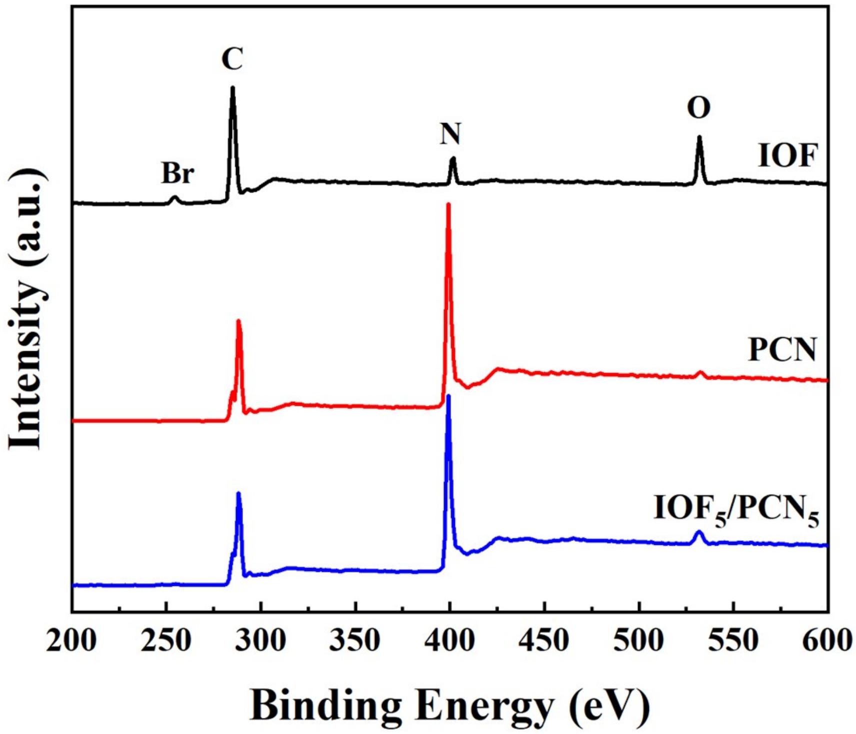


Figure S3 XPS survey spectra of IOF, PCN and IOF_5/PCN_5

Section S1.4 The Eg, E_{VB} and E_{CB} of IOF, PCN and IOF_5/PCN_5

Table S1 The Eg, E_{VB} and E_{CB} of IOF, PCN and IOF_5/PCN_5

Entry	Samples	Eg (eV)	E_{VB} a (eV)	E_{CB} (eV)
1	IOF	3.25	1.86	-1.39
2	PCN	2.9	1.66	-1.25
3	IOF_5/PCN_5	2.9	1.84	-1.06

Section S1.5 schematic diagram of the band structureof IOF, PCN and IOF_5/PCN_5

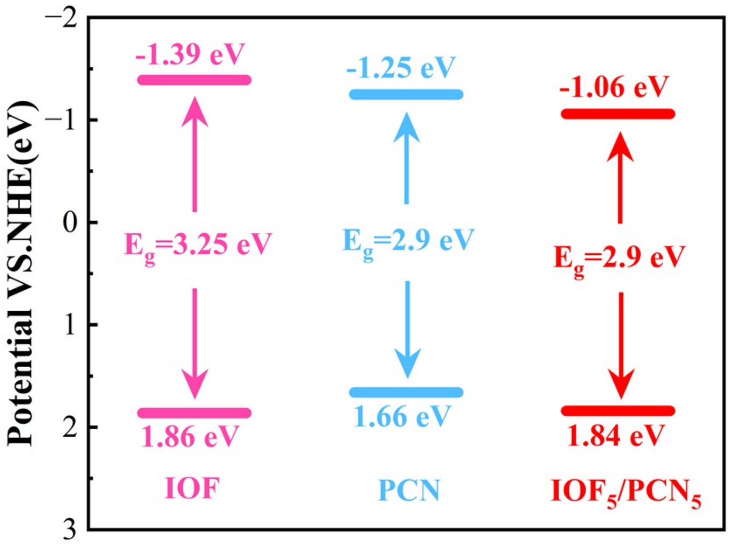


Figure S4 schematic diagram of the band structureof IOF, PCN and IOF_5/PCN_5

Section S1.6 Comparison of catalytic performance between IOF_5/PCN_5 and previously reported benzylamine coupling reaction materials

Table S2 Comparison of catalytic performance between IOF_5/PCN_5 and previously reported benzylamine coupling reaction materials

Entry	catalyst	Catalyst amount (mg)	Time (h)	Light	Conv. (%)	Sel. (%)
1[1]	CeR/g-C_3N_4	50 mg	3 h	300 W Xe lamp	82	99
2[2]	NiTiFe-LDH	15 mg	26 h	Blue LED	95	93
3[3]	Cd-MOFs	10 mg	6 h	300 W Xe lamp	98	99
4[4]	HNU-64	10 mg	7 h	300W Xe lamp (>400nm)	93	99
5[5]	ClBD-BTT	10 mg	6 h	300 W Xe LAMP	82	99
6	IOF_5/PCN_5	10 mg	6 h	300 W Xe lamp	98	99

Section S1.7 H_2O_2 production of IOF, PCN and IOF_5/PCN_5

Table S3 H_2O_2 production of IOF, PCN and IOF_5/PCN_5

catalyst	H_2O_2 yield(umol/g/h)
PCN	131.25
IOF	135.28
IOF_5/PCN_5	282.45

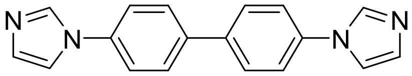
Reaction conditions: catalyst (10 mg) in deionized water (50 mL), purged with O_2 and stirred for 30 min in the dark (to achieve dissolved oxygen saturation), followed by irradiation with a xenon lamp for 2 h. The generated H_2O_2 was determined by iodometric titration.

Section S2.Theoretical calculations

Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Section S3. ^{1}H NMR and ^{13}C NMR

Section S3.1 ^{1}H NMR, ^{13}C NMR of **BIBP**



BIBP(4,4'-di(1H-imidazol-1-yl)-1,1'-biphenyl)：^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.41 (s, 2H), 7.95 (d, J=8.0 Hz, 4H), 7.89 (s, 2H), 7.84 (d, J=8.0 Hz, 4H), 7.20 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 137.8, 136.8, 136.0, 130.5, 128.4, 121.2, 118.4.

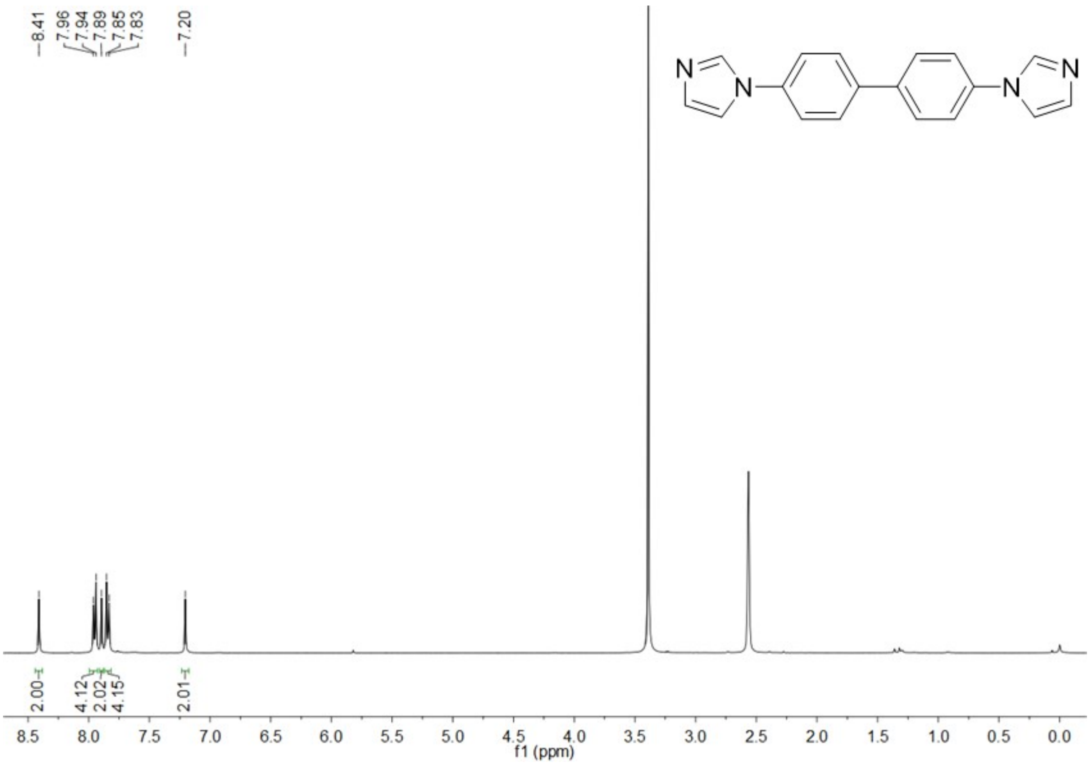


Figure S3.1 ^{1}H NMR of spectra of BIBP

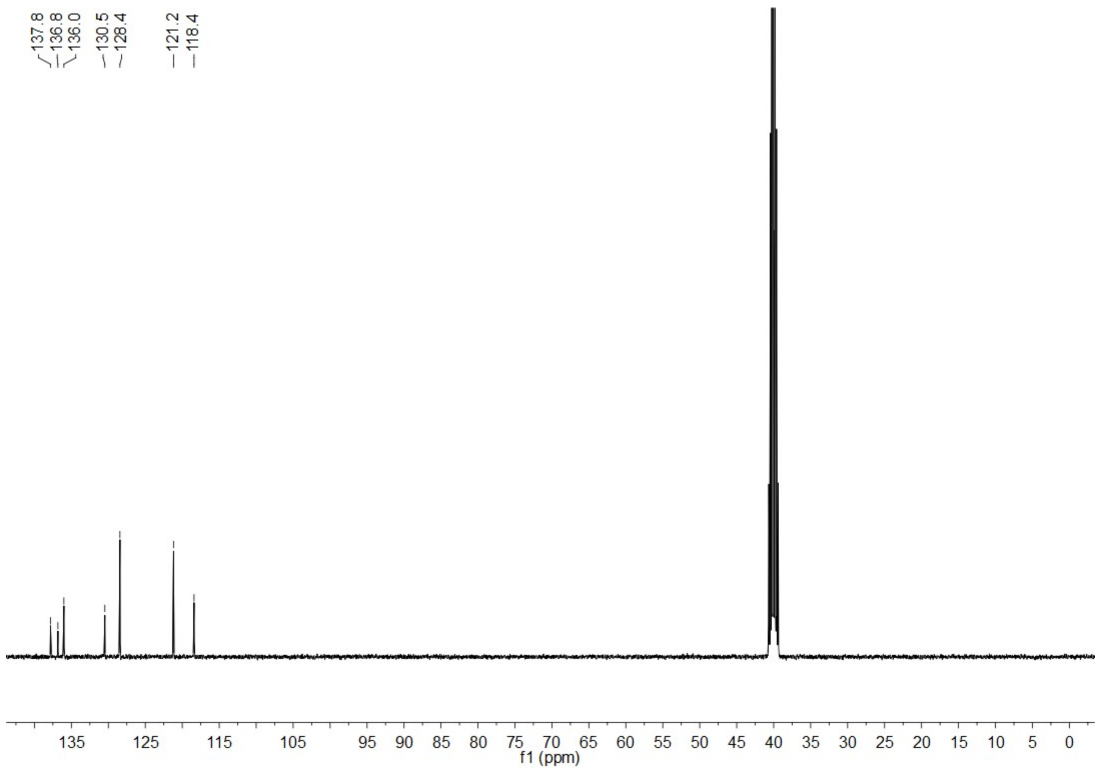
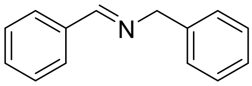


Figure S3.2 ^{13}C NMR of spectra of BIBP

Section S3.2 ^{1}H NMR, ^{13}C NMR of $[Be_2A][H]$



$[Be_2A][H]$((E)-N-benzyl-1-phenylmethanimine): ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.51 (s, 1H), 7.78 (dd, J1=4.0 Hz, J2=8.0 Hz, 2H), 7.46 (dd, J1=1.6 Hz, J2=5.2 Hz, 4H), 7.34 (t, J=4.0 Hz, 4H), 4.78 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 162.3, 140.1, 136.5, 131.2, 129.2, 128.8, 128.4, 128.4, 127.3, 64.4.

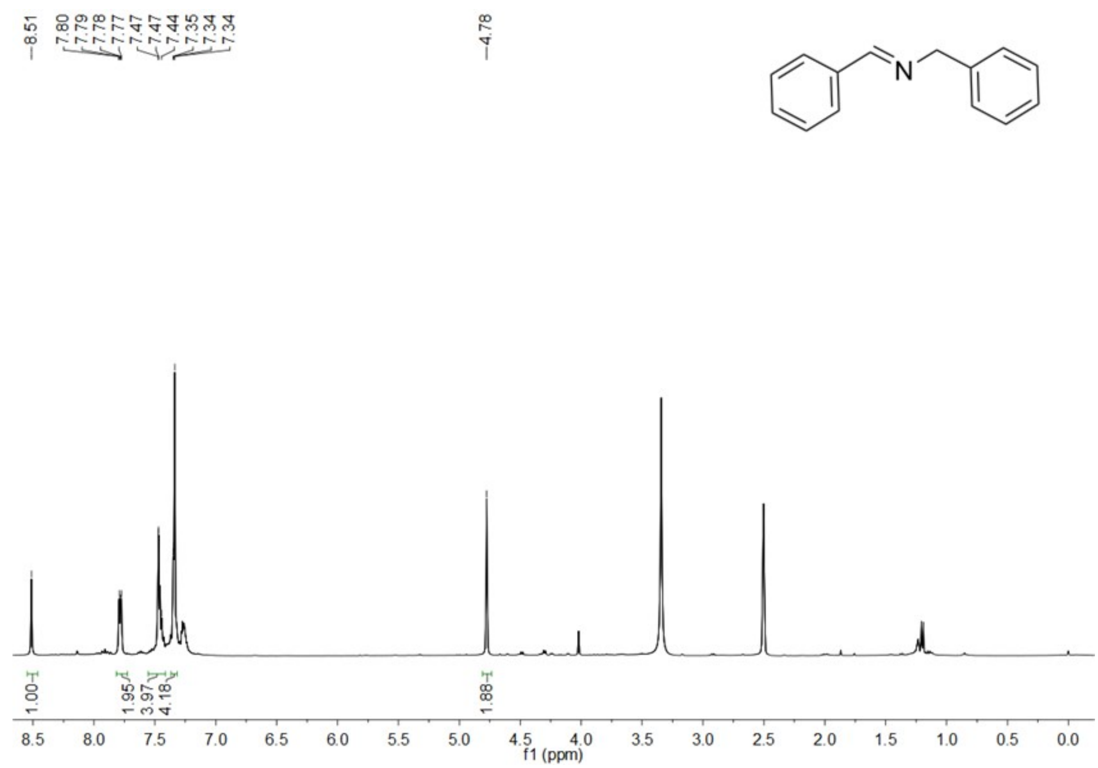


Figure S3.3 ^{1}H NMR of spectra of [Be_2A][H]

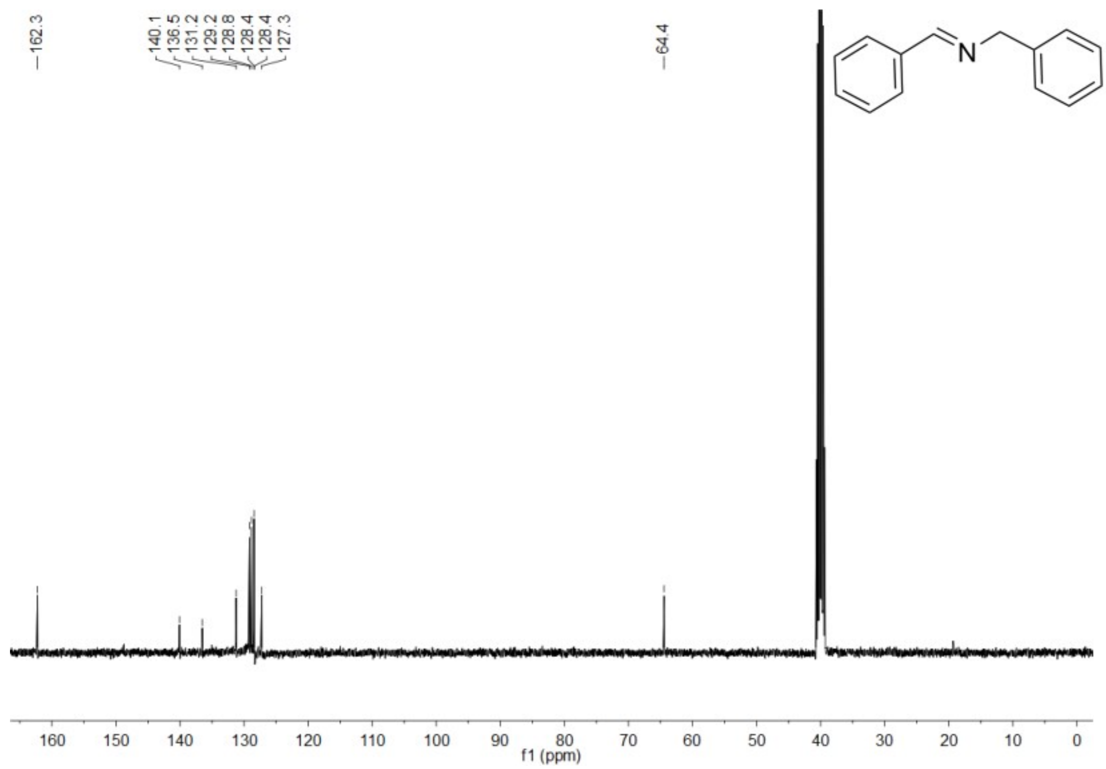
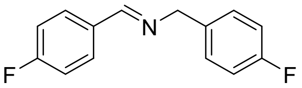


Figure S3.4 13C NMR of spectra of [Be2A][H]

Section S3.3 ^{1}H NMR, ^{13}C NMR of $[Be_2A][F]$



$[Be_2A][F]$((E)-N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine): ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.50 (s, 1H), 7.85 (q, J=5.6 Hz, 2H), 7.37 (q, J=6.0 Hz, 2H), 7.30 (t, J=8.0 Hz, 2H), 7.17 (t, J=8.0 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 161.1, 130.7, 130.63, 130.2, 130.2, 116.3, 116.1, 115.6, 115.4, 63.4.

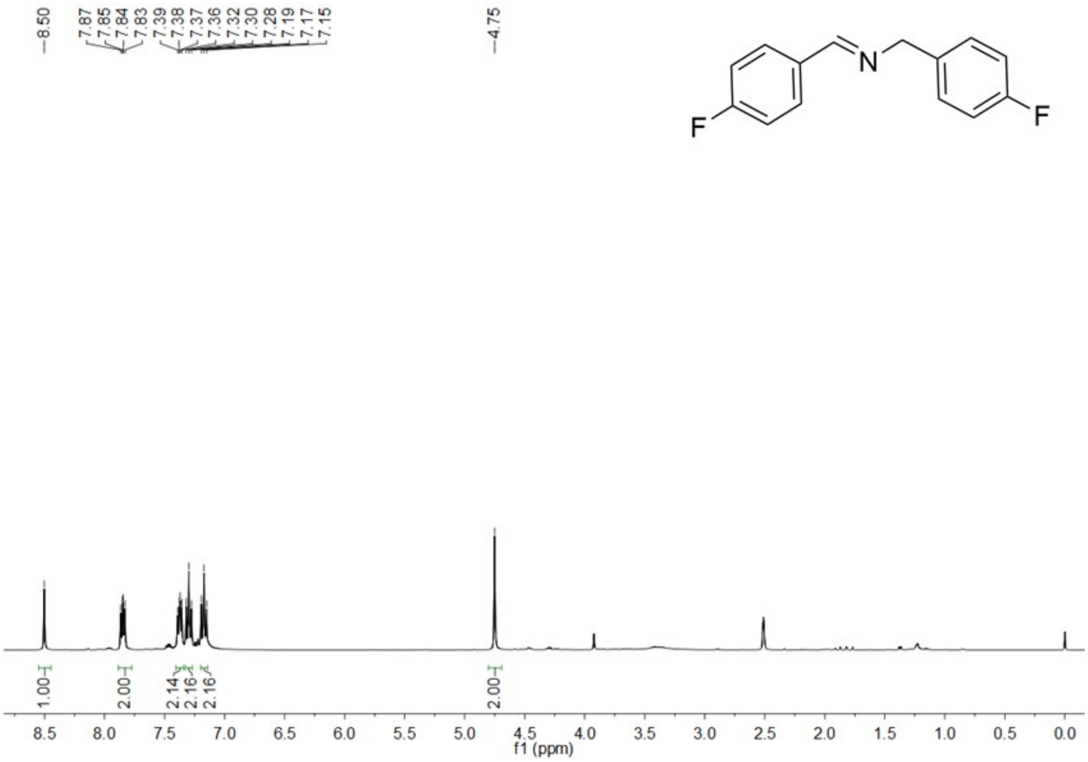
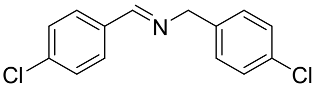


Figure S3.5 ^{1}H NMR of spectra of $[Be_2A][F]$

Figure S3.6 ^{13}C NMR of spectra of $[Be_2A][F]$

Section S3.4 ^{1}H NMR, ^{13}C NMR of $[Be_2A][Cl]$



$[Be_2A][Cl]$((E)-N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine): ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.44 (s, 1H), 7.74 (d, *J*=8.0 Hz, 2H), 7.46 (d, *J*=8.0 Hz, 2H), 7.32

(q, 8.0 Hz, 4H), 4.70 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.5, 139.0, 135.9, 135.3, 131.9, 130.2, 130.1, 129.3, 128.8, 63.3.

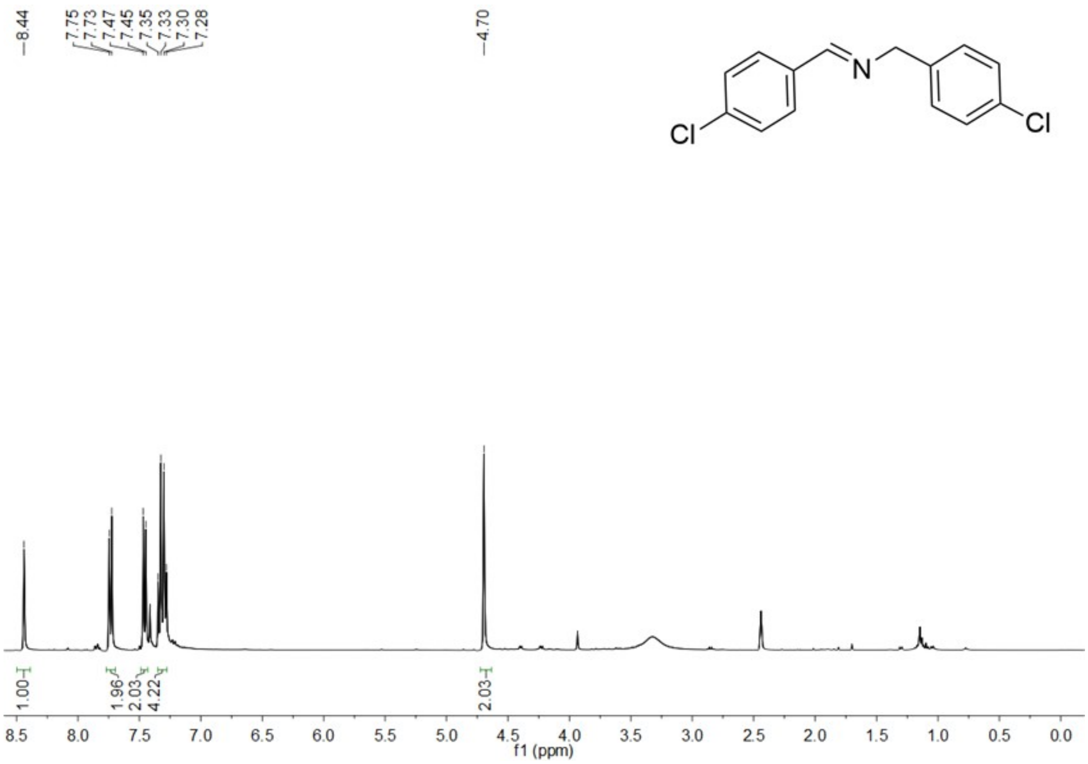
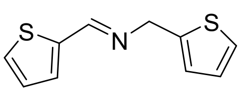


Figure S3.7 ^{1}H NMR of spectra of [Be_2A][Cl]

Figure S3.8 ^{13}C NMR of spectra of [Be_2A][Cl]

Section S3.5 ^{1}H NMR, ^{13}C NMR of [Th_2A][H])



[Th_2A][H])((E)-1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine): ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.59 (s, 1H), 7.70 (d, *J*=4.0 Hz, 1H), 7.52 (d, *J*=4.0 Hz, 1H), 7.43 (t, *J*=4.0 Hz, 1H), 7.16 (t, *J*=4.0 Hz, 1H), 7.01 (d, *J*=4.0 Hz, 2H), 4.89 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.3, 142.8, 142.4, 132.4, 130.4, 128.3, 127.4, 125.6, 125.5, 58.2.

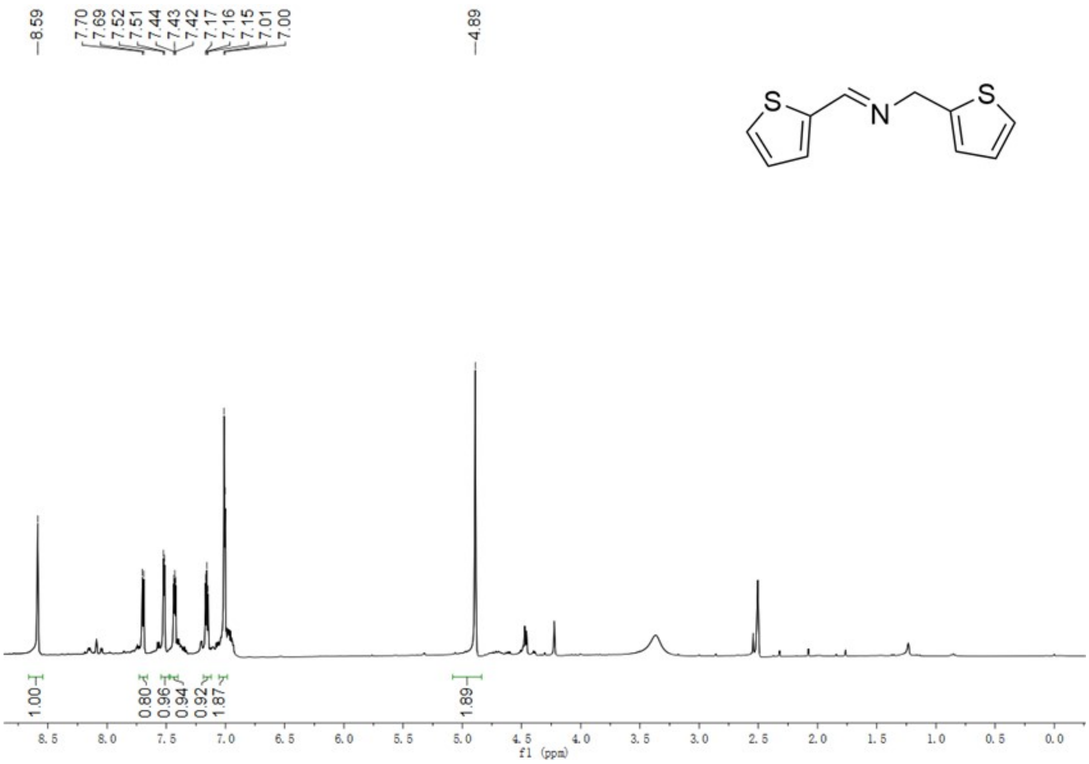


Figure S3.9 ^{1}H NMR of spectra of $[Th_2A][H]$

Figure S3.10 ^{13}C NMR of spectra of $[Th_2A][H]$

References

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3. J. Shi, J. Zhang, T. Liang, D. Tan,eta l. Bipyridyl-Containing Cadmium-Organic Frameworks for Efficient Photocatalytic Oxidation of Benzylamine, *ACS Applied Materials & Interfaces,* 2019, **11**, 30953-30958.
4. G. Che, W. Yang, C. Wang et al., Efficient Photocatalytic Oxidative Coupling of Benzylamine over Uranyl-Organic Frameworks Inorganic Chemistry, 2022, **61**, 12301-12307.
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