Supporting information

Ternary Assembly of Pyrazine 2,3-dicarboxylic acid with a Ditopic-Amine

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General:

Infrared spectra of the solid samples were recorded on a Perkin-Elmer Spectrum-Two FT-IR spectrophotometer in the region 4000-400 cm^{-1} using attenuated total reflectance method. Powder X-ray diffraction patterns were recorded using Bruker powder X-ray diffractometer D2 phaser. X-ray photoelectronic Spectroscopy analyses were done using Physical Electronics PHI 5000 Versa Probe-III. Merck hplc grade methanol with, 99.90% purity was used as solvent for the synthesis of the salt and ionic cocrystal. The crystallizations were done in open air conditions with relative humidity 75-80 %.

Crystallisation of the salt H_3anthraimmida·pyzda·$2H_2O$·CH_3OH: To a well-stirred solution of Hanthraimmida (31.6 mg, 0.10 mmol) in methanol (10 ml), pyrazine 2,3-dicarboxylic acid (16.72 mg, 0.10 mmol) was added. The resulting solution was stirred for one hour at room temperature, filtered and kept undisturbed for evaporation. Yellow block shaped crystals were formed within 2-3 hours. Isolated yield: 46.89 mg. IR (Neat, cm^{-1}): 3390 (m, br), 3136 (m), 2963 (m), 2820 (m), 1676 (s), 1588 (s), 1541 (s), 1448 (m), 1365 (s), 1346 (s), 1300 (m), 1228 (m), 1192 (m), 1156 (m), 1101 (s), 1082 (s), 1026 (m), 905 (m), 877 (w), 845 (m), 826 (s), 790 (s), 751 (s), 730 (s), 630 (m), 601 (m), 538 (m), 431 (m), 416 (m).

Crystallisation of the ternary Cocrystal H_3anthraimmida·pyzda·H_2pyzda·H_2O:

A similar procedure for the salt was used but the concentration of pyrazine 2,3-dicarboxylic acid (33.44 mg, 0.20 mmol) was doubled and it was added to the solution of Hanthraimmida (31.6 mg, 0.10 mmol) in methanol (10 ml). The resulting solution was stirred for one hour at room temperature. The solution was filtered and kept undisturbed for evaporation. Light yellow flake shaped crystals were formed after two days. Isolated yield: 52.23 mg. IR (Neat, cm^{-1}): 3413 (m, br), 3058 (m), 2808 (m), 1655 (s), 1567 (s), 1446 (m), 1342 (m), 1301 (m), 1157 (m), 1096 (s), 1059 (m), 971 (w), 840 (s), 810 (m), 784 (s), 730 (s), 701 (s), 645 (w), 558 (w), 460 (w), 413 (s).

Crystallographic Study: The X-ray single crystal diffraction data for the salt and the ionic cocrystal were collected by Bruker D8 Quest diffractometer at room temperature. Data refinement and cell reductions were carried out by Bruker SAINT Software. Data reduction and cell refinements were performed using SAINT and XPREP software. Structures were solved by direct methods using SHELXS-97 and were refined by full-matrix least-squares on F^2 using SHELXL-14. All non-hydrogen atoms were refined in anisotropic approximation against F^2 of all reflections. Hydrogen atoms were placed at their geometric positions by riding and refined in the isotropic approximation. The crystallographic parameters are listed in the Table 1S.

Computational methodology: Density Functional Theory (DFT) calculations of all the compounds were performed with the B3LYP functional[1s,2s] using 6-31G+(d,p) as the basis set.[2s] Calculations were performed using the Gaussian 09W package.[3s] Gauss View (version 5.0.9) software[4s] was used to visually analyze the calculated data. In each case to generate equivalent compositions by exchange of positions of protons, the positions of the labile protons of the crystallographic information (CIF) file were exchanged at different positions by using the Gauss View program. To create the new assemblies from the CIF file, Gauss View was used by omitting the not required molecules for theoretical studies.

References:

1S. Tirado-Rives, J. and Jorgensen, W. L.; *J. Chem. Theory Comput.*, 2008, **4**, 297–306.
2S. Meng, S.; Li, W.; Yin, X. and Xie, J.; *Comput. Theor. Chem.*, 2013, **1006**, 76–84.
3S. Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Petersson, G.; Nakatsuji, H.; *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2016.
4S. Dennington II, R. D.; Keith, T. A.; Millam, J.; Nielsen, A. B.; Holder, A. J.; *GaussView, Version 5.0.9*, Gaussian, Inc., Wallingford, CT, 2009.

Table 1S: Crystallographic parameters of the binary salt and the ionic cocrystal

Parameters	H_3anthraimmida·pyzda·$2H_2O$·CH_3OH	H_3anthraimmida·pyzda·H_2pyzda·H_2O
Formula	C_{28} H_{33} N_5 O_7	C_{33} H_{31} N_7 O_9
CCDC	2453172	2099503
Mol.wt.	551.59	669.65
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	10.504(3)	8.214(2)
b(Å)	11.035(3)	11.435(3)
c (Å)	12.357(4)	17.873(5)
α (°)	72.607(8)	101.983(8)
β (°)	81.828(9)	96.261(8)
γ (°)	87.451(9)	101.317(8)
V ($Å^3$)	1353(7)	1590.4(8)
Density, g cm^{-3}	1.354	1.398
Abs. coeff., mm^{-1}	0.099	0.104
F (000)	584	700
Total no. of reflections	5932	5635
Reflections, I > 2σ(I)	4570	2905
Max. θ/°	27.115	25.049
Ranges (h, k, l)	−13 ≤ h ≤ 13	−9 ≤ h ≤ 9
	−14 ≤ k ≤ 14	−13 ≤ k ≤ 13
	−15 ≤ l ≤ 15	−21 ≤ l ≤ 21
Complete to 2θ (%)	99.7	99.9
Data/restraints/parameters	5932/0/369	5635/2/459
GooF (F^2)	1.053	1.025
R indices [I > 2σ(I)]	0.0613	0.0760
wR_2 [I > 2σ(I)]	0.1456	0.1756
R indices (all data)	0.0813	0.1497
wR_2 (all data)	0.1629	0.2227

Table 2S: Hydrogen bond parameters of the compounds.

Compounds	D-H···A	d_{D-H} (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D-H···A (°)
H_3anthraimmida·pyzda·$CH_3OH·2H_2O$	N(1) –H(1)...O(2) [1-x,1-y,-z]	0.86	2.56	3.108(4)	122
	N(1) –H(1)...O(3) [1-x,1-y,-z]	0.86	1.96	2.737(3)	150
	N(3) –H(3A)...O(4) [x,y,z]	0.89	1.82	2.693(2)	167
	N(3) –H(3B)...O(4) [1-x,1-y,1-z]	0.89	1.94	2.789(2)	159
	O(5) –H(5C)...O(1) [1-x,1-y,-z]	0.85	2.05	2.861(3)	161
	O(5) –H(5D)...O(6) [x,y,z]	0.85	2.08	2.921(4)	171
	O(6) –H(6C)...O(7) [1+x,y,z]	0.85	1.96	2.793(5)	168
	O(6) –H(6D)...O(2) [1+x,y,z]	0.85	1.93	2.777(4)	177
	O(7) –H(7)...O(1) [-x,1-y,-z]	0.82	2.06	2.863(4)	167
	C(2) –H(2)...O(5) [1-x,1-y,-z]	0.93	2.44	3.251(4)	145
	C(4) –H(4B)...N(4) [1+x,y,z]	0.97	2.49	3.232(3)	133
	C(6) –H(6A)...N(2) [x,y,z]	0.97	2.60	2.967(3)	102
	C(20) –H(20)...N(5) [1-x,1-y,1-z]	0.93	2.45	3.346(3)	162
H_3anthraimmida·pyzda·H_2pyzda·H_2O	N(3) –H(3N')...O(9) [x,y,z]	0.89	1.97	2.809(5)	158
	N(3) –H(3N)...O(3) [1+x,y,z]	0.89	1.96	2.725(5)	143
	N(1) –H(1N)...O(4) [1+x,1+y,z]	0.81(7)	2.09(7)	2.844(6)	154(7)
	N(1) –H(1N)...N(5) [1+x,1+y,z]	0.81(7)	2.42(7)	2.987(6)	128(6)
	O(9) –H(9O')...O(1) [x,y,z]	0.91(5)	1.98(5)	2.890(5)	174(5)
	O(9) –H(9O)...N(6) [x,y,z]	0.89(3)	2.19(4)	3.049(5)	161(5)
	O(5) –H(5O)...O(4) [1+x,y,z]	0.86(6)	1.67(6)	2.505(6)	162(5)
	O(8) –H(8O)...O(1) [x,-1+y,z]	0.82	1.73	2.519(5)	161
	C(2) –H(2)...O(2) [1-x,2-y,-z]	0.93	2.45	3.292(7)	150
	C(1) –H(3)...O(6) [x,1+y,z]	0.93	2.39	3.311(6)	172
	C(4) –H(4A)...O(7) [x,1+y,z]	0.97	2.59	3.422(6)	143
	C(5) –H(5A)...O(2) [1+x,y,z]	0.97	2.47	3.297(6)	143
	C(5) –H(5B)...N(4) [x,y,z]	0.97	2.57	3.338(6)	136
	C(17) –H(17)...O(9) [1-x,2-y,1-z]	0.93	2.58	3.463(7)	158

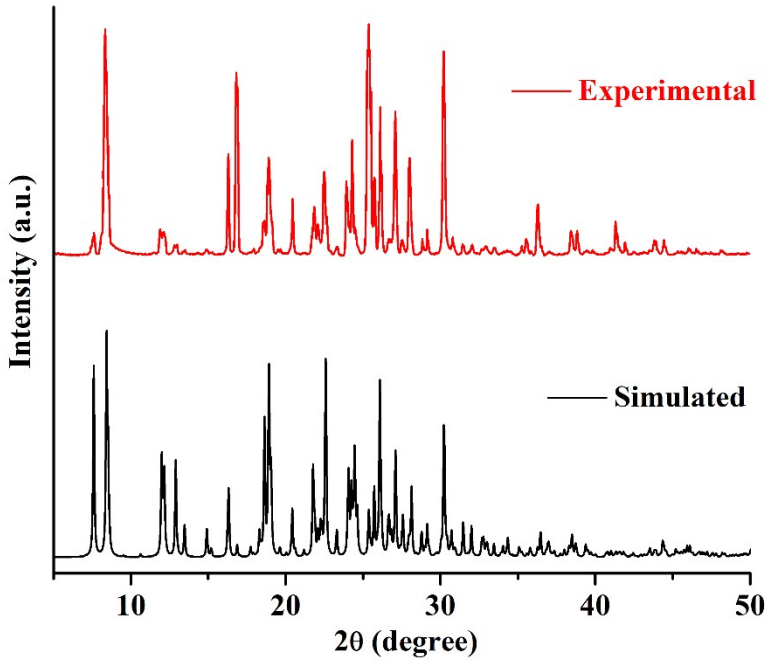


Figure 1S: Powder X-ray diffraction patterns of the H_3anthraimmida·pyzda·$2H_2O$·CH_3OH (Red = Experimental, Black = Simulated; Simulated pattern generated from crystallographic information file).

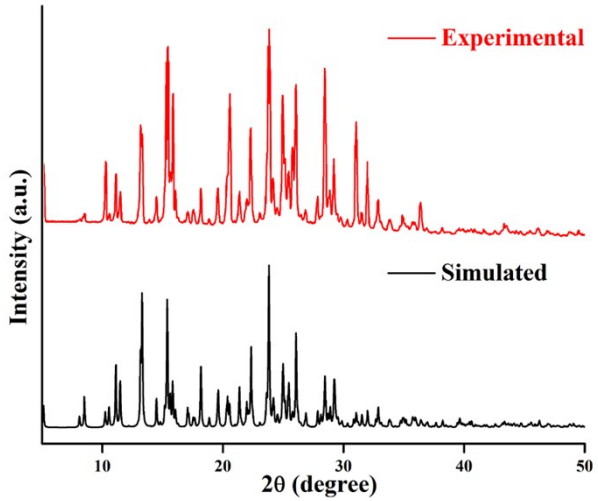


Figure 2S: Powder X-ray diffraction patterns of the H_3anthraimmida·pyzda·H_2pyzda·H_2O (Red = Experimental, Black = Simulated; Simulated pattern generated from crystallographic information file).

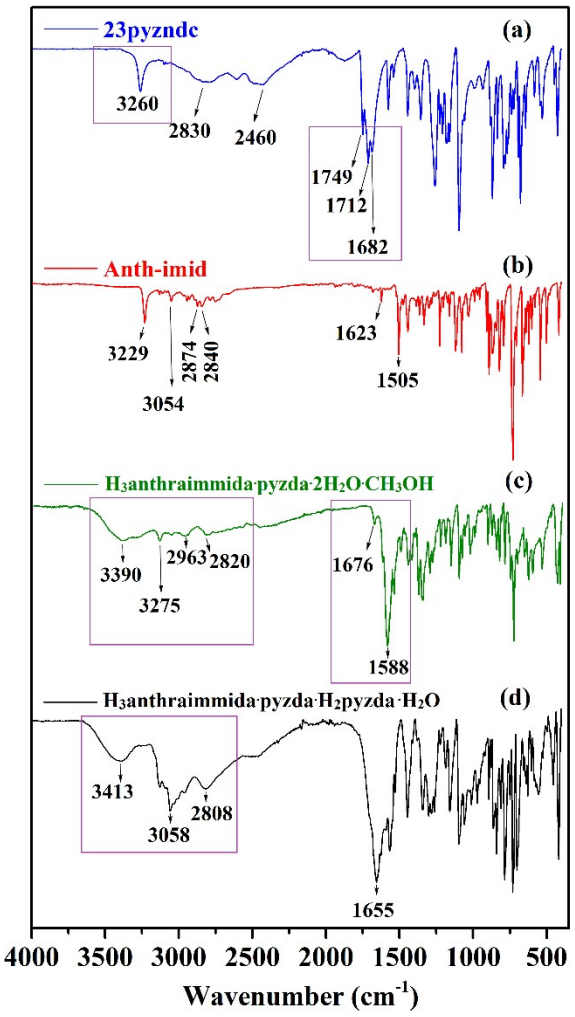


Figure 3S: IR-spectra of (a) pyrazine 2,3-dicarboxylic acid (blue), (b) Hanthraimmida (red), (c) H_3anthraimmida·pyzda·$2H_2O$·CH_3OH (olive) (d)H_3anthraimmida·pyzda·H_2pyzda·H_2O (black).

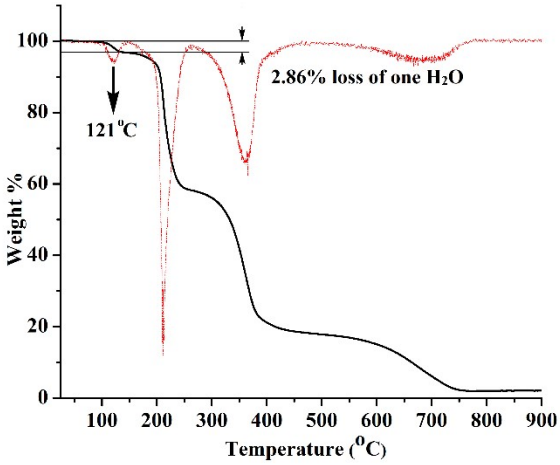


Figure 4S: Thermogram of ionic cocrystal H_3anthraimmida·H_2pyzda·pyzda·H_2O (Heating rate 10°C/min under nitrogen atmosphere).

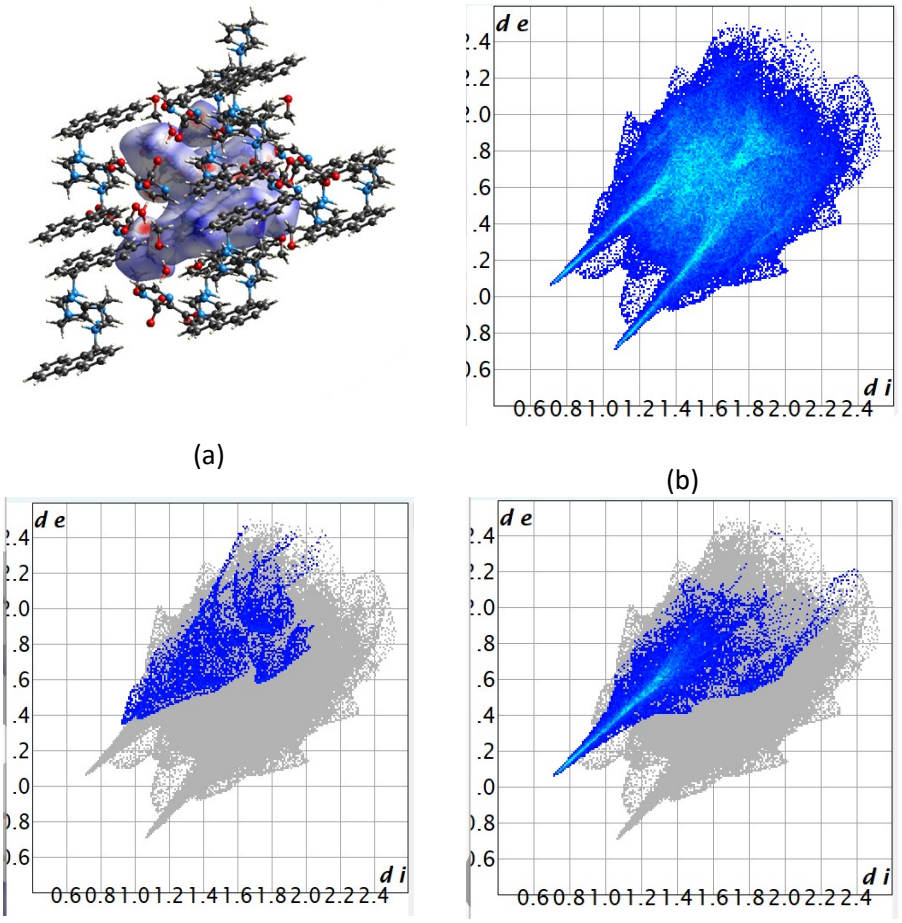


Figure 5S: (a) Hirshfeld surface showing the species within 3.8 Å of the surface and (b) de vs di fingerprint plot, (c) and (d) fingerprint of the all atoms present inside the surface interacting with oxygen (12.3 %), and nitrogen atoms (4.4%) located outside the surface, respectively of the binary salt H_3anthraimmida·pyzda·$2H_2O$·CH_3OH.

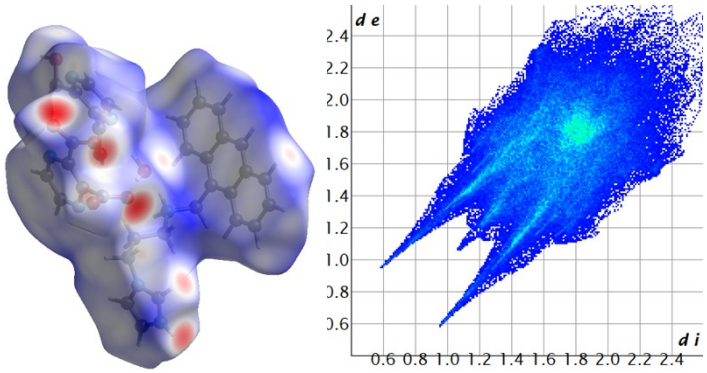
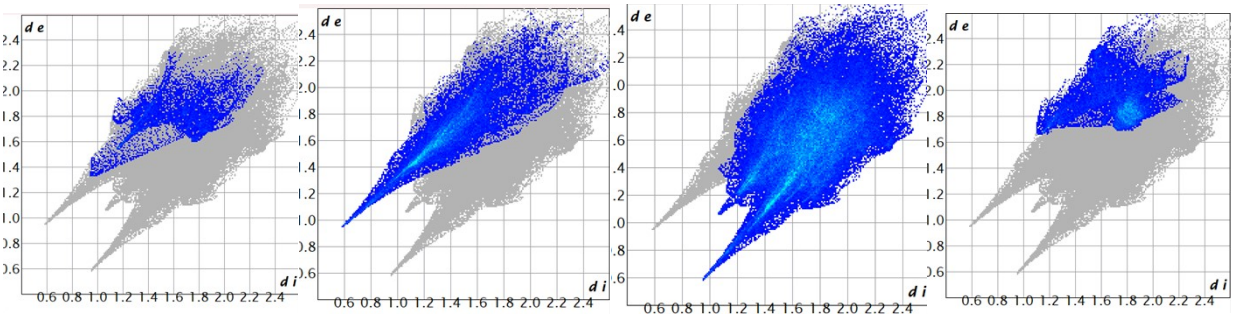
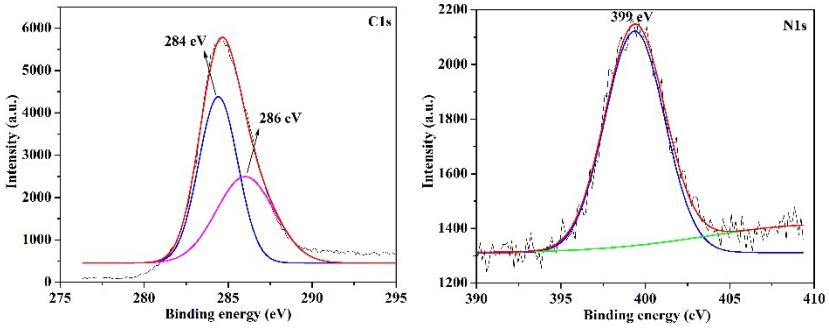


Figure 6S: Hirshfeld surface and de vs di fingerprint plot of the ionic cocrystal.



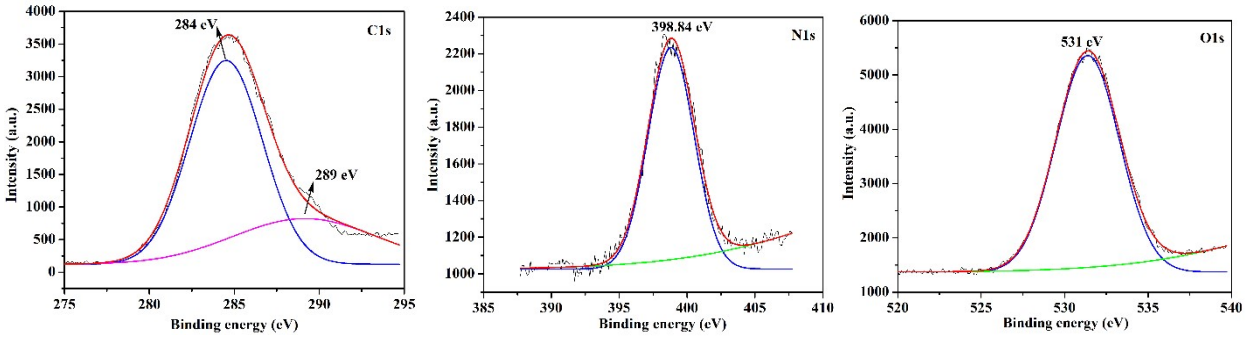
(a) (b) (c) (d)

Figure 7S: The Finger-print plots for all atoms present inside the surface interacting with (a) nitrogen, (b) oxygen, (c) hydrogen and (d) carbon atoms located outside the surface.



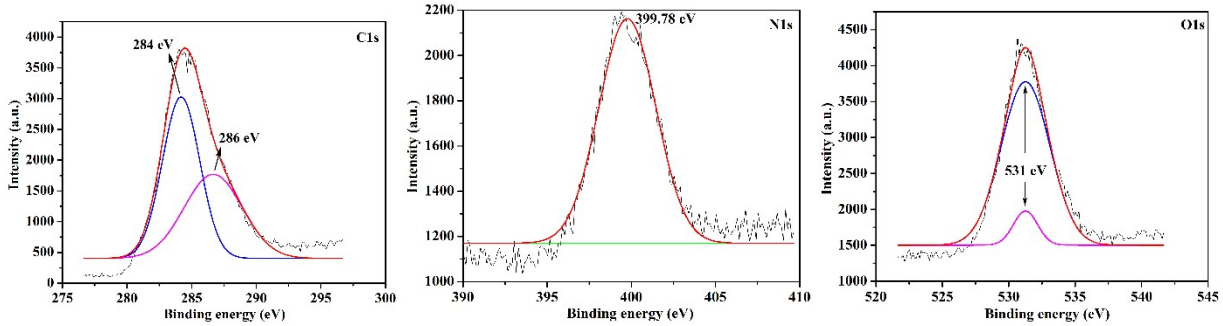
(a) (b)

Figure 8S: XPS spectra (black lines smoothened one shown in red) and the deconvoluted peaks (different colored lines) of Hanthraimmida: (a) C1s; (b) N1s.



(a) (b) (c)

Figure 9S: XPS spectra (black lines smoothened one shown in red) and the deconvoluted peaks (different colored lines) of H_2pyzda: (a) C1s; (b) N1s; (c) O1s.



(a) (b) (c)

Figure 10S: XPS spectra (black lines smoothened one shown in red) and the deconvoluted peaks (different colored lines) of H_3anthraimmida·H_2pyzda·pyzda·H_2O: (a) C1s; (b) N1s; (c) O1s.