Electronic Supplementary Information (ESI)

Structure controlled solvatochromism and halochromic fluorescence switching of 2,2'-bipyridine based donor-acceptor derivatives

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1. FT-IR Spectra

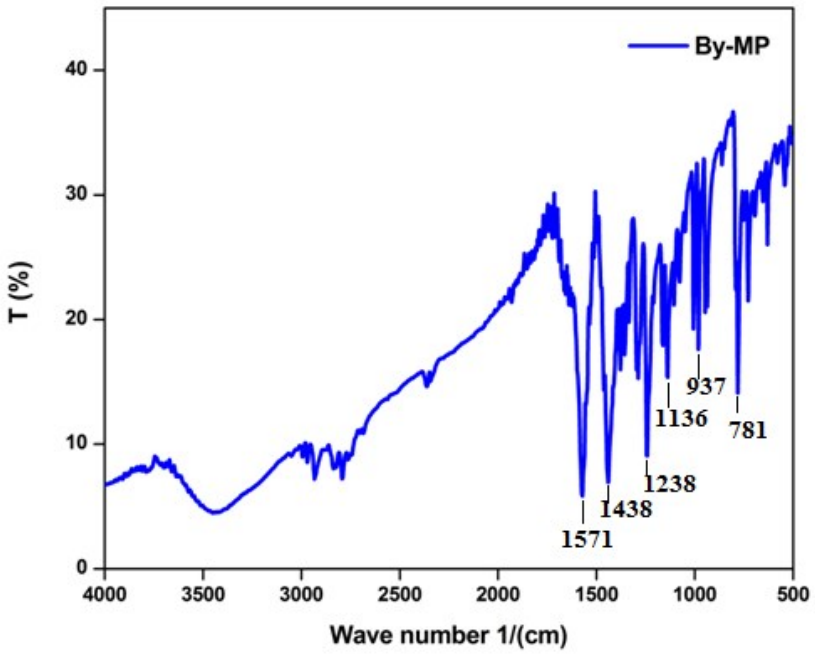

Fig. S1 FT-IR spectrum of Bpy-1MP.

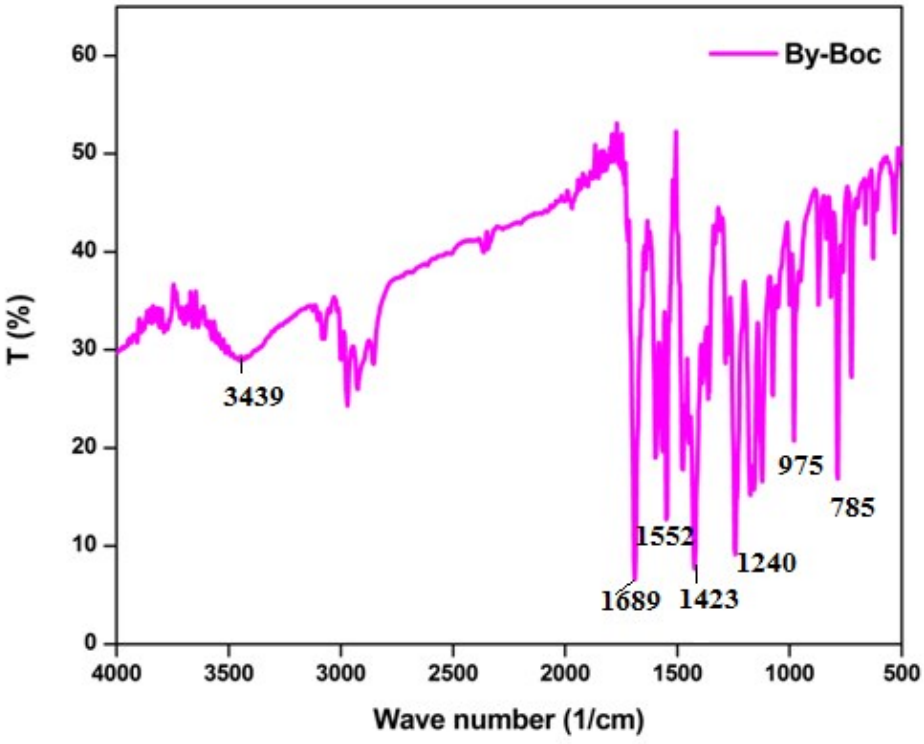

Fig. S2 FT-IR spectrum of Bpy-BP.

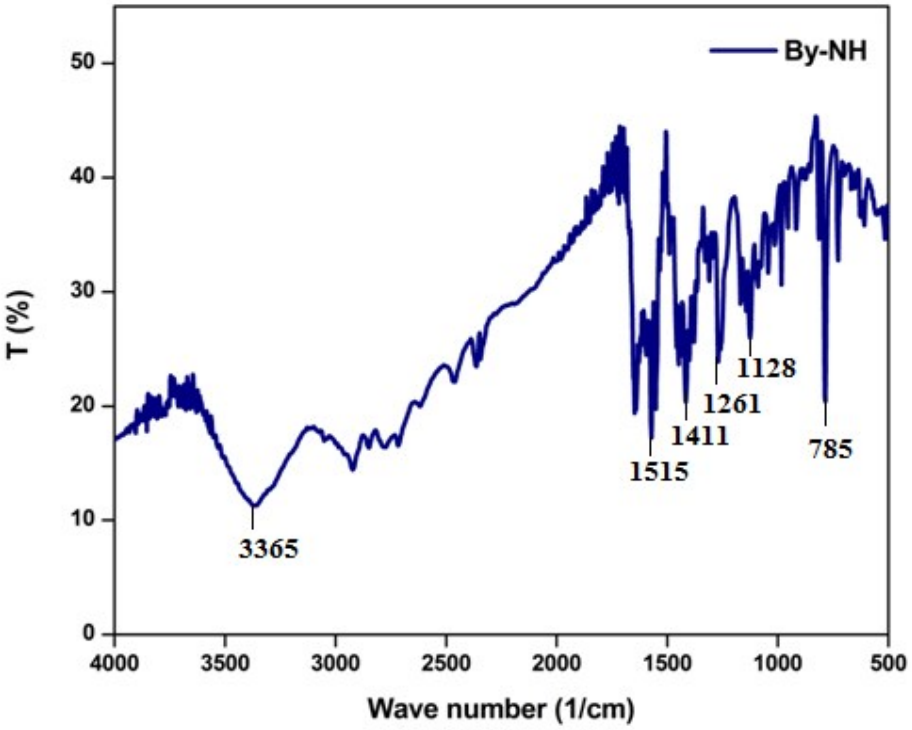

Fig. S3 FT-IR spectrum of Bpy-Pep.

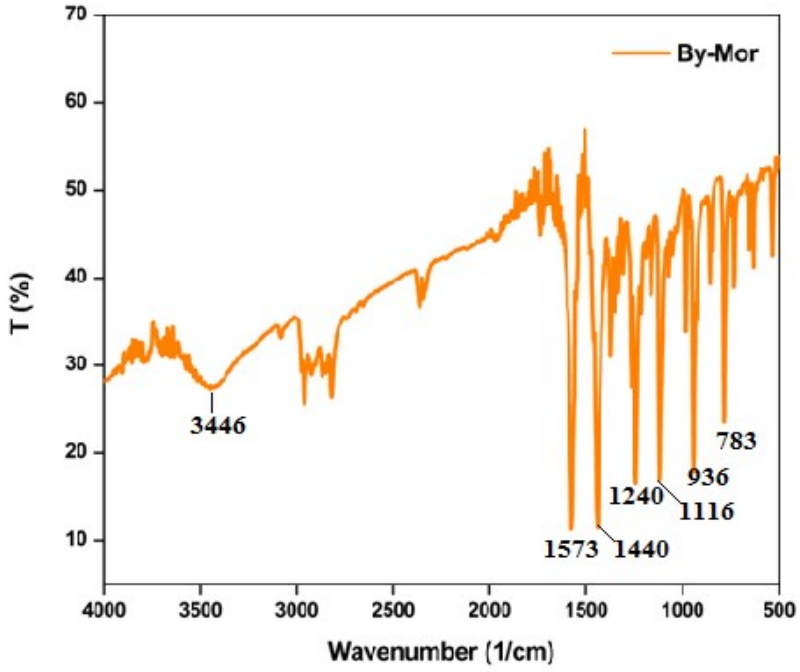

Fig. S4 FT-IR spectrum of Bpy-Mor.

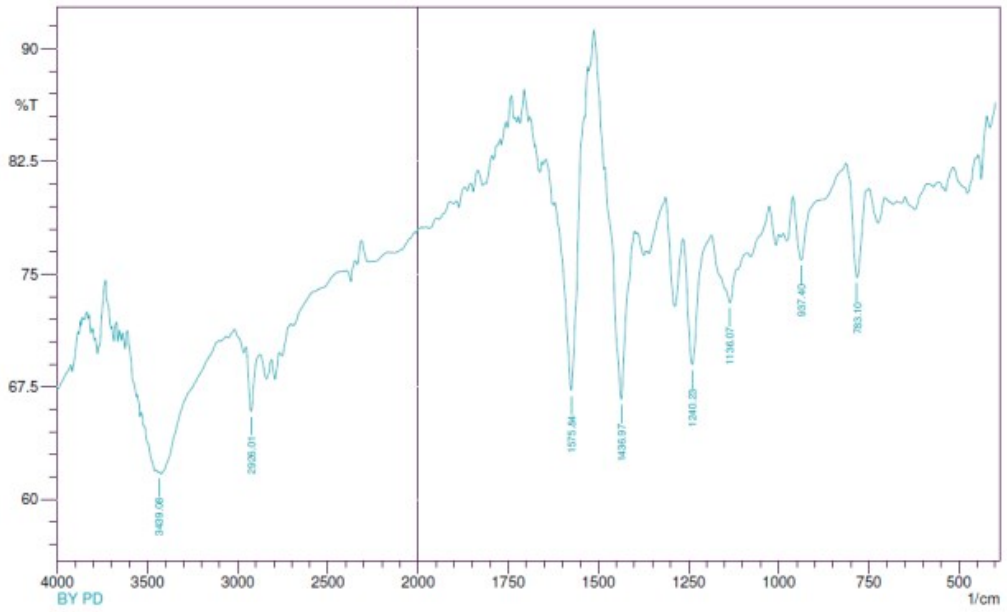

Fig. S5 FT-IR spectrum of Bpy-Pip

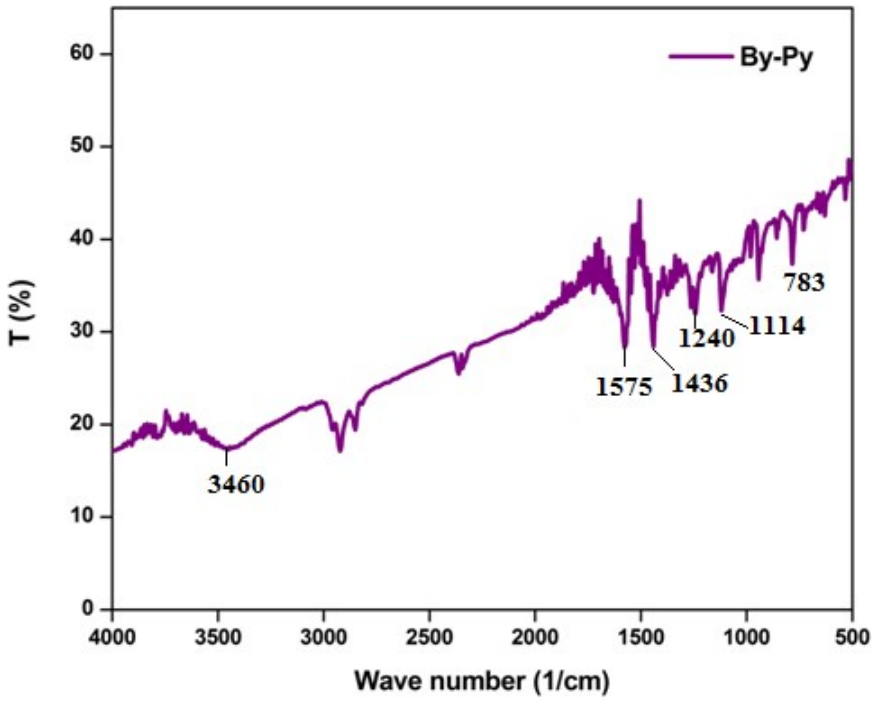

Fig. S6 FT-IR spectrum of Bpy-Pyr.

2. NMR Studies

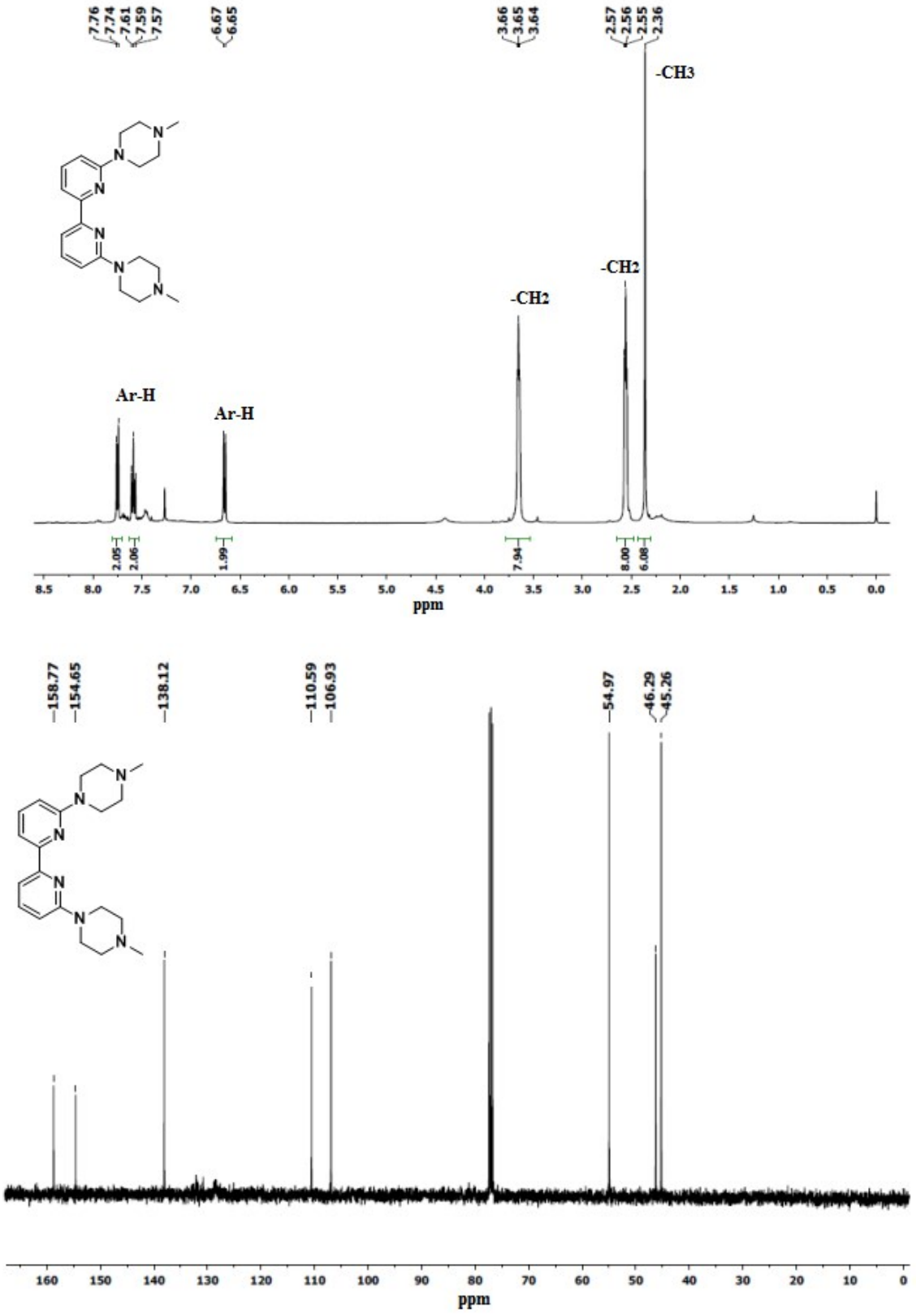

Fig. S7 ^{1}H & ^{13}C NMR spectrum of Bpy-1MP.

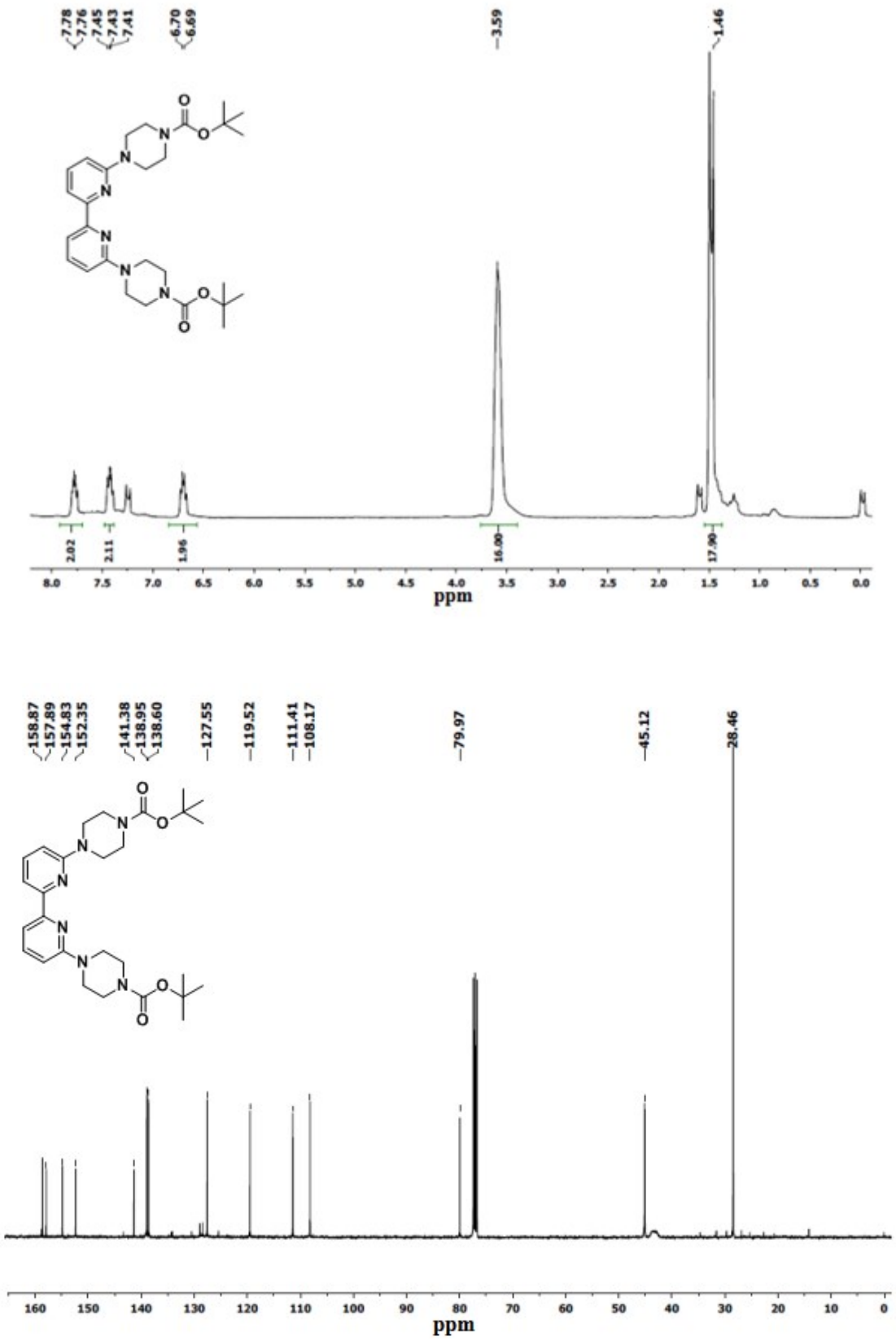

Fig. S8 ^{1}H & ^{13}C NMR spectrum of Bpy-BP.

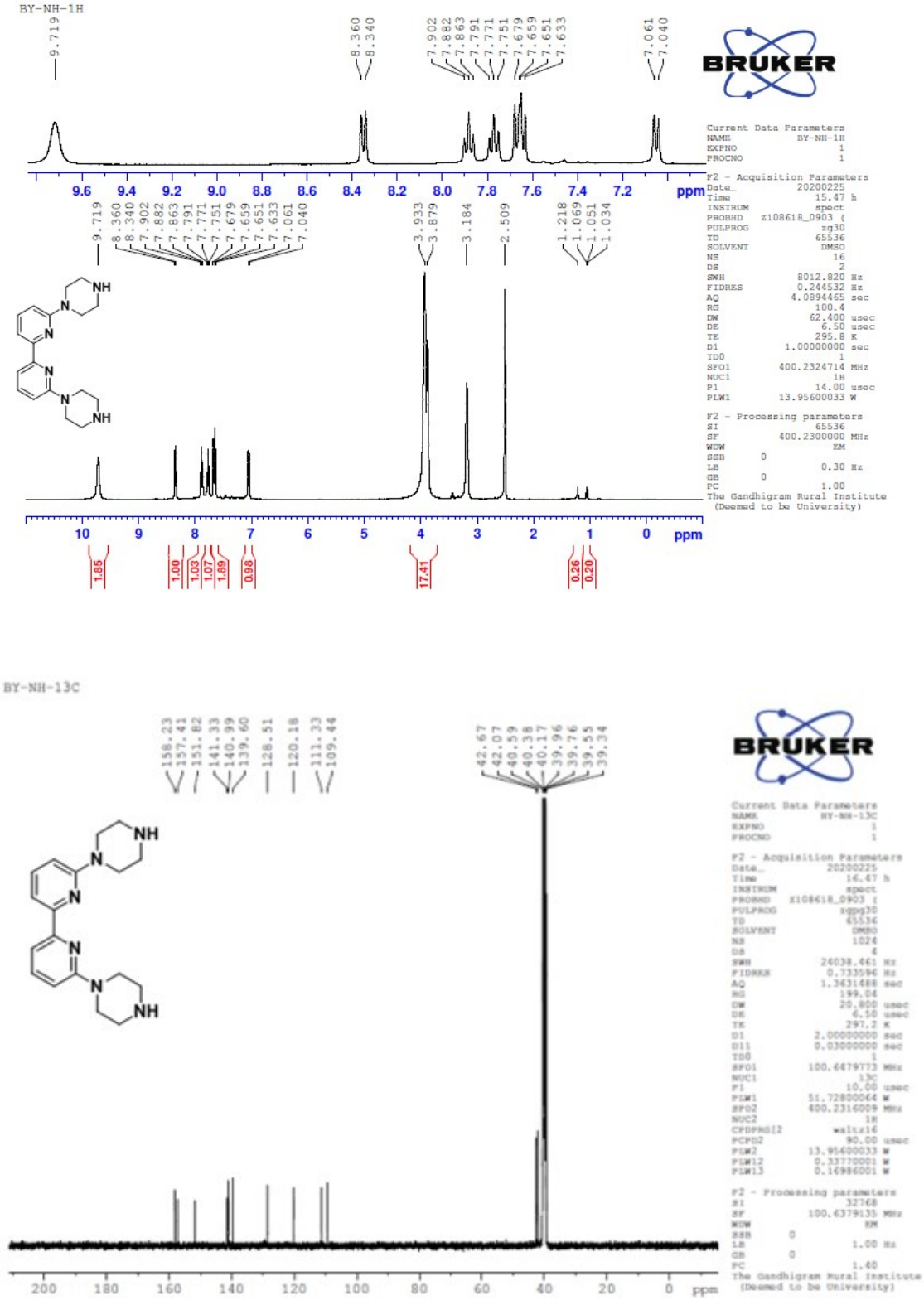

Fig. S9 ^{1}H & ^{13}C NMR spectrum of Bpy-Pep

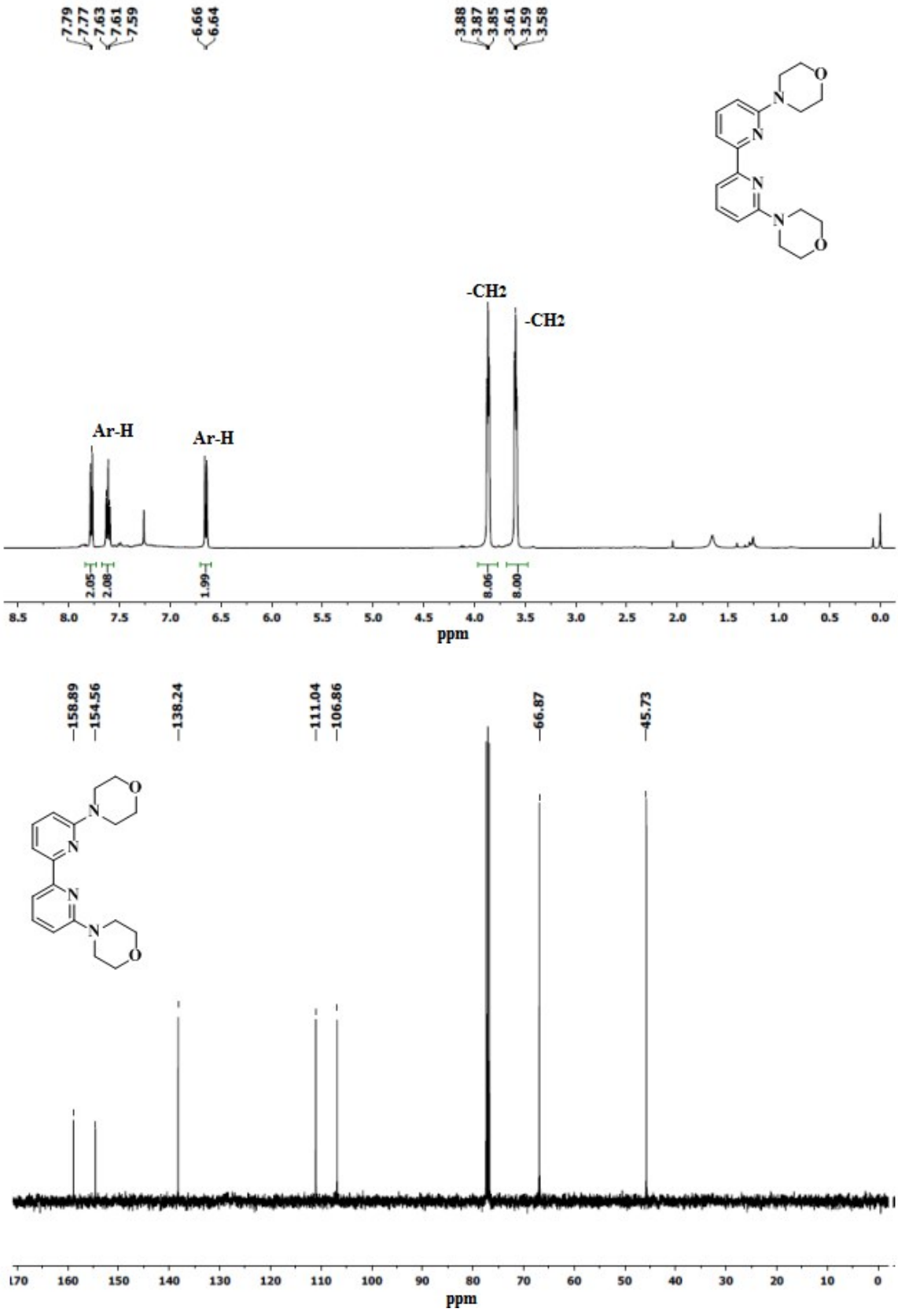

Fig. S10 ^{1}H & ^{13}C NMR spectrum of Bpy-Mor.

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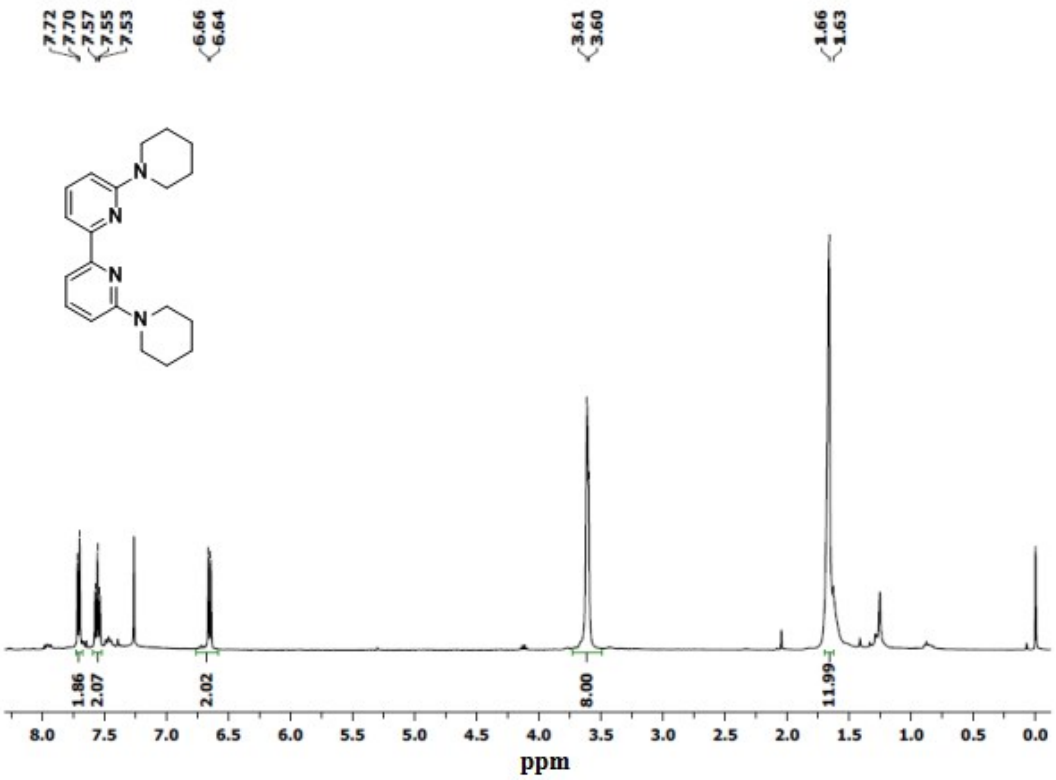

7.72
7.70
7.57
7.55
7.53
6.66
6.64
3.61
3.60
1.66
1.63
1.86
2.07
2.02
8.00
11.99
ppm

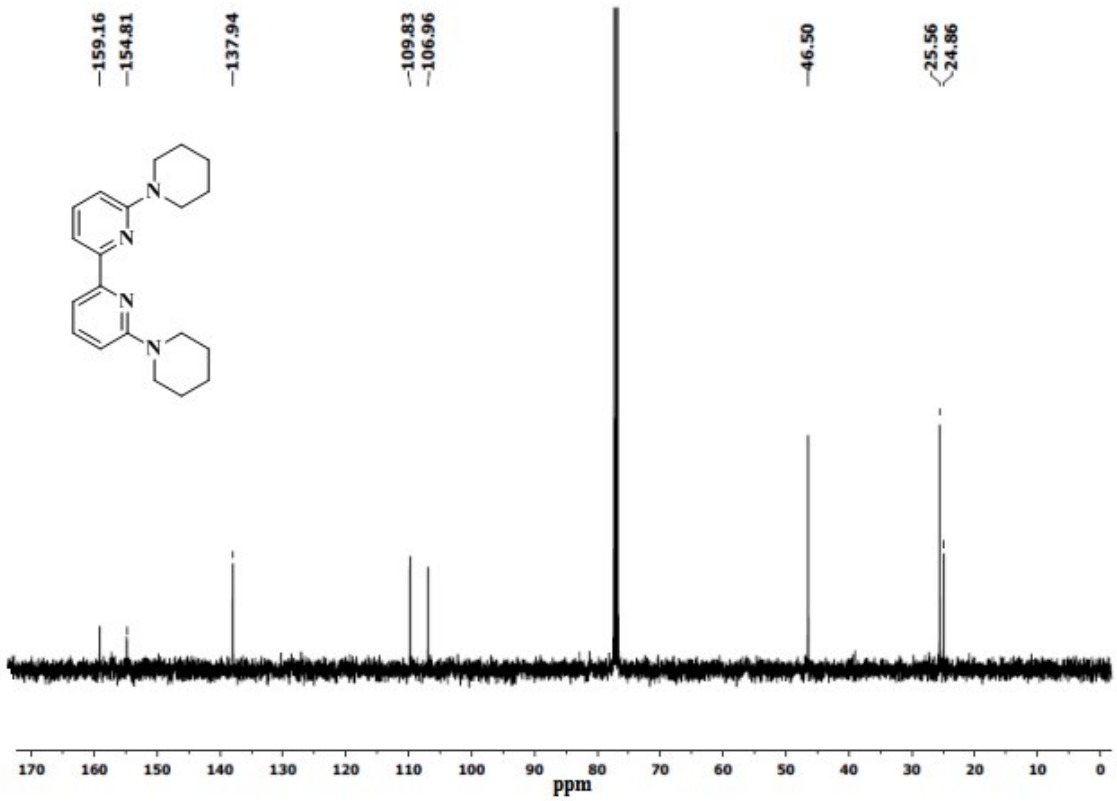
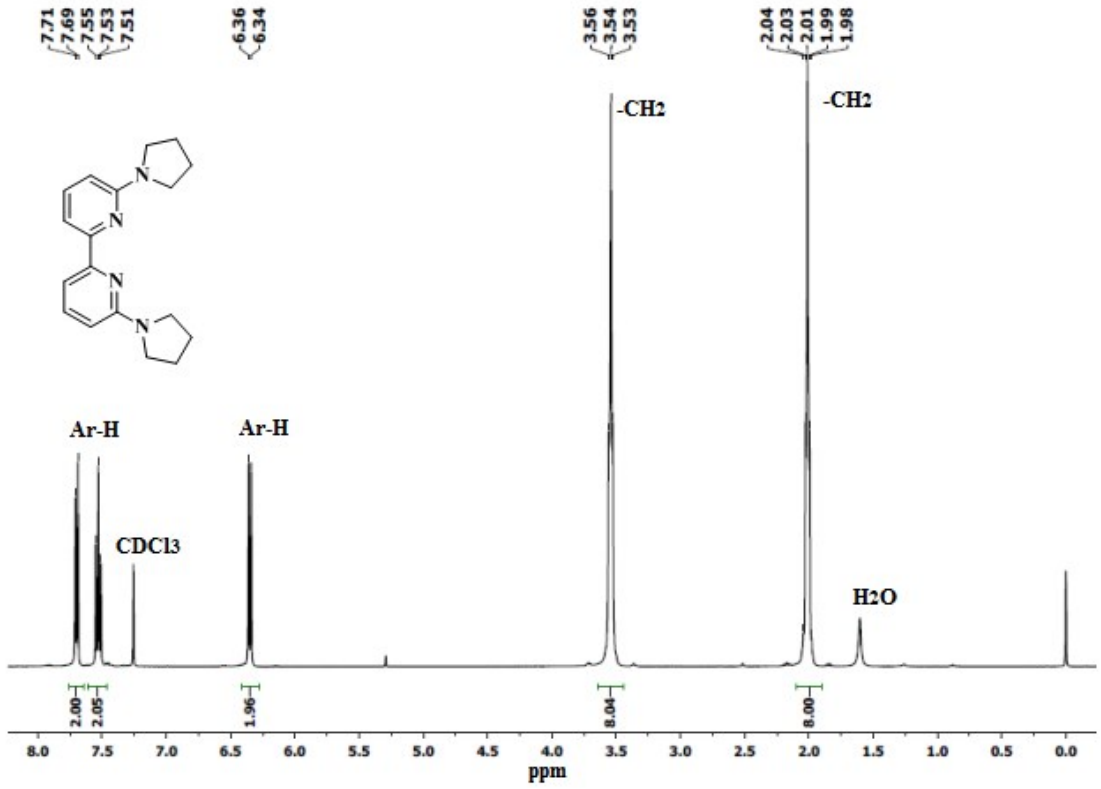

159.16
154.81
137.94
109.83
106.96
46.50
25.56
24.86
ppm

Fig. S11 ^{1}H & ^{13}C NMR spectrum of Bpy-Pip.



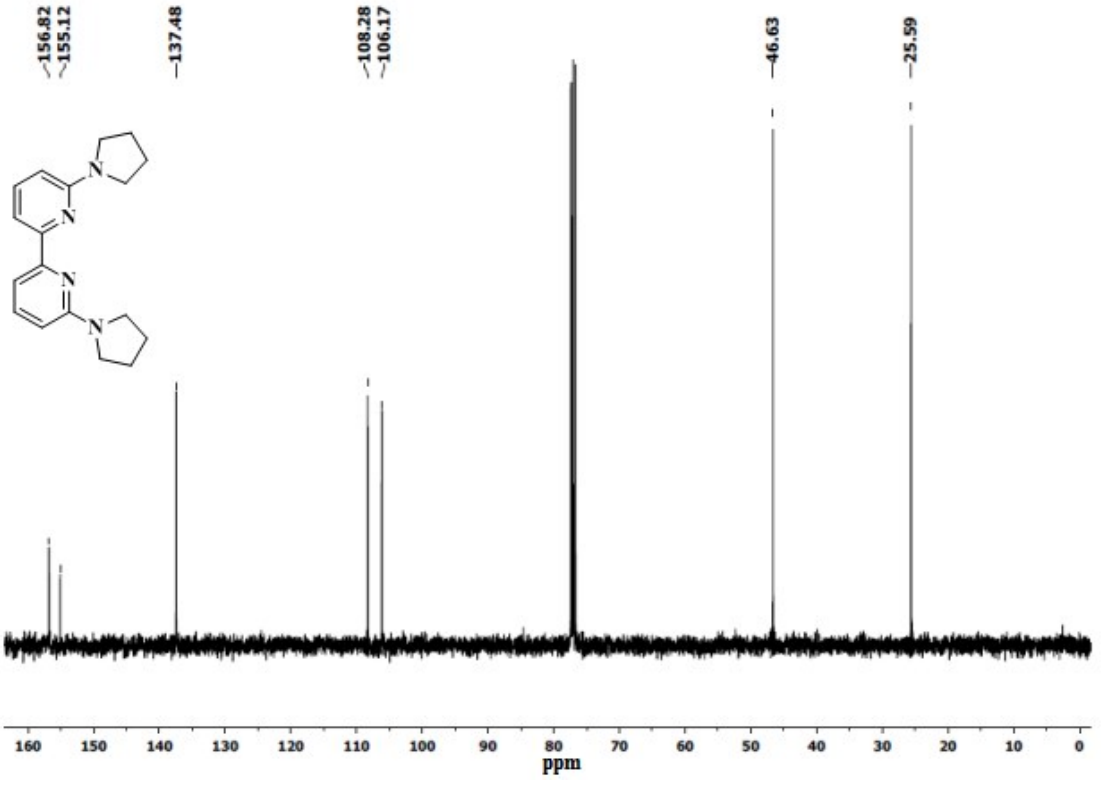


Fig. S12 ^{1}H & ^{13}C NMR spectrum of Bpy-Pyr.

3. **Mass analysis**

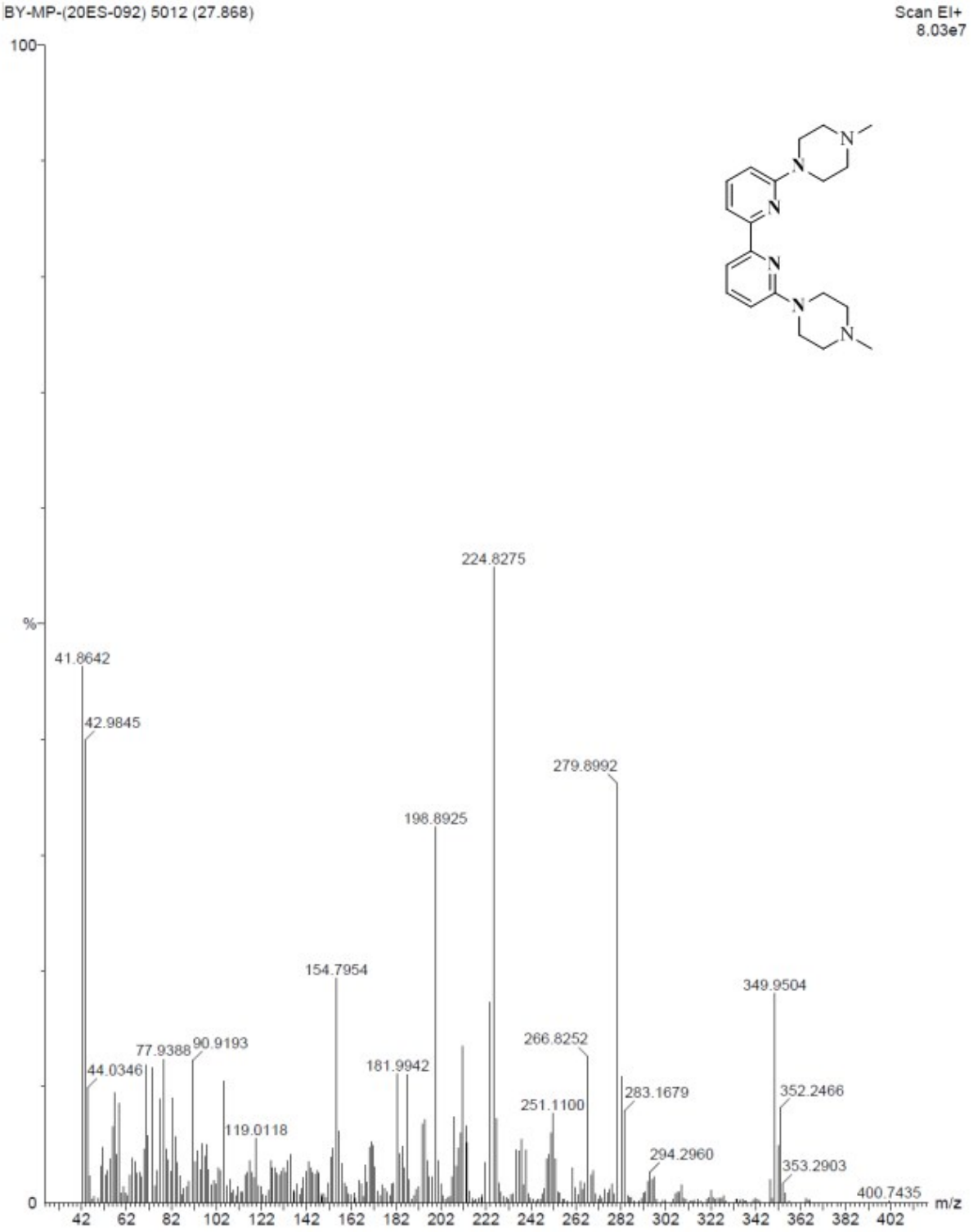


Fig. S13 ESI-MS spectrum for Bpy-1MP

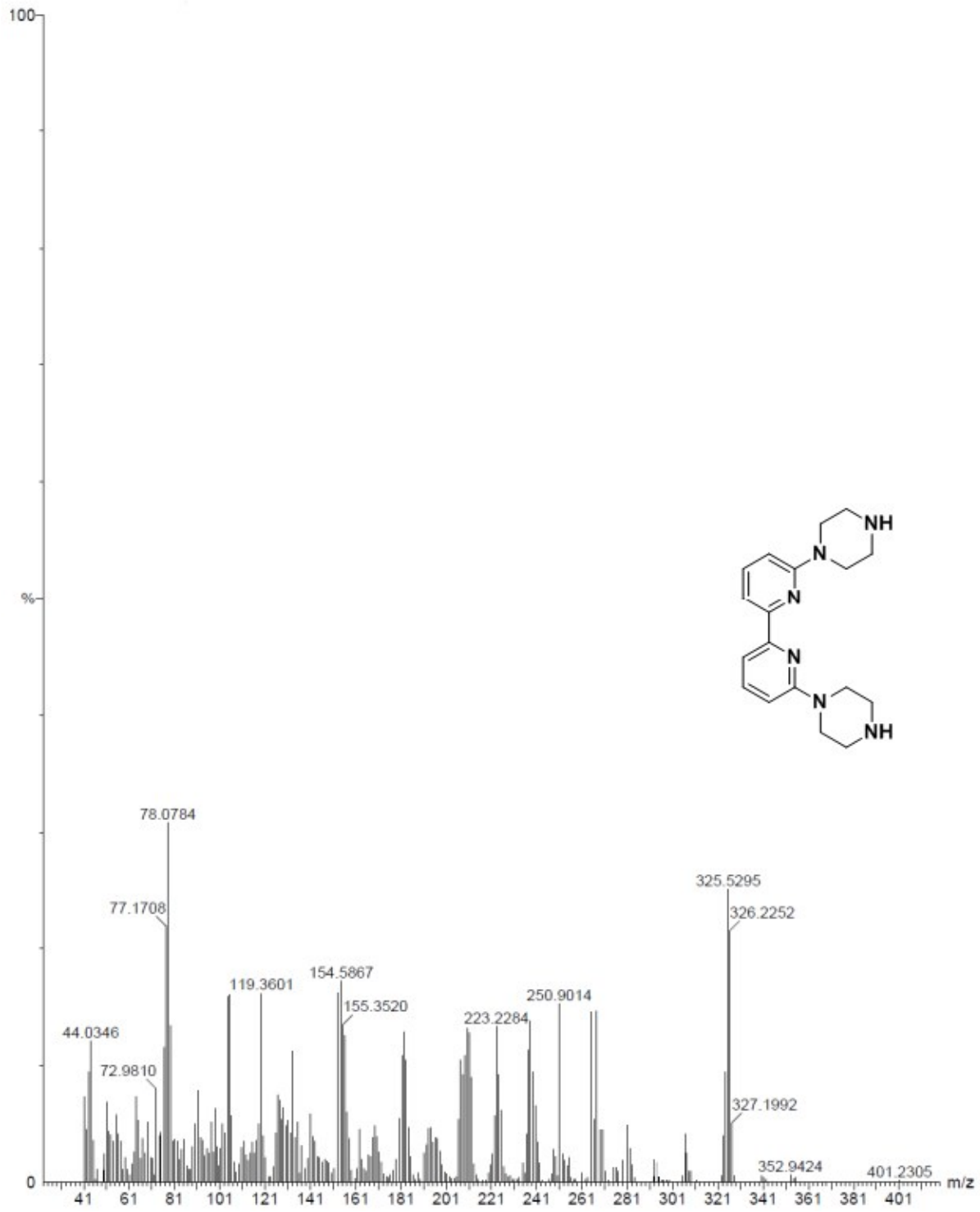


Fig. S14 ESI-MS spectrum for Bpy-Pep.

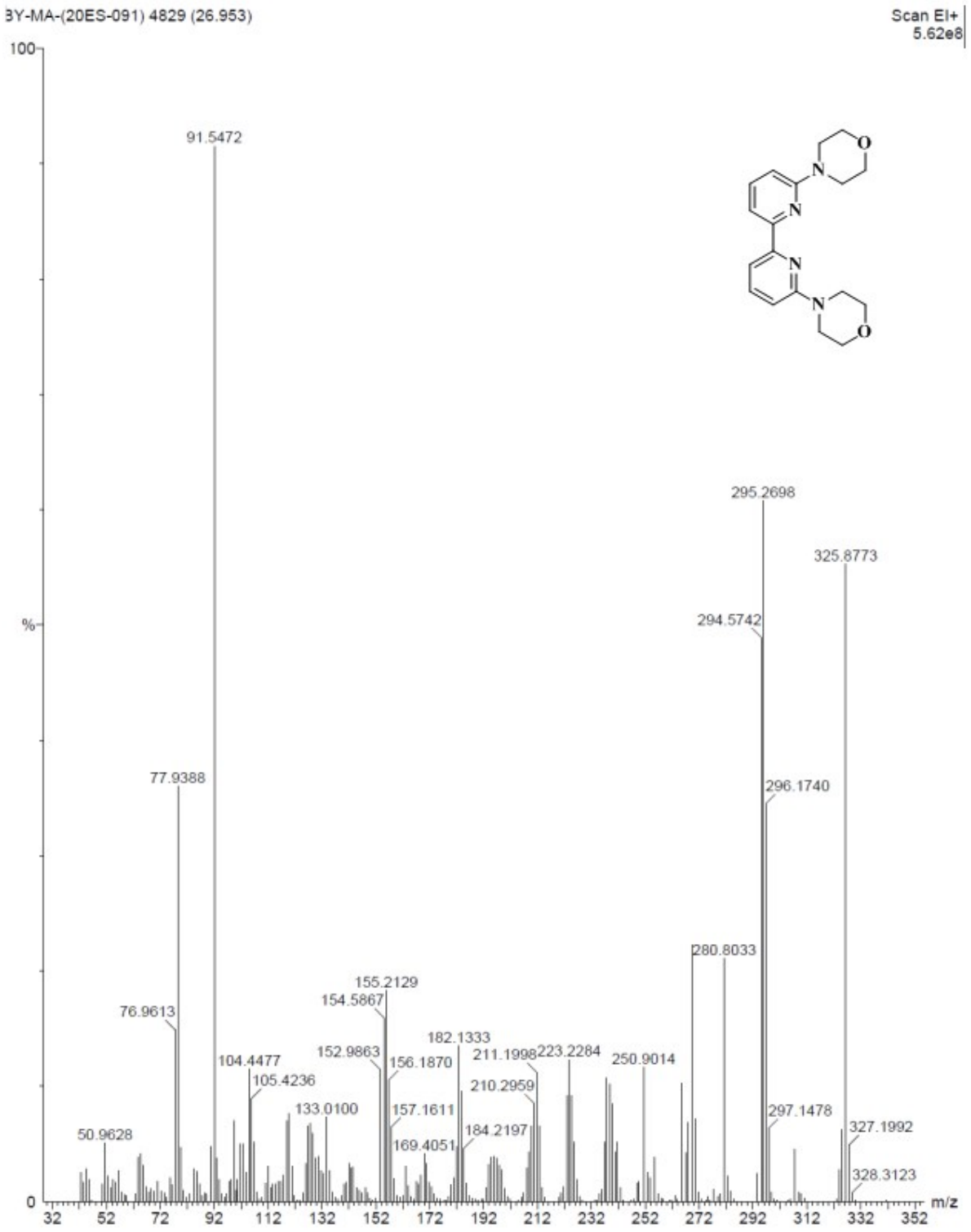


Fig. S15 ESI-MS spectrum for Bpy-Mor

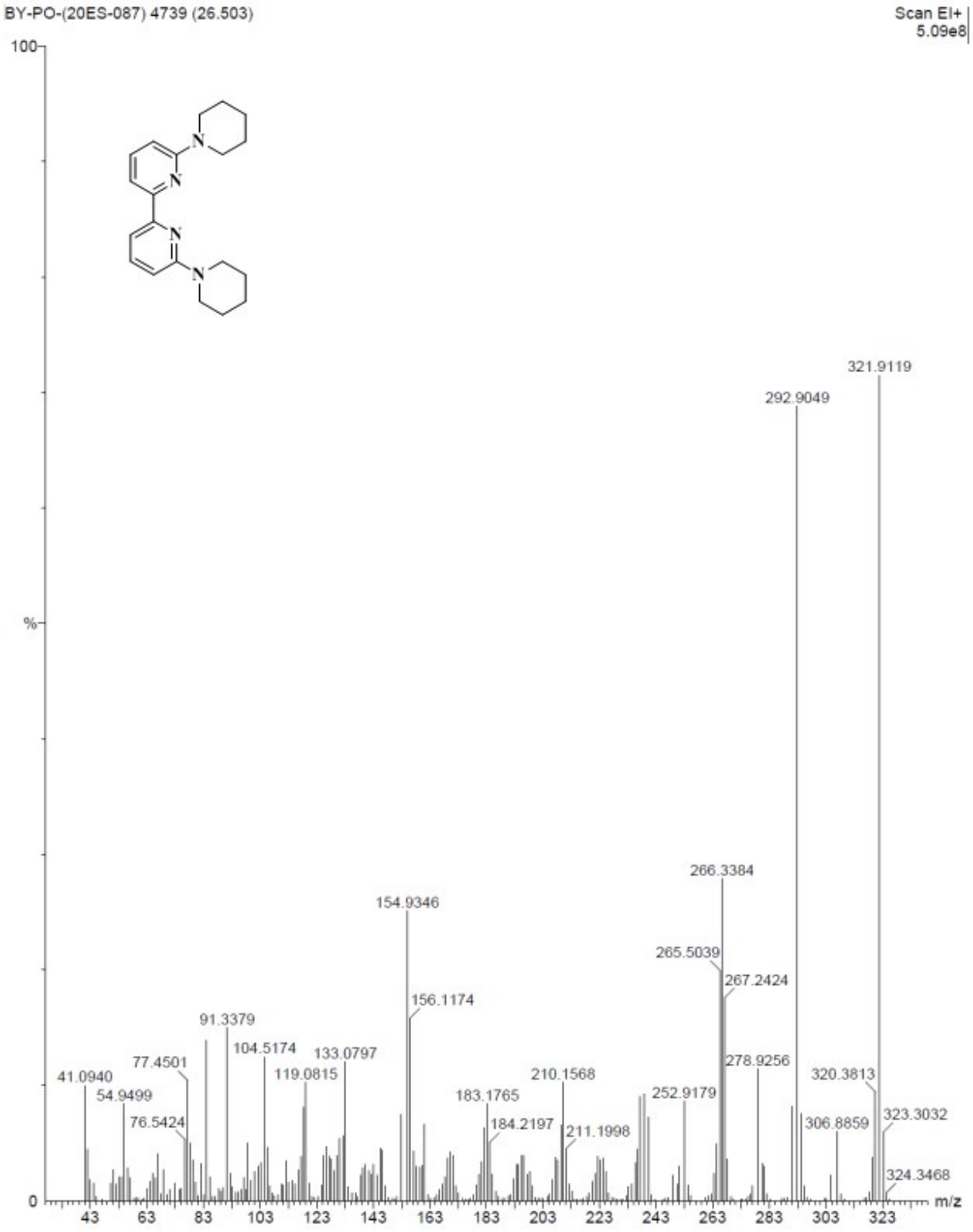


Fig. S16 ESI-MS spectrum for Bpy-Pip.

4. Single Crystal X-ray crystallography studies

A single crystal of Bpy-1MP, Bpy-Pyr and (Bpy-MorH)PF_6 was coated with paratone-N oil and the diffraction data were measured at 100 K with synchrotron radiation (l = 0.60999 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program[1] was used for data collection (the detector distance is 63 mm, omega scan; Do = 31, the exposure time is 2 s per frame) and HKL3000sm (Ver. 703r)[2] was used for cell refinement, reduction and absorption correction. The crystal structure of AAP-Ru, ADABS-Ru(II) and P2P-Ru(II) was solved by the direct method using the SHELX-XT (2014/4) program and refined by full-matrix least square calculations using the SHELX-XL (2014/7) program package.[3] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned an isotropic displacement coefficient of Uiso(H) = 1.2 or 1.5Ueq, and their coordinates were allowed to ride on their respective atoms.

Table S1. Crystal data and structure refinement for Bpy-1MP, Bpy-Pyr and (Bpy-MorH)PF_6.

Compound	**Bpy-1MP**	**Bpy-Pyr**	**(Bpy-MorH)PF_6**
Empirical formula	$C_{20}H_{28}N_6$	$C_{18}H_{22}N_4$	$C_{18}H_{23}F_6N_4O_2P$
Formula weight	352.48	294.39	472.37
T [K]	220(2)	220(2)	220(2)
λ [Å]	0.630	0.630	0.630
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	4.8930(10)	7.0750(14)	7.1800(14)
b, Å	10.170(2)	7.3030(15)	14.821(3)
c, Å	18.638(4)	14.865(3))	19.057(4)
α, deg	90	90	90
β, deg	91.05(3)	96.04	98.31(3)
γ, deg	90	90	90
V (Å^3)	927.3(3)	763.8(3)	2006.7(7)
Z	2	2	4
d_{calc} (mg/cm^3)	1.262	1.280	1.564
μ (mm^{-1})	0.062	0.062	0.158
R[I>2σ(I)]	R_1 = 0.0492 wR_2 =0.1444	R_1 = 0.0465 wR_2=0.1369	R_1 = 0.1179 wR_2 = 0.3022
R (all data)	R_1 = 0.0542 wR_2=0.1481	R_1 = 0.0501 wR_2=0.1418	R_1 = 0.1510 wR_2 = 0.3195
Largest diff. Peak/hole [e Å^{-3}]	0.437/ -0.276	0.381 /-0.261	1.497/-0.500

Table S2. Selected Bond lengths [Å] and angles [°] for compound **Bpy-1MP**

N(1)-C(5)	1.3374(13)	N(1)-C(1)	1.3454(12)
N(2)-C(5)	1.3978(12)	N(2)-C(6)	1.4608(13)
N(2)-C(9)	1.4616(13)	N(3)-C(7)	1.4567(14)
N(3)-C(10)	1.4586(14)	N(3)-C(8)	1.4588(14)
C(1)-C(2)	1.3851(15)	C(1)-C(1)#1	1.493(2)
C(2)-C(3)	1.3856(16)	C(3)-C(4)	1.3790(15)
C(4)-C(5)	1.4041(15)	C(6)-C(7)	1.5165(15)
C(5)-N(1)-C(1)	118.88(9)	C(5)-N(2)-C(6)	118.84(9)
C(5)-N(2)-C(9)	116.83(8)	C(6)-N(2)-C(9)	112.16(8)
C(7)-N(3)-C(10)	109.80(9)	C(7)-N(3)-C(8)	109.08(8)
C(10)-N(3)-C(8)	110.47(10)	N(1)-C(1)-C(2)	122.83(9)
N(1)-C(1)-C(1)#1	115.97(11)	C(2)-C(1)-C(1)#1	121.20(11)
C(1)-C(2)-C(3)	117.83(10)	C(4)-C(3)-C(2)	120.39(10)
C(3)-C(4)-C(5)	118.12(10)	N(1)-C(5)-C(4)	121.95(9)
N(1)-C(5)-N(2)	116.02(9)	N(2)-C(5)-C(4)	122.01(9)
N(2)-C(6)-C(7)	109.89(9)	N(2)-C(6)-H(6A)	109.7
N(3)-C(7)-C(6)	112.34(8)	N(3)-C(8)-C(9)	111.30(10)
N(2)-C(9)-C(8)	111.09(9)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

Table S3. Selected bond lengths [Å] and angles [°] for compound **Bpy-Pyr**

N(1)-C(5)	1.3454(12)	N(1)-C(1)	1.3464(13)
N(2)-C(5)	1.3602(13)	N(2)-C(9)	1.4549(12)
N(2)-C(6)	1.4650(12)	C(1)-C(2)	1.3887(12)
C(1)-C(1)#1	1.4962(17)	C(2)-C(3)	1.3961(13)
C(3)-C(4)	1.3725(14)	C(4)-C(5)	1.4162(12)
C(6)-C(7)	1.5256(14)	C(7)-C(8)	1.5232(16)
C(8)-C(9)	1.5236(15)	C(5)-N(2)-C(9)	124.30(8)
C(5)-N(1)-C(1)	118.38(8)	C(5)-N(2)-C(6)	122.35(8)
C(9)-N(2)-C(6)	112.60(8)	N(1)-C(1)-C(2)	123.33(9)
N(1)-C(1)-C(1)#1	116.15(9)	C(2)-C(1)-C(1)#1	120.51(10)
C(1)-C(2)-C(3)	117.58(9)	C(4)-C(3)-C(2)	120.57(8)
C(3)-C(4)-C(5)	118.06(9)	N(1)-C(5)-N(2)	116.59(8)
N(1)-C(5)-C(4)	122.07(9)	N(2)-C(5)-C(4)	121.34(9)
N(2)-C(6)-C(7)	104.18(9)	C(8)-C(7)-C(6)	104.52(8)
C(7)-C(8)-C(9)	104.03(8)	N(2)-C(9)-C(8)	102.65(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S4. Selected bond lengths [Å] and angles [°] for Compound **(Bpy-MorH)PF_6**

O(1)-C(8)	1.414(7)	O(1)-C(7)	1.417(6)
O(2)-C(16)	1.414(6)	O(2)-C(17)	1.417(5)
N(1)-C(5)	1.337(5)	N(1)-C(1)	1.346(5)
N(2)-C(5)	1.373(5)	N(2)-C(9)	1.455(5)
N(2)-C(6)	1.459(6)	N(3)-C(14)	1.356(5)
N(3)-C(10)	1.370(5)	N(4)-C(14)	1.338(5)
N(4)-C(18)	1.475(5)	N(4)-C(15)	1.475(5)
C(1)-C(2)	1.384(5)	C(1)-C(10)	1.486(5)
C(2)-C(3)	1.393(6)	C(3)-C(4)	1.377(6)
C(4)-C(5)	1.420(5)	C(6)-C(7)	1.494(6)
C(8)-C(9)	1.514(7)	C(10)-C(11)	1.357(5)
C(11)-C(12)	1.413(6)	C(12)-C(13)	1.355(6)
C(13)-C(14)	1.420(5)	C(15)-C(16)	1.506(6)
C(17)-C(18)	1.517(6)	C(8)-O(1)-C(7)	109.9(4)
C(16)-O(2)-C(17)	109.9(3)	C(5)-N(1)-C(1)	118.8(3)
C(5)-N(2)-C(9)	120.0(3)	C(5)-N(2)-C(6)	118.5(3)
C(9)-N(2)-C(6)	113.6(4)	C(14)-N(3)-C(10)	125.4(3)
C(14)-N(4)-C(18)	122.3(3)	C(14)-N(4)-C(15)	121.7(3)
C(18)-N(4)-C(15)	113.6(3)	N(1)-C(1)-C(2)	124.3(3)
N(1)-C(1)-C(10)	113.7(3)	C(2)-C(1)-C(10)	121.9(3)
C(1)-C(2)-C(3)	116.6(4)	C(4)-C(3)-C(2)	120.5(4)
C(3)-C(4)-C(5)	118.9(3)	N(1)-C(5)-N(2)	116.7(3)
N(1)-C(5)-C(4)	120.8(3)	N(2)-C(5)-C(4)	122.5(3)
N(2)-C(6)-C(7)	111.1(4)	O(1)-C(7)-C(6)	113.1(4)
O(1)-C(8)-C(9)	112.8(4)	N(2)-C(9)-C(8)	108.9(4)
C(11)-C(10)-N(3)	118.8(3)	C(11)-C(10)-C(1)	127.8(4)
N(3)-C(10)-C(1)	113.4(3)	C(10)-C(11)-C(12)	118.3(4)
C(13)-C(12)-C(11)	121.6(4)	C(12)-C(13)-C(14)	120.3(4)
N(4)-C(14)-N(3)	119.6(3)	N(4)-C(14)-C(13)	124.9(4)
N(3)-C(14)-C(13)	115.5(4)	N(4)-C(15)-C(16)	110.1(4)
O(2)-C(16)-C(15)	111.3(4)	O(2)-C(17)-C(18)	110.3(4)
N(4)-C(18)-C(17)	108.9(3)		

5. Photophysical Properties

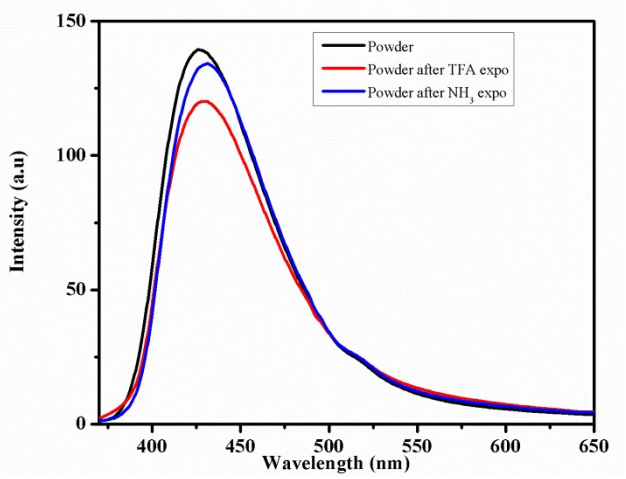


Fig. S17 Solid state fluorescence spectra of Bpy-1MP before and after exposure to TFA vapor followed by NH_3 vapor exposure.

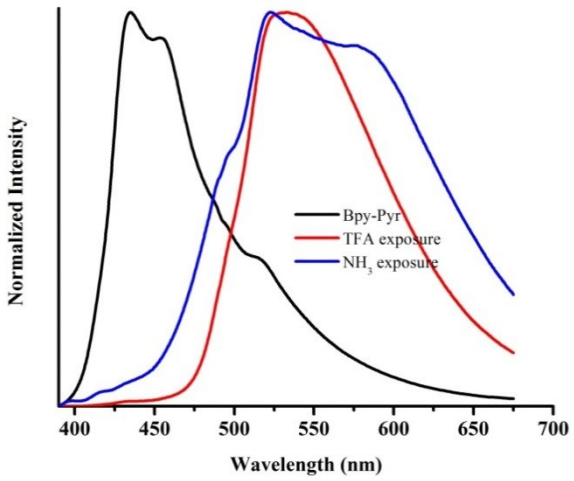


Fig. S18 Fluorescence spectra of Bpy-pyr before and after exposure to TFA vapor followed by NH_3 vapor exposure.

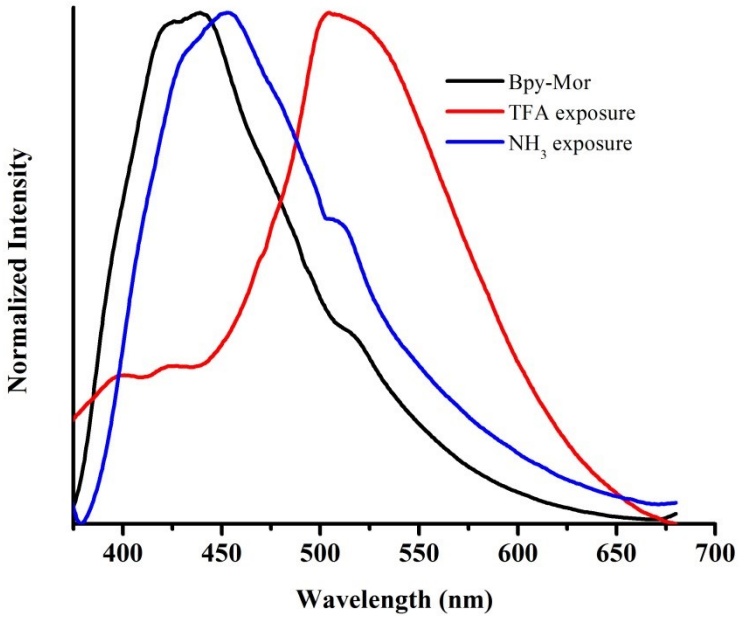


Fig. S19 Fluorescence spectra of Bpy-Mor before and after exposure to TFA vapor followed by NH_3 vapor exposure.

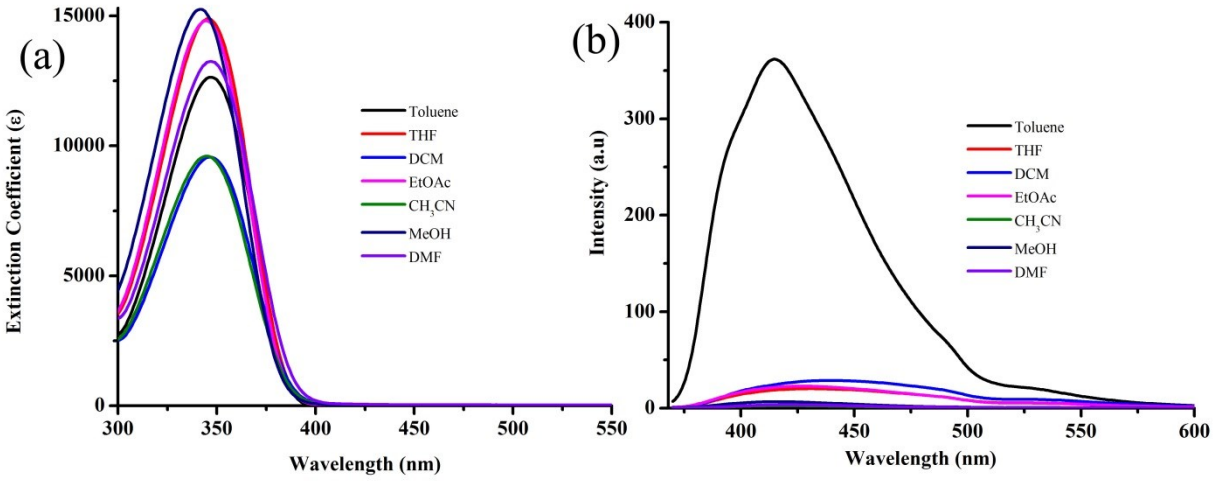


Fig. S20 (a) Absorption spectra of Bpy-1MP in different solvents. (b) Fluorescence spectra of Bpy-1MP in different solvents.

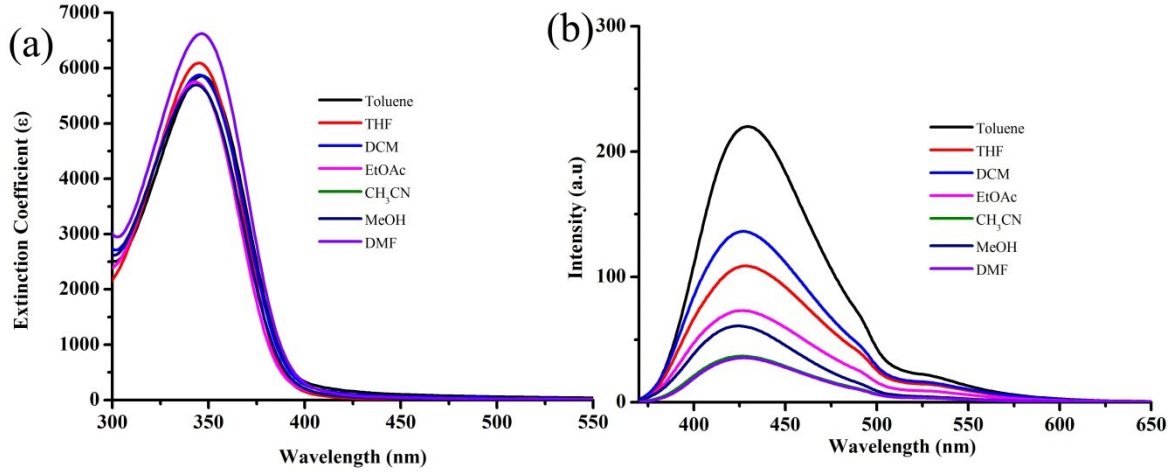


Fig. S21 (a) Absorption spectra of Bpy-BP in different solvents. (b) Fluorescence spectra of Bpy-BP in different solvents.

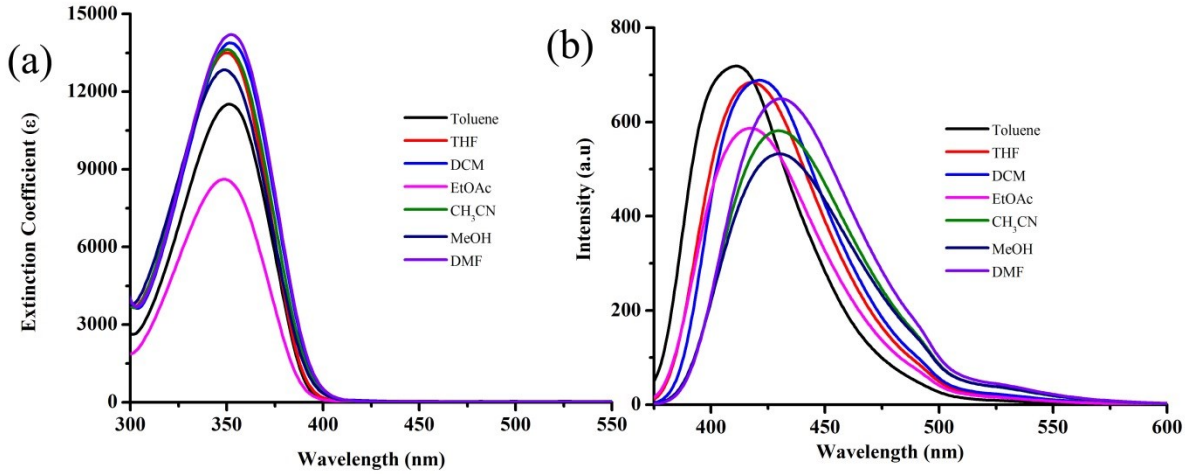


Fig. S22 (a) Absorption spectra of Bpy-Pep in different solvents. (b) Fluorescence spectra of Bpy-Pep in different solvents.

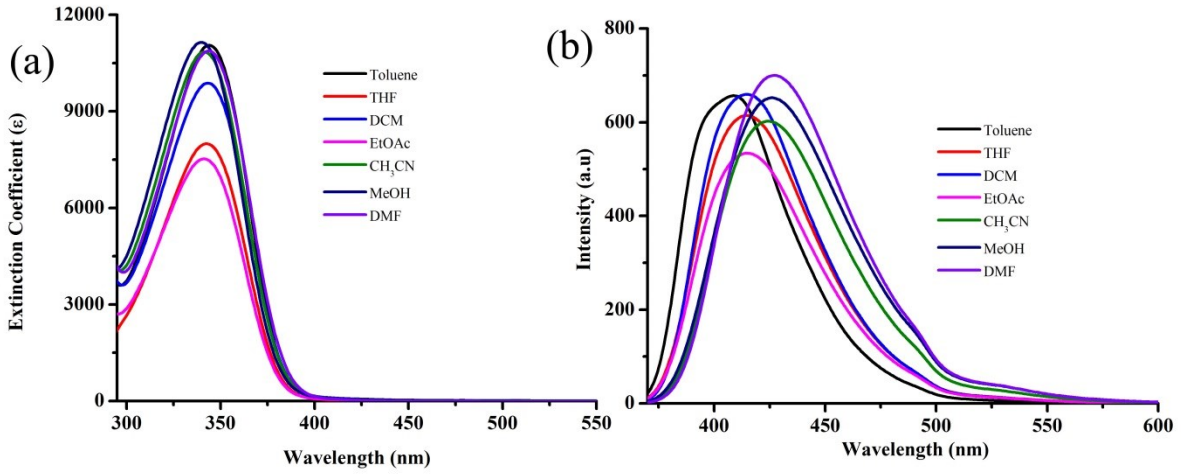


Fig. S23 (a) Absorption spectra of Bpy-Mor in different solvents. (b) Fluorescence spectra of Bpy-Mor in different solvents.

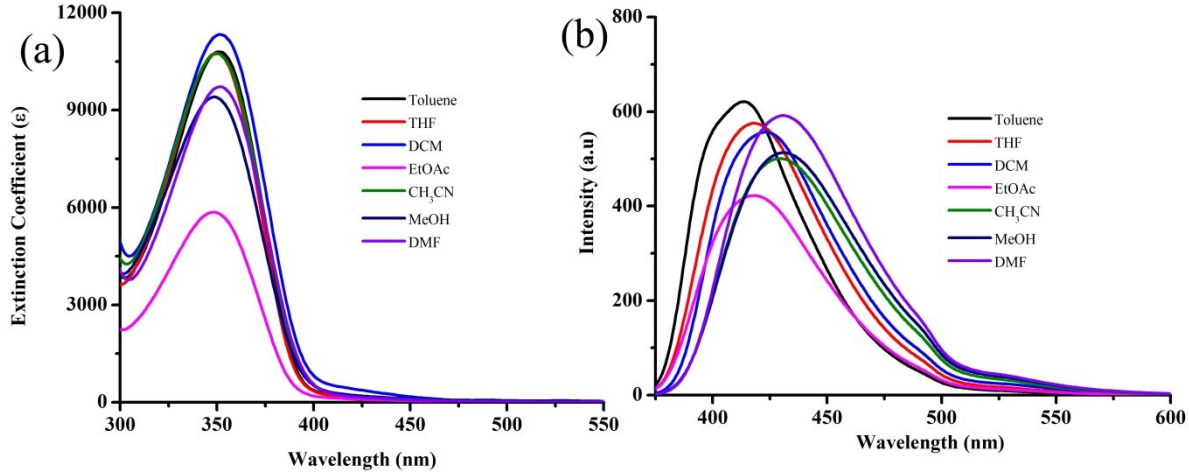


Fig. S24 (a) Absorption spectra of Bpy-Pip in different solvents. (b) Fluorescence spectra of Bpy-Pip in different solvents.

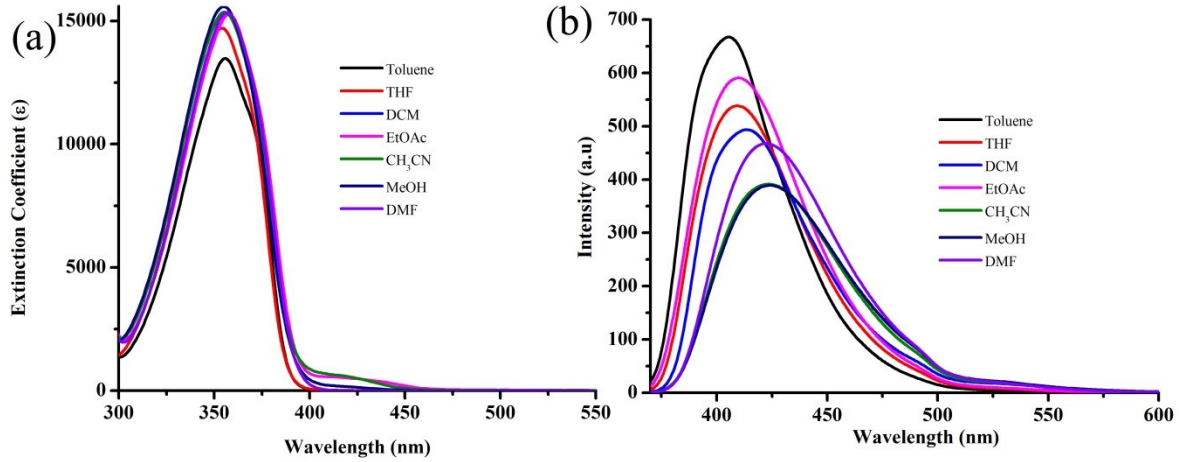


Fig. S25 (a) Absorption spectra of Bpy-Pyr in different solvents. (b) Fluorescence spectra of Bpy-Pyr in different solvents.

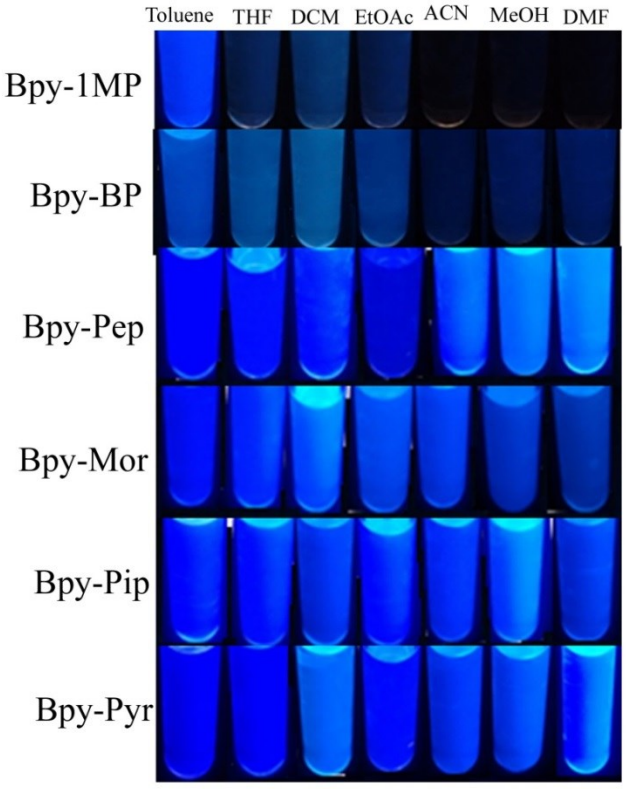


Fig. S26 Digital images of emission color of Bpy-BP, Bpy-Pep, Bpy-Mor, Bpy-Pip and Bpy-Pyr at different solvents under 365 nm irradiation.

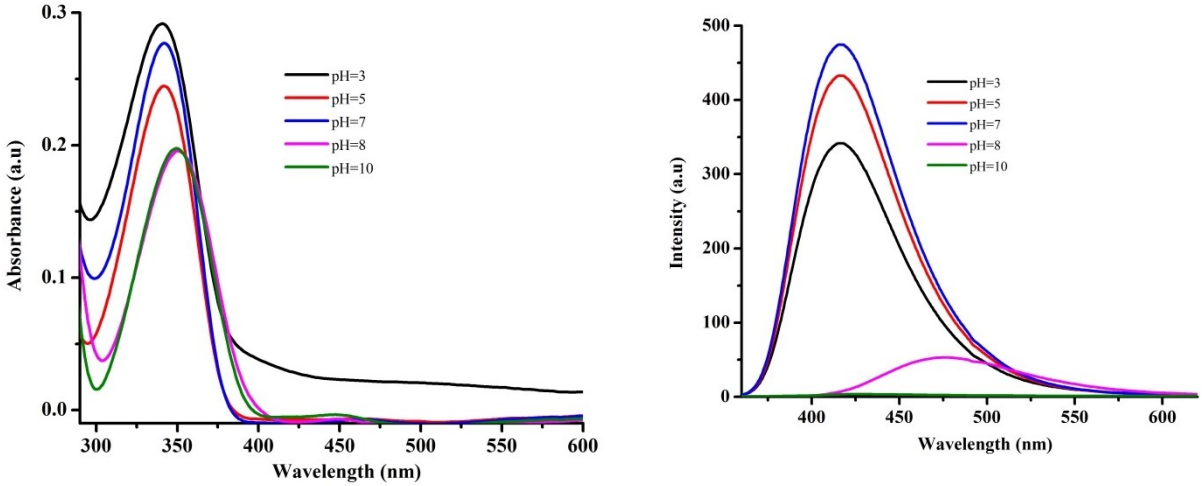


Fig. S27 (a) Absorption spectra of Bpy-1MP at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-1MP at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

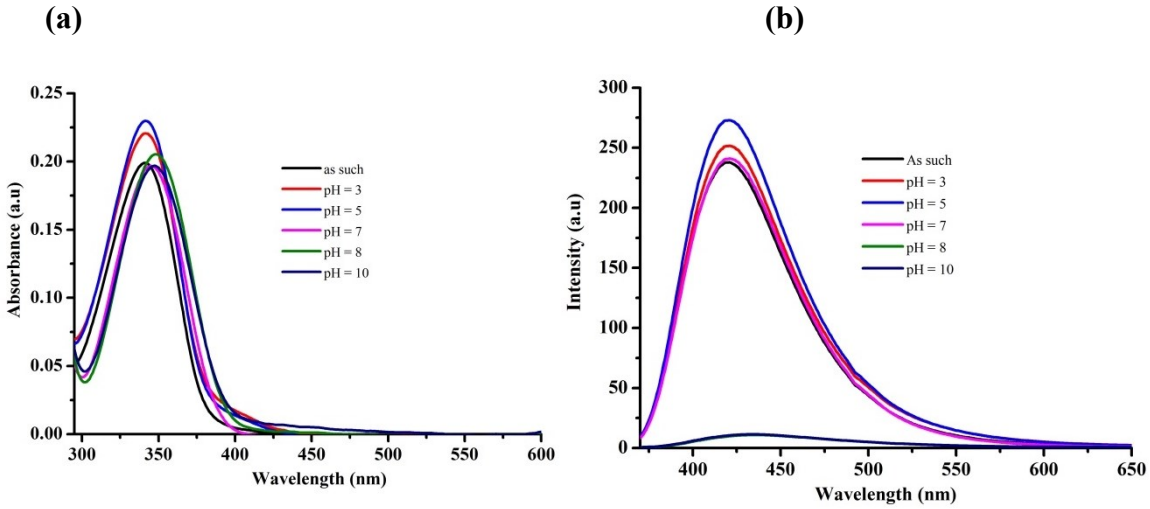


Fig. S28 (a) Absorption spectra of Bpy-BP at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-BP at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

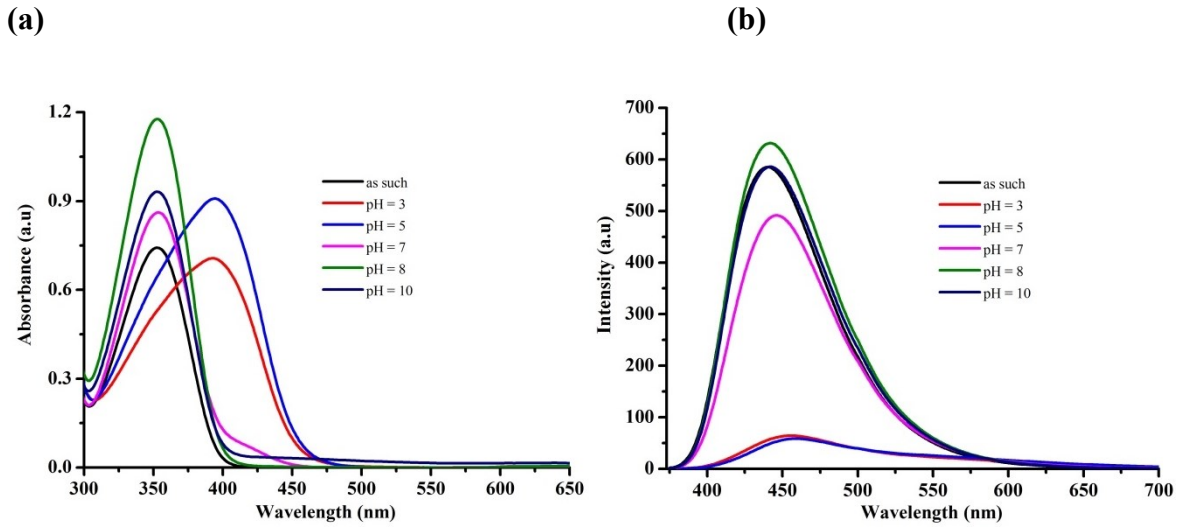


Fig. S29 (a) Absorption spectra of Bpy-Pep at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-Pep at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

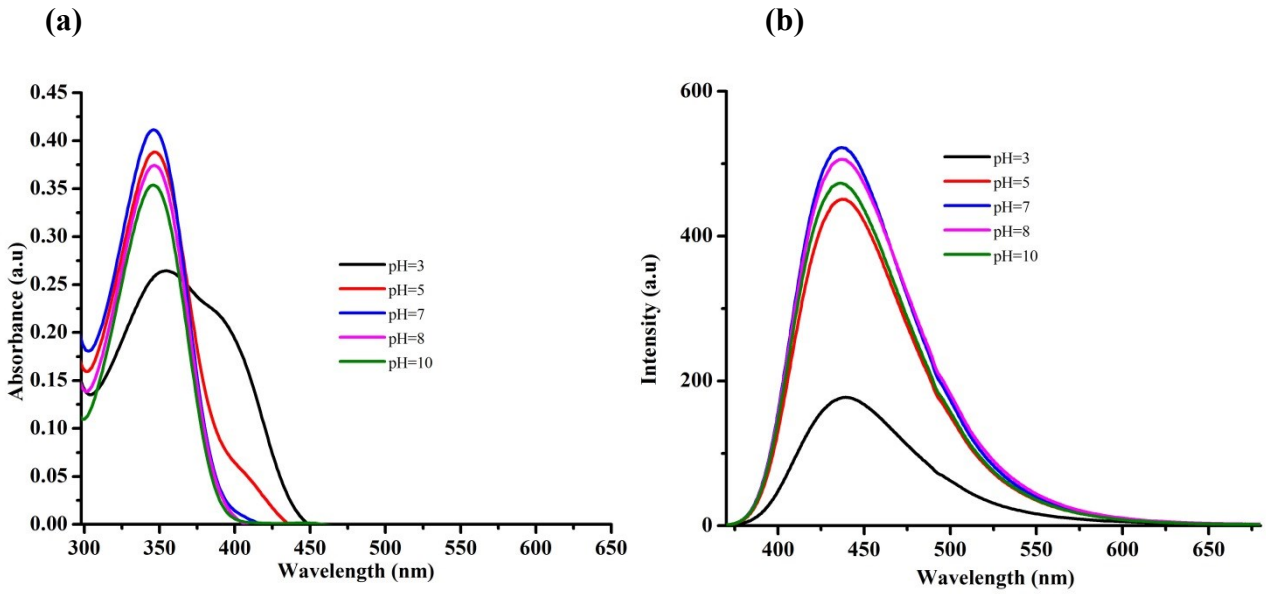


Fig. S30 (a) Absorption spectra of Bpy-Mor at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-Mor at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

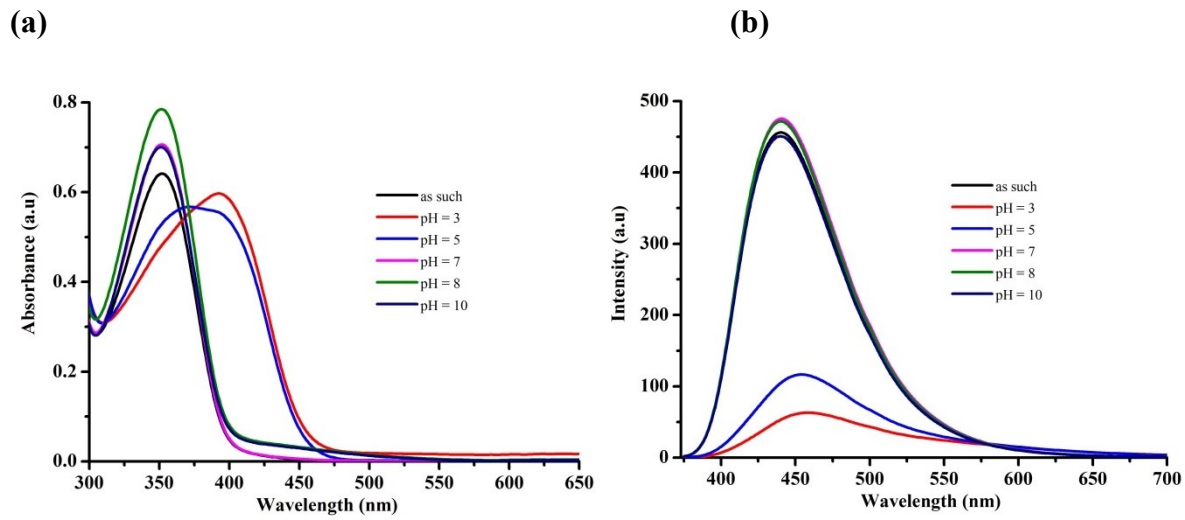


Fig. S31 (a) Absorption spectra of Bpy-Pip at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-Pip at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

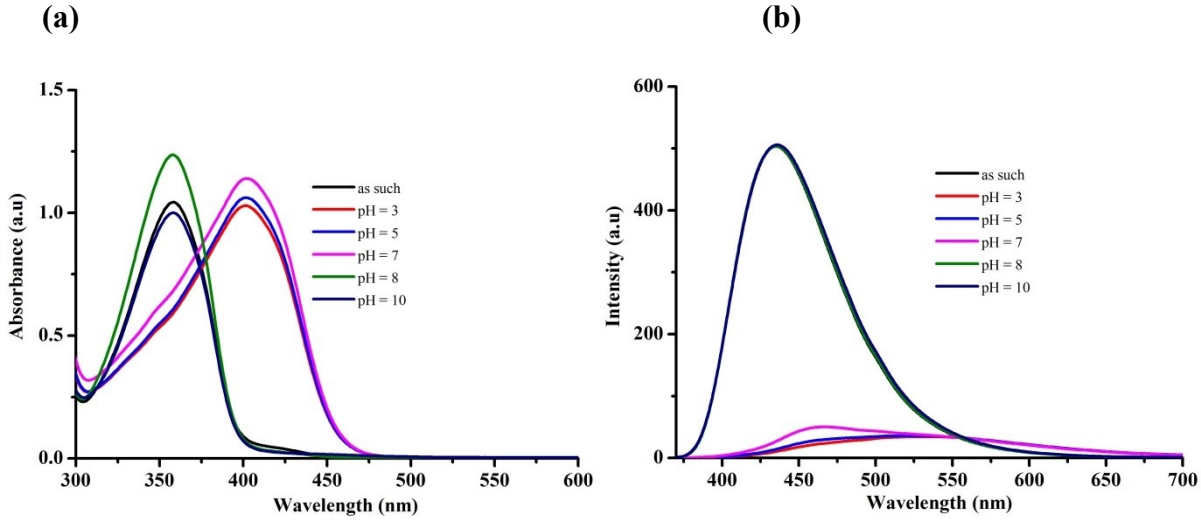


Fig. S32 (a) Absorption spectra of Bpy-Pyr at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent. (b) Fluorescence spectra of Bpy-Pyr at different pH conditions (pH 3, 5, 7, 8 and 10) in DMF solvent.

6. References

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