Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Self-reversible Mechanochromism and Aggregation Induced Emission in Neutral Triarylmethanes and Their Application in Water Sensing

Thekke Thattariyil Divya[a], Kalluruttimmal Ramshad[a], Velluvakandi Chaluvalappil Saheer[b], Lakshmi Chakkumkumarath[a]*

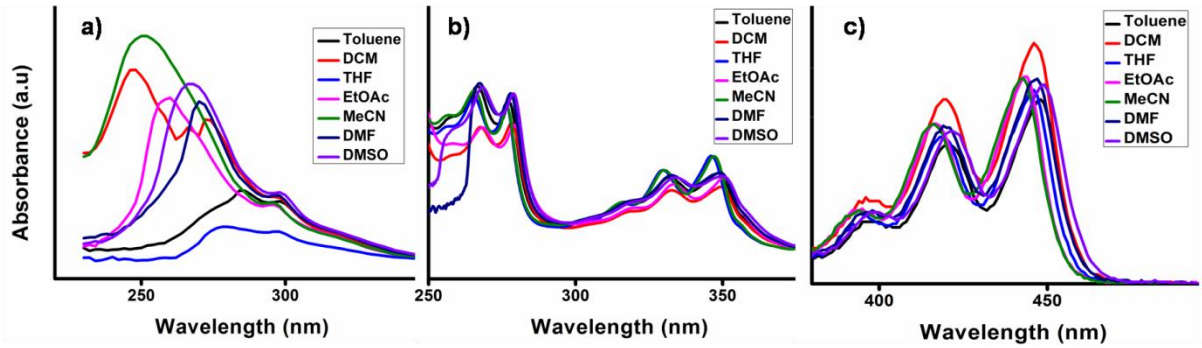


Fig. S1 The absorption spectra of (5×10^{-5} M) solution of a) **PhMBD**, b) **PyMBD**, c)**PrMBD** in different solvents.

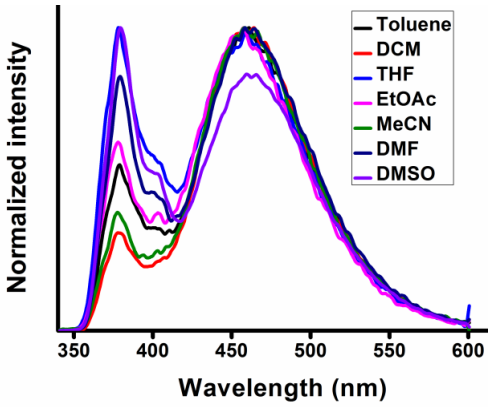


Fig. S2 The emission spectra of pyrene (2×10^{-3} M) in different solvents.

Table S1: The spectral data of **PhMBD** in different solvents.

Solvent	Absorbance (nm)	Emission (nm)	Stokes shift (nm)	Quantum yield
Toluene	298, 288	405	107	0.366
Dichloromethane	297, 252	437	185	0.478
THF	298, 278	448	150	0.445
Ethyl acetate	296,262	439	177	0.363
Acetonitrile	296, 251, 219	502	251	0.29
DMF	297, 273	491	218	0.519
DMSO	298, 270	513	243	0.611

Table S2: The spectral data of **PyMBD** in different solvents.

Solvent	Absorbance (nm)	Emission (nm)	Stokes shift (nm)	Quantum yield
Toluene	351, 333, 282	432	81	0.097
Dichloromethane	349, 332, 278, 267	494	145	0.041
THF	348, 332, 277, 266	508	160	0.031
Ethyl acetate	347, 330, 276, 267	501	154	0.020
Acetonitrile	347, 330, 276, 266	580, 415	233	0.016
DMF	349, 332, 277, 267	583, 420	234	0.10
DMSO	350, 334, 278, 268	600, 430	250	0.087

Table S3: The spectral data of **PrMBD** in different solvents.

Solvent	**Absorbance (nm)**	**Emission (nm)**	**Stokes shift (nm)**	**Quantum yield**
Toluene	448, 420, 395	473, 453	25	0.49
Dichloromethane	446, 419, 396	475	29	0.148
THF	446, 418, 396	468	22	0.028
Ethyl acetate	444, 417, 393	468	24	0.024
Acetonitrile	443, 416, 394	466	23	0.006
DMF	447, 419, 396	471	24	0.014
DMSO	449, 421, 397	471	22	0.017

Table S4: Comparison of solid and solution state properties of compounds

Compound	**Physical state**	**$\lambda_{ab.max.}$ (nm)**	**$\lambda_{em.max}$ (nm)**	**Stokes shift (nm)**	**ϕ_f**	**ϕ_{agg}**	**α_{AIE}**	**CIE Co – ordinates(x,y)**
PhMBD	In CH_3CN	296, 251, 219	502	251	0.305	0.3	0.98	(0.210, 0.378)
	Solid	308	424	116	0.027			(0.184, 0.164)
PyMBD	In CH_3CN	347, 330, 276, 266	580	233	0.016	0.29	18	(0.432,0.458)
	Solid	374, 312, 262	435	61	0.08			(0.165, 0.216)
PrMBD	In CH_3CN	443, 416, 394	466	23	0.006	0.14	23	(0.281, 0.389)
	Solid	397	610	213	0.011			(0.524, 0.385)

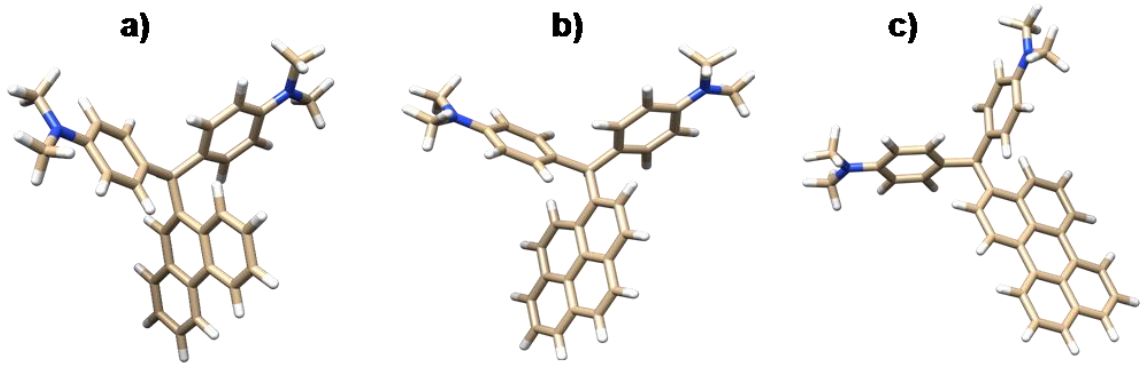


Fig. S3 Optimized Structure of a) **PhMBD** b) **PyMBD** c) **PrMBD** in acetonitrile.

Table S5: Computed electronic transitions, excitation energies and oscillator strengths.

Molecule	State	Transition	Wave function coefficients	Excitation Energy (eV)	Oscillator Strength
PhMBD	1	115 → 116	0.70358	2.8570 eV 433.96 nm	0.0182
	2	114 →116	0.70487	3.1106 eV 398.58 nm	0.0017
	3	115 →117	-0.70249	366.71	0.0026
PyMBD	1	121 →122	0.70476	2.4970 eV 496.54 nm	0.0020
	2	120 →122	0.70476	2.8864 eV 429.55 nm	0.0060
	3	118 →123 119 →122	0.15 0.69	3.3964 eV 365.04 nm	0.4707
PrMBD	1	134 → 135	-0.70254	2.1341 eV 580.97 nm	0.0017
	2	132 →135 133 → 135	-0. 61371 -0.34567	2.4889 eV 498.14 nm	0.0652
	3	132 →135 133 → 135	0.34825 -0.61260	2.6025 eV 476.40 nm	0.4440

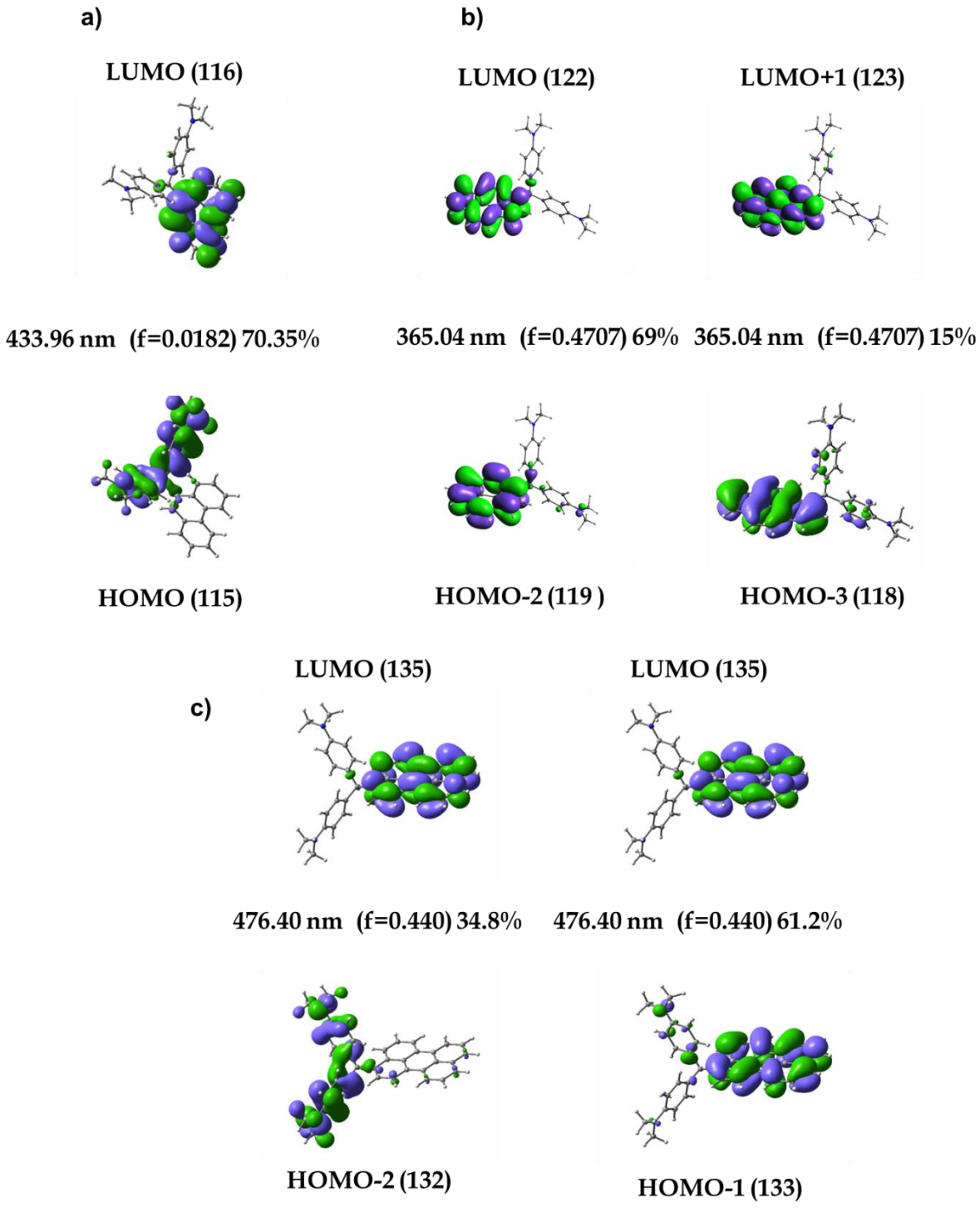


Fig.S4 The major electronic transitions based on oscillator strength of a) **PhMBD** b) **PyMBD** c) **PrMBD.**

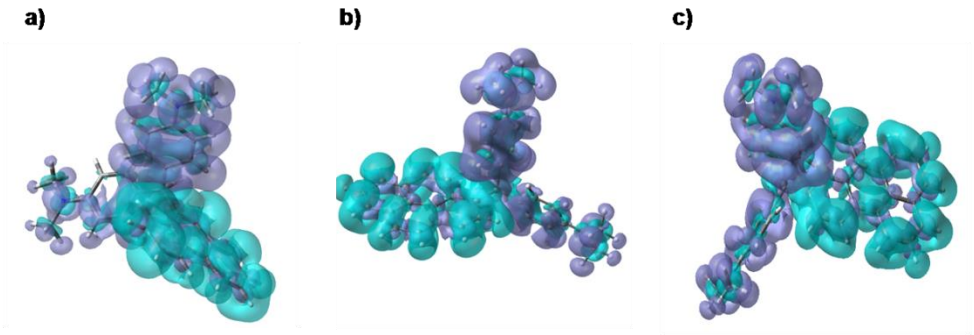


Fig.S5 The electron difference density isosurface between ground and excited states of a) **PhMBD** b) **PyMBD** c) **PrMBD.**

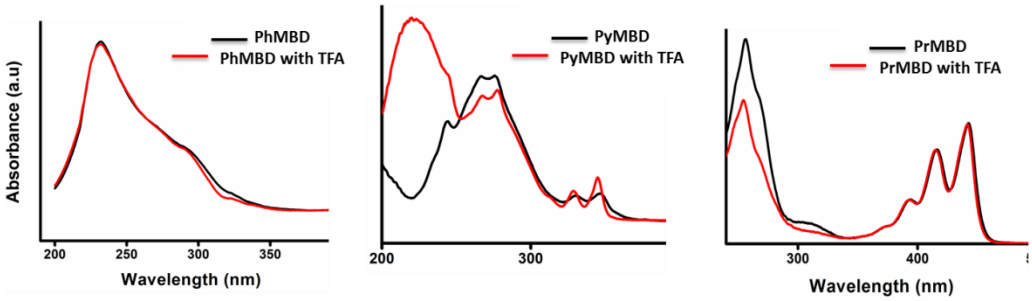


Fig. S6 The absorption of **PhMBD**, **PyMBD** & **PrMBD** in the presence of TFA.

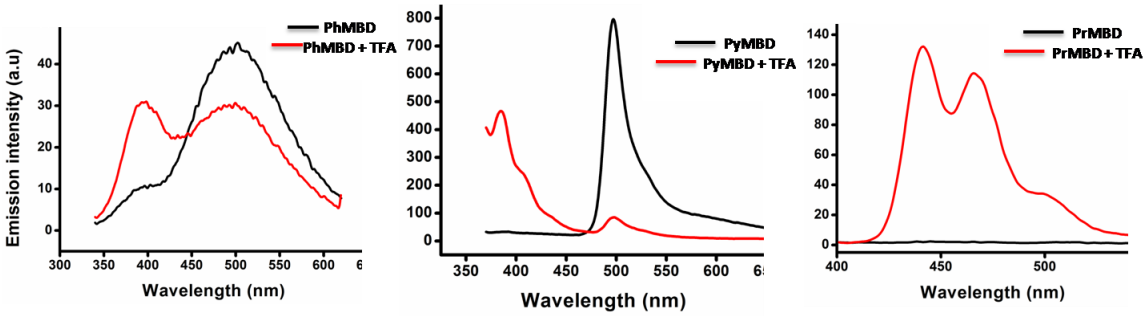


Fig. S7 The emission spectra of **PhMBD**, **PyMBD** & **PrMBD** in the presence of TFA.

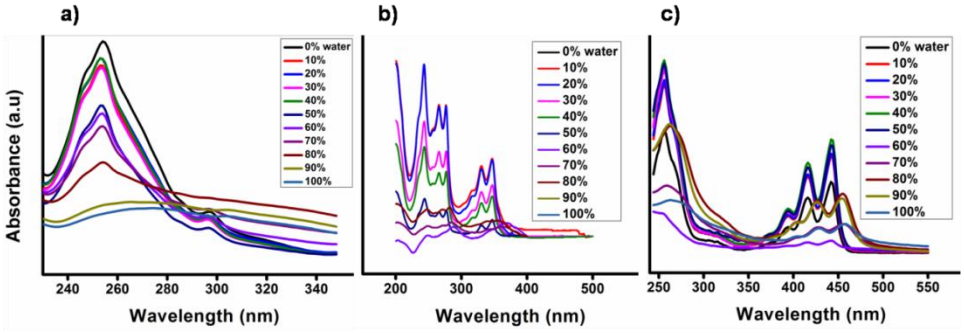


Fig. S8 The absorption spectra of (5×10^{-5} M) solution of a) **PhMBD**, b) **PyMBD**, c) **PrMBD** in acetonitrile containing different percentages of water.

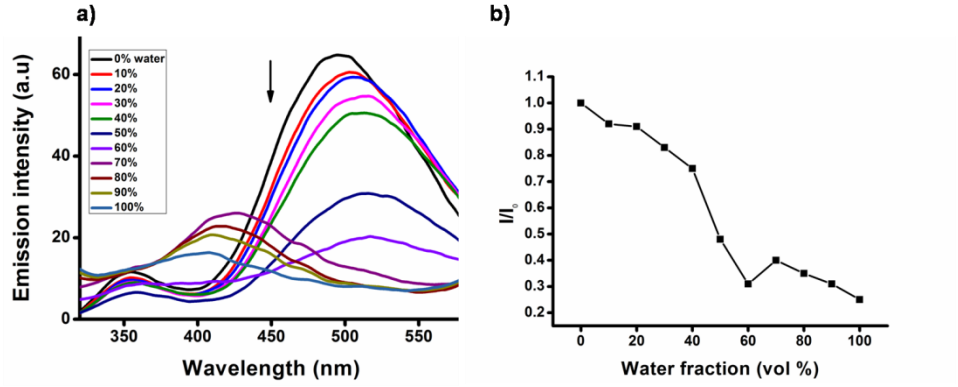


Fig. S9 (a) The emission spectrum and (b) calibration curve of **PhMBD** (5×10^{-5} M) in CH_3CN-H_2O mixtures with different water fractions. λ_{ex} = 300 nm.

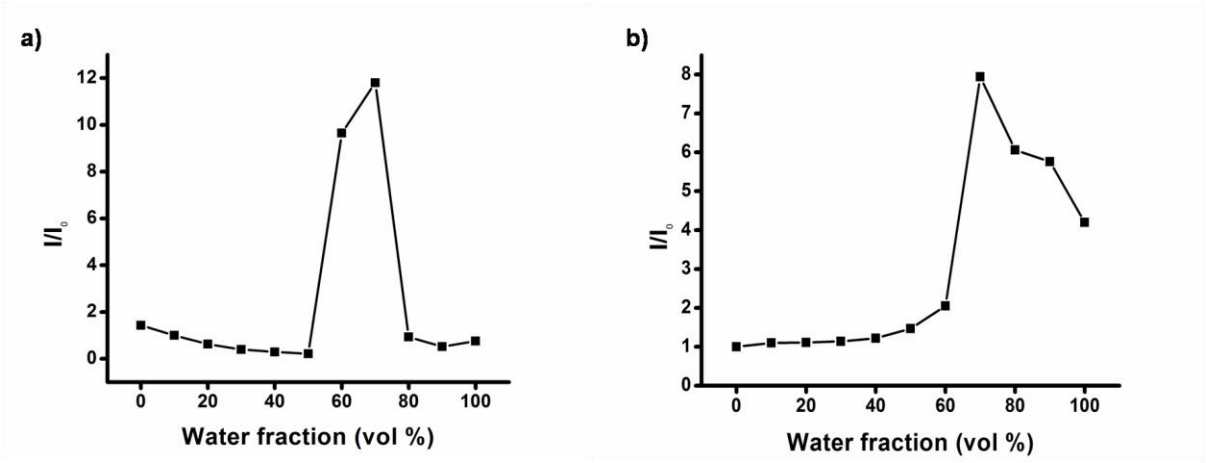


Fig. S10 The calibration curve of 5×10^{-5} M (a) **PyMBD** λ_{ex} = 350 nm. (b) **PrMBD** λ_{ex} = 380 nm in CH_3CN - H_2O mixtures with different water fractions.

		Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 212.4	Peak 1:	201.1	100.0	97.92
PdI: 0.397	Peak 2:	0.000	0.0	0.000
Intercept: 0.883	Peak 3:	0.000	0.0	0.000

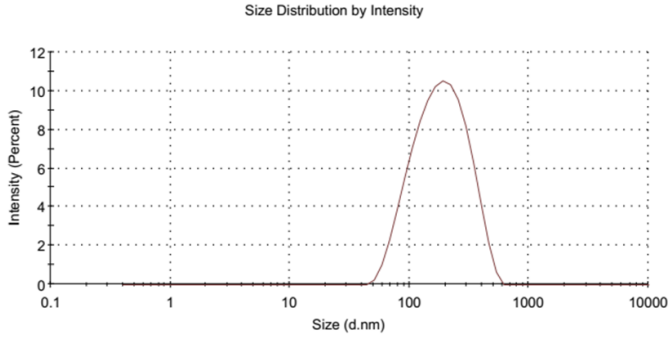


Fig. S11 DLS images of **PhMBD** (1:1 H_2O/CH_3CN) concentration (5×10^{-5} M).

		Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 3629	Peak 1:	98.83	100.0	7.207
PdI: 1.000	Peak 2:	0.000	0.0	0.000
Intercept: 0.684	Peak 3:	0.000	0.0	0.000

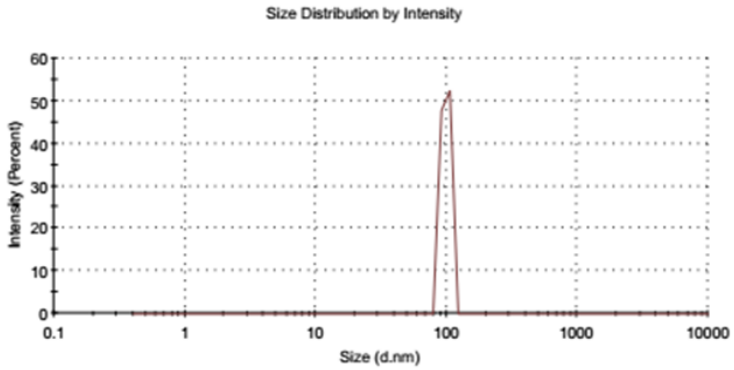


Fig. S12 DLS images of **PyMBD** (1:1 H_2O/CH_3CN) concentration (5×10^{-5} M).

		Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 1206	Peak 1:	245.7	100.0	21.00
PdI: 0.907	Peak 2:	0.000	0.0	0.000
Intercept: 0.910	Peak 3:	0.000	0.0	0.000

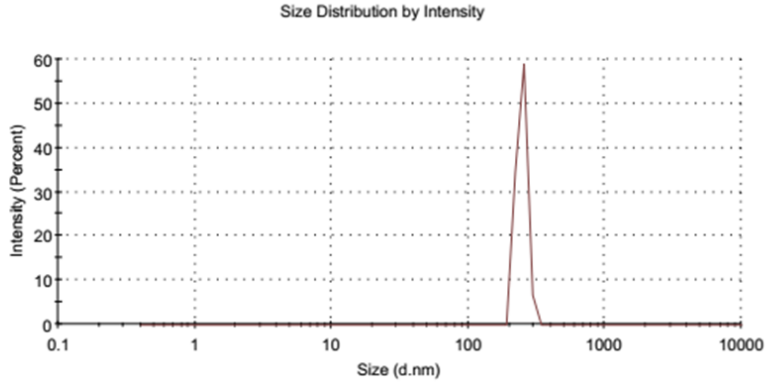


Fig. S13 DLS images of **PrMBD** (1:1 H_2O/CH_3CN) concentration (5×10^{-5} M).

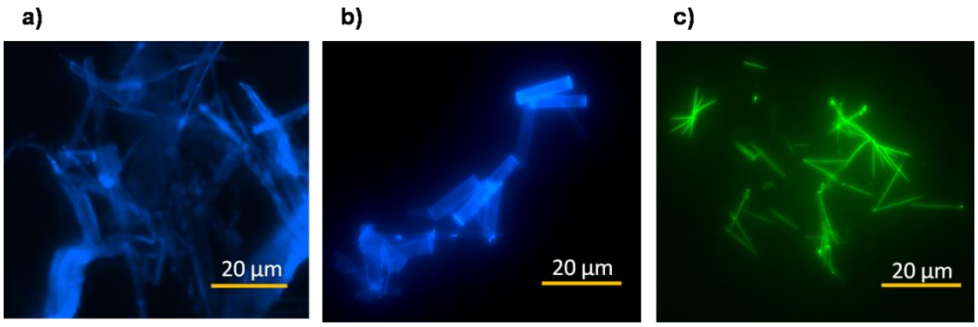


Fig. S14 The fluorescent microscopic images of a) **PhMBD** (f_w 70%), b) **PyMBD** (f_w 70%), c) **PrMBD** (f_w 60%) in CH_3CN-H_2O mixtures, concentration (5×10^{-5} M).

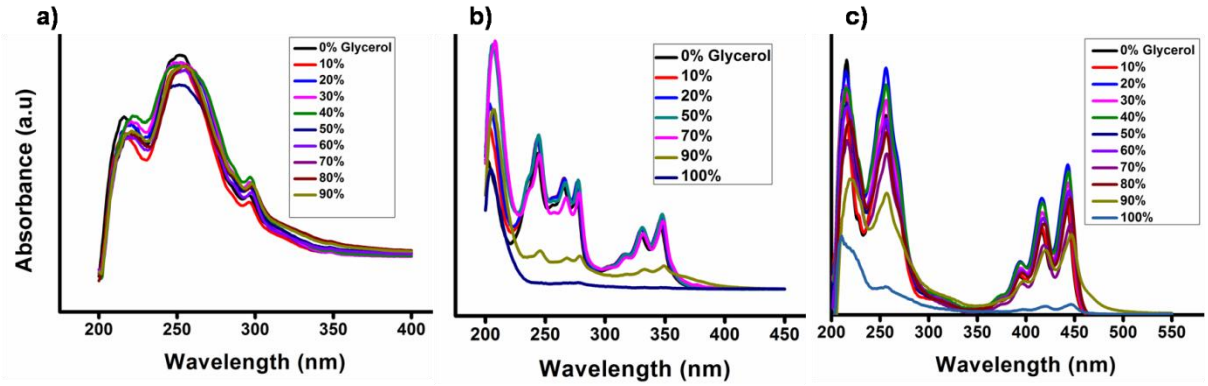


Fig. S15 The absorption spectrum of (5×10^{-5}M) solutions of a) **PhMBD** b) **PyMBD** c) **PrMBD** in methanol containing different percentages of glycerol.

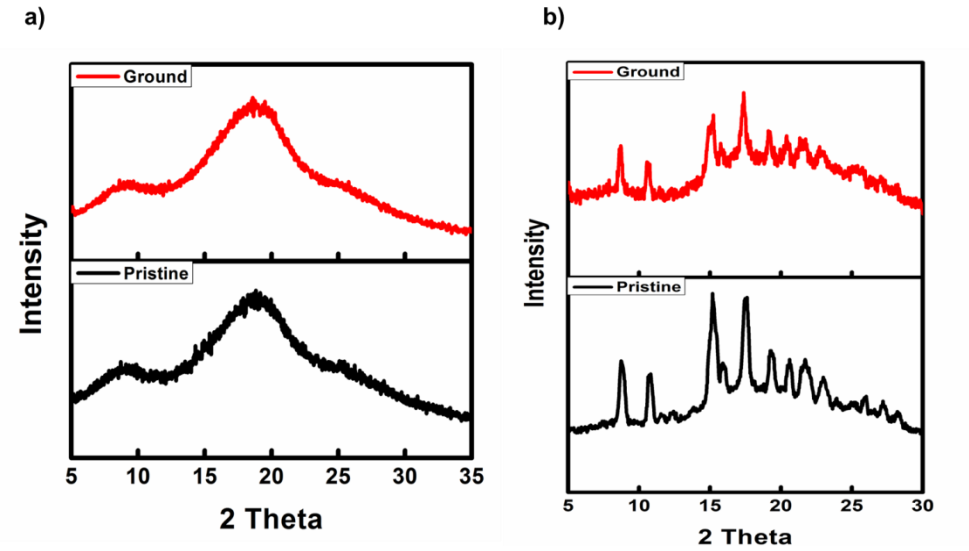


Fig. S16 The PXRD spectra of a) **PhMBD** b) **PyMBD** before and after grinding.

Table S6: The 2θ values of the pristine, ground and aged sample

Pristine	**Ground**	**After 17 hr**
2 Theta	**2 Theta**	**2 Theta**
6.9	6.77	6.86
8.88	8.57	8.61
9.8	12.25	9.62
10.54	13.26	10.46
11.29	15.67	11.02
11.99	16.59	12.30
12.38	13.30	
13.44	19.09	14.75
14.18	19.84	15.28
14.57	20.28	15.67
15.72	20.97	16.68
16.33	22.42	17.60
16.77	25.18	19.13
17.65	25.93	19.88
18.78	27.77	20.36
19.22		21.11
21.02		21.50
21.50		22.47
21.8		23.34
22.60		25.23
23.34		25.97
24.05		26.85
24.49		27.86
25.32		28.39
26.02		28.60
		29.53

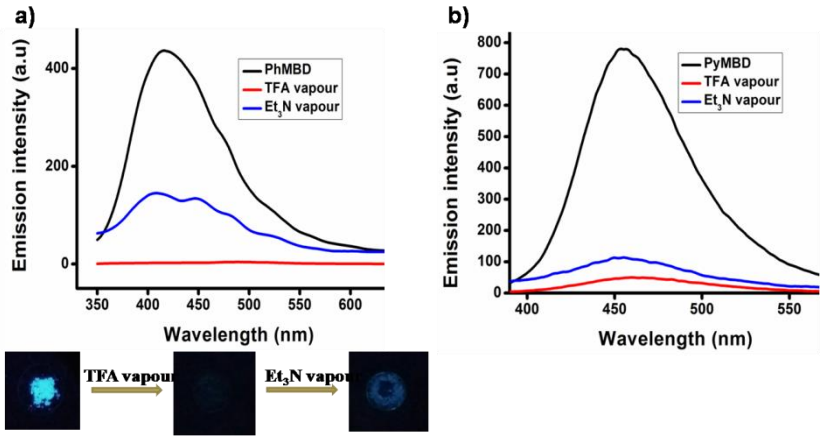


Fig.S17 The emission spectra of a) **PhMBD** b) **PyMBD** exposed to TFA and Et_3N vapour.

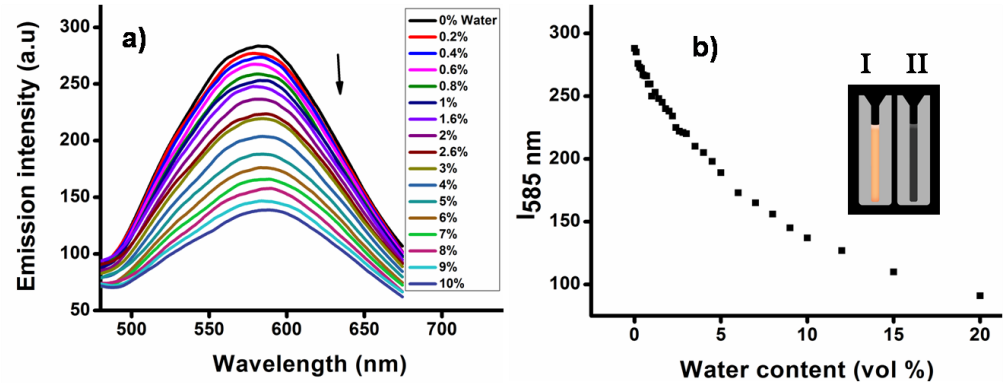
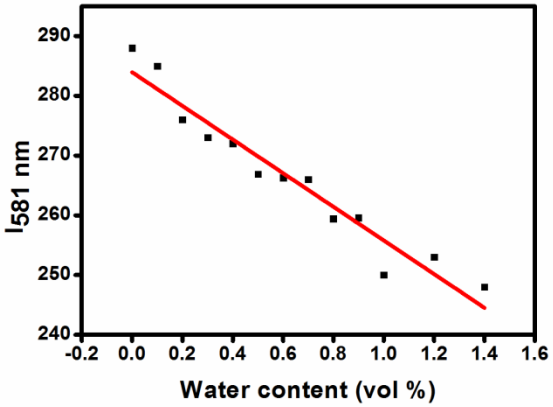
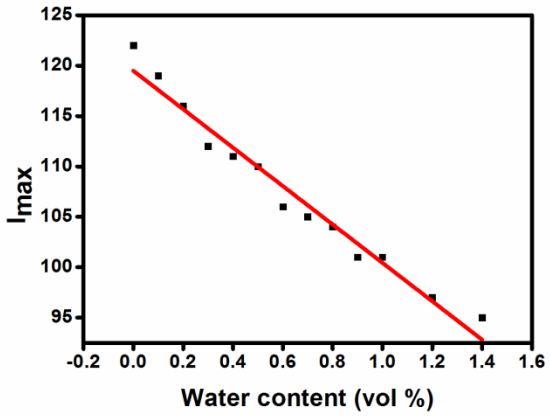


Fig. S18 a) The emission spectra and b) calibration curve and photographs of **PyMBD** (5×10^{5} M in acetonitrile) in presence of different percentages of water in acetonitrile [I-pure solvent, II-with the addition of 20% water (when viewed under UV lamp of 365 nm)].



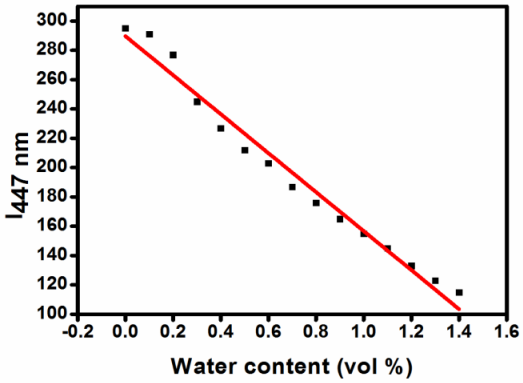
Equation	y = a + b*x		
Weight	No Weighting		
Residual	114.49977		
Pearson's	-0.96876		
Adj. R-Sq	0.93291		
		Value	Standard
B	Intercept	283.9518	1.62326
B	Slope	-28.16215	2.17366

Fig. S19 Calibration curve of **PyMBD** (5×10^{-5}M) in lower concentration range, with error bars for calculating the DL and QL as a function of water content in acetonitrile.



Equation	y = a + b*x		
Weight	No Weighting		
Residual	24.96508		
Pearson's	-0.98475		
Adj. R-Sq	0.96699		
		Value	Standard
B	Intercept	119.48953	0.75797
B	Slope	-19.05726	1.01497

Fig. S20 Calibration curve of **PyMBD** (5×10^{-5}M) in lower concentration range, with error bars for calculating the DL and QL as a function of water content in dioxane.



Equation	y = a + b*x		
Weight	No Weighting		
Residual	1075.79643		
Pearson's	-0.98932		
Adj. R-Sq	0.97712		
		Value	Standard
B	Intercept	289.725	4.472
B	Slope	-133.0357	5.43644

Fig. S21 Calibration curve of **PrMBD** (5×10^{-5}M) in lower concentration range, with error bars for calculating the DL and QL as a function of water content in dioxane.

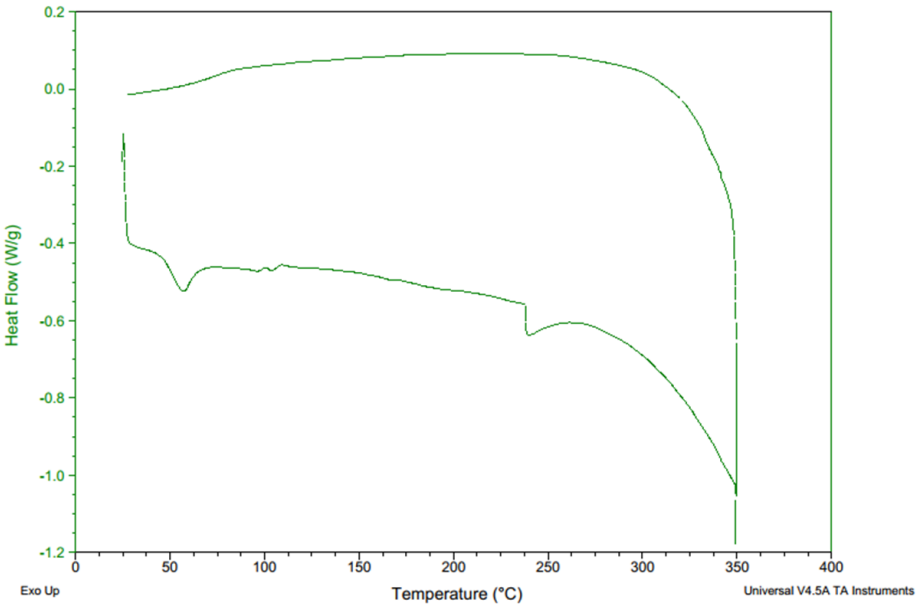


Fig.S22 The DSC curve of **PhMBD.**

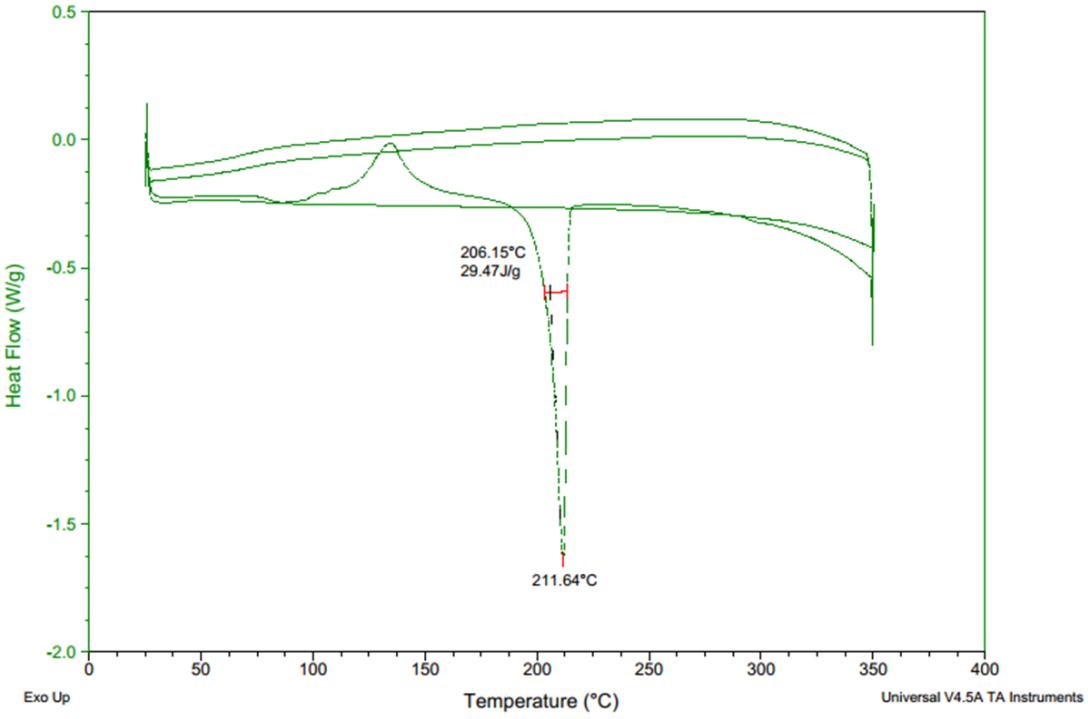


Fig.S23 The DSC curve of **PyMBD.**

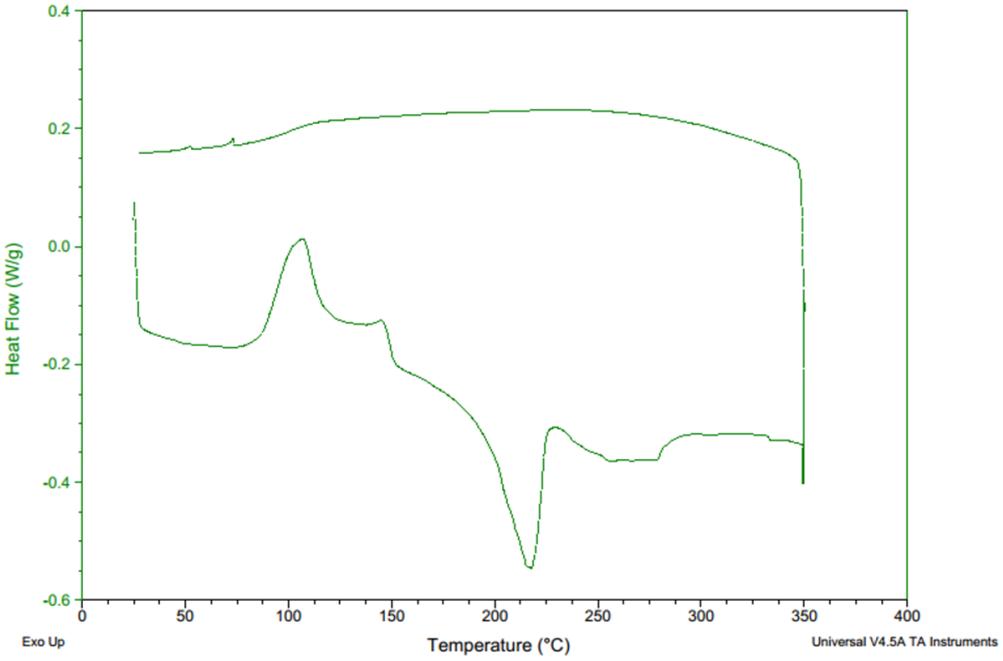


Fig.S24 The DSC curve of **PrMBD.**

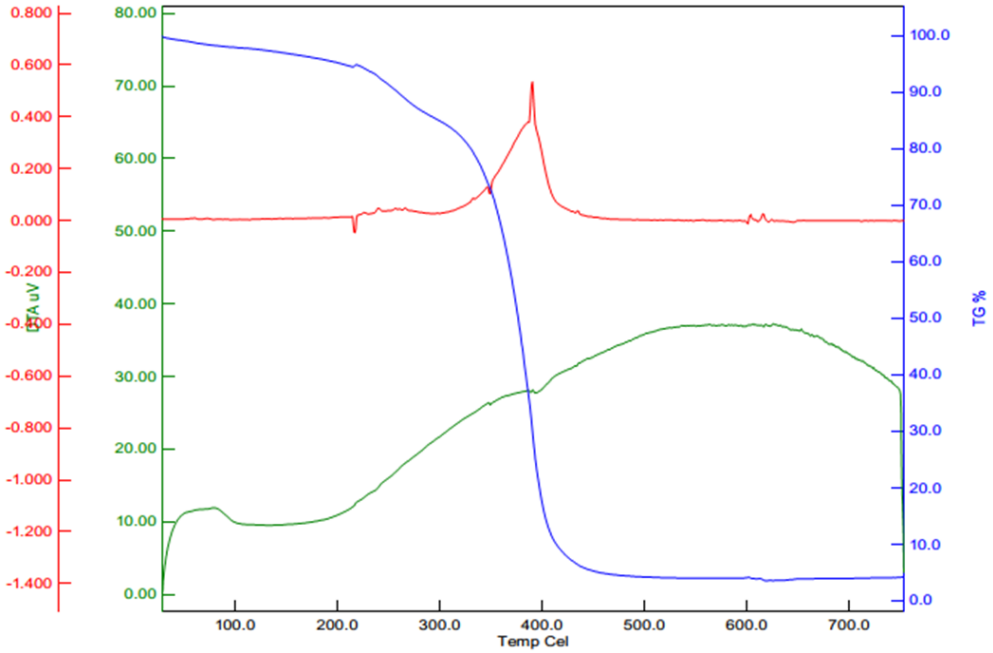


Fig.S25 DTA, TG and DTG curves of **PhMBD.**

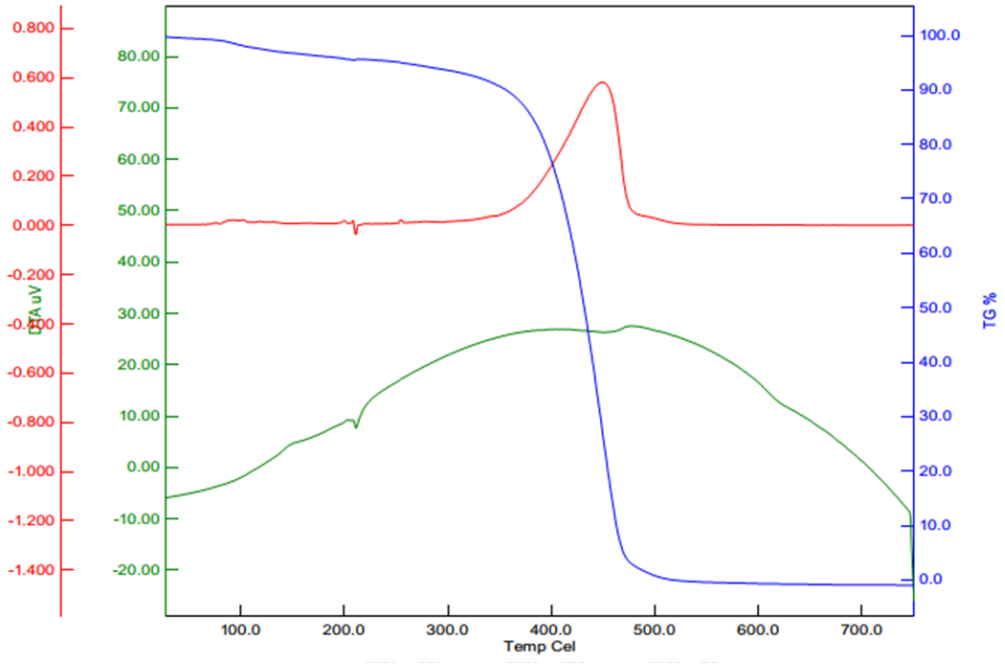


Fig.S26 DTA, TG and DTG curves of **PyMBD.**

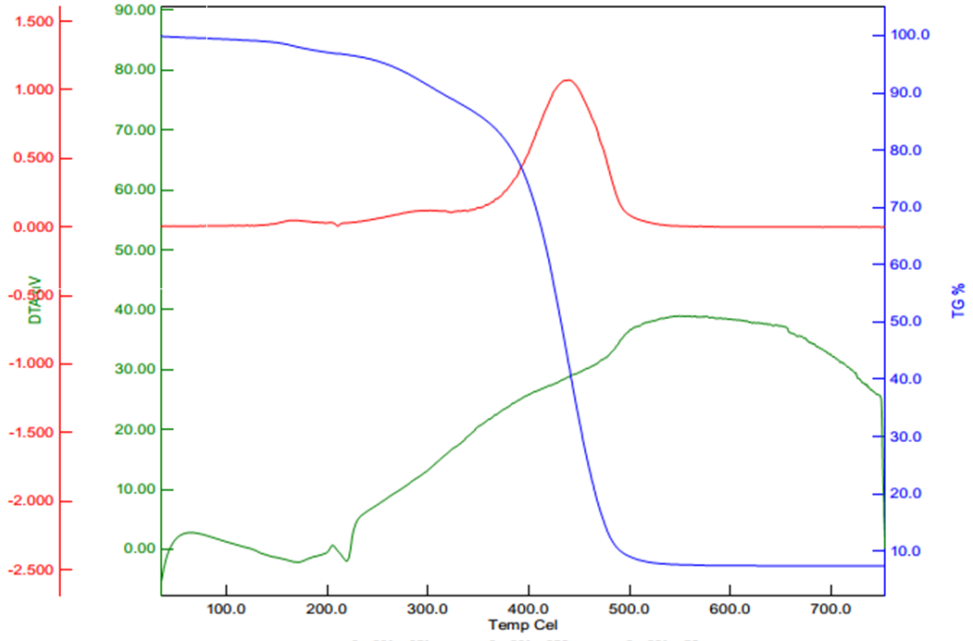


Fig.S27 DTA, TG and DTG curves of **PrMBD.**

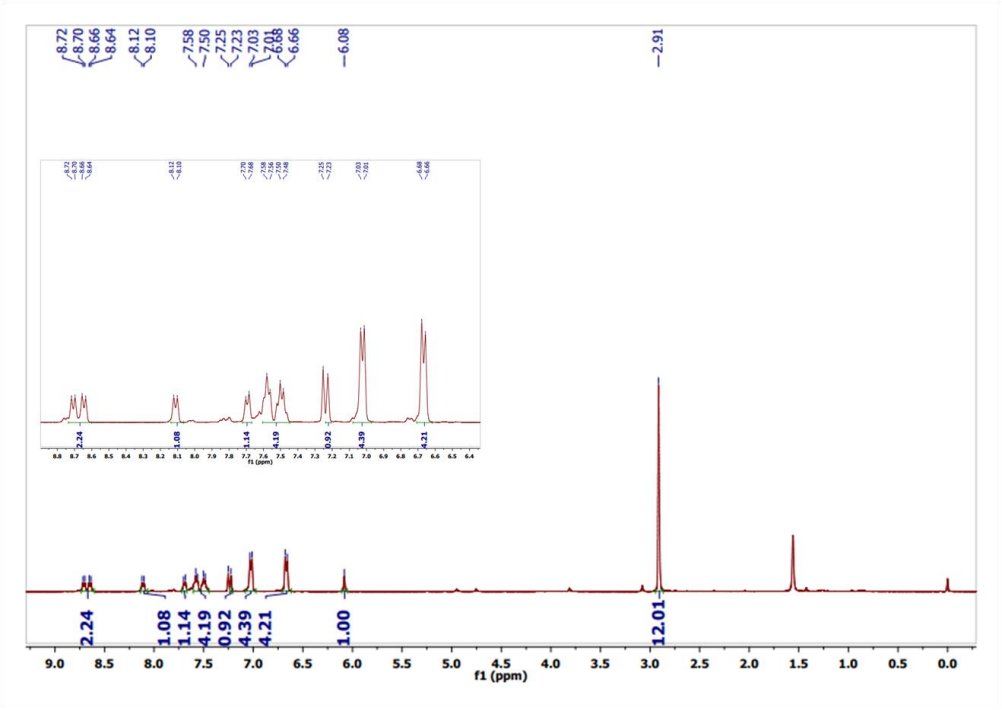


Fig.S28 ^{1}HNMR of **PhMBD** (400MHz, $CDCl_3$).

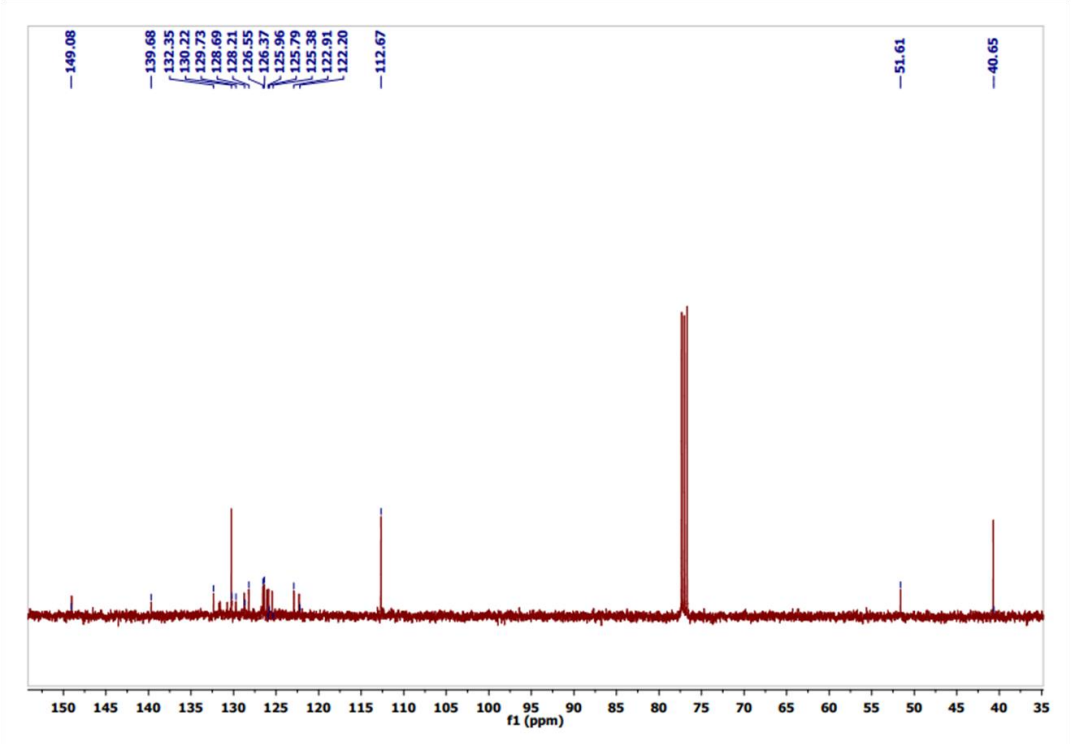


Fig. S29. ^{13}C NMR of **PhMBD** (100MHz, $CDCl_3$).

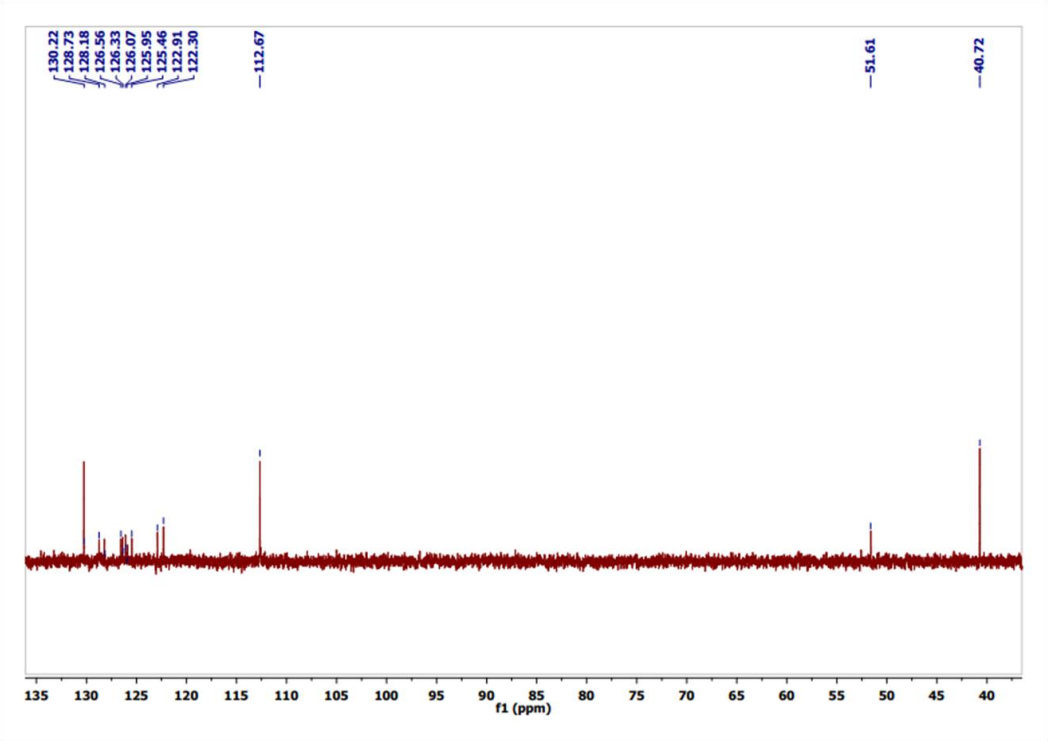


Fig. S30. DEPT-135 of **PhMBD** (100MHz, $CDCl_3$).

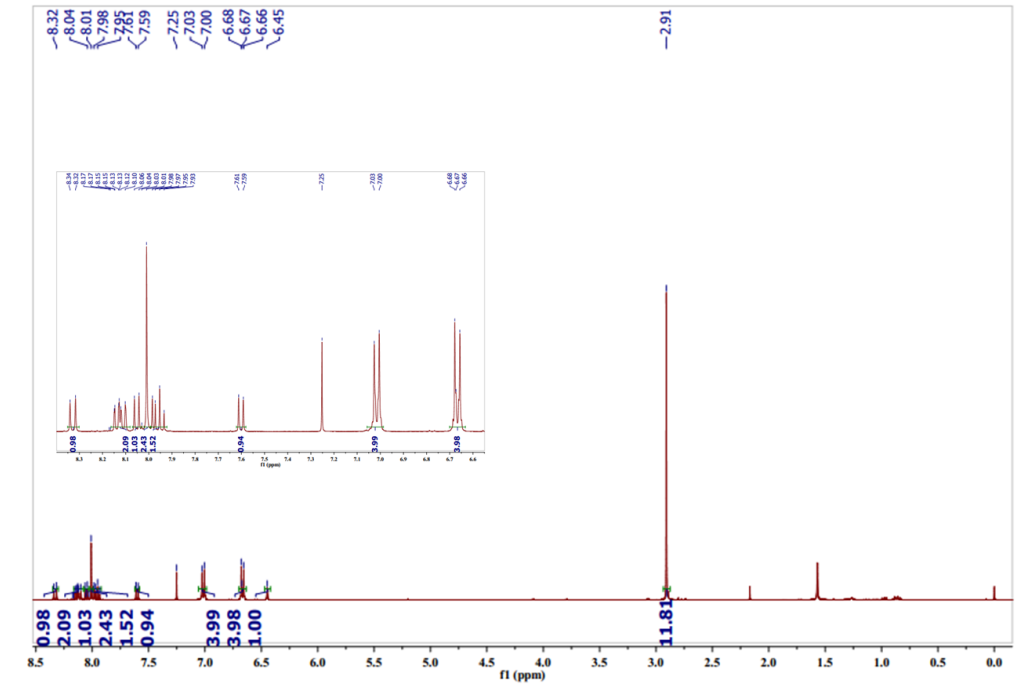


Fig.S31 ^{1}HNMR of **PyMBD** (400MHz, $CDCl_3$).

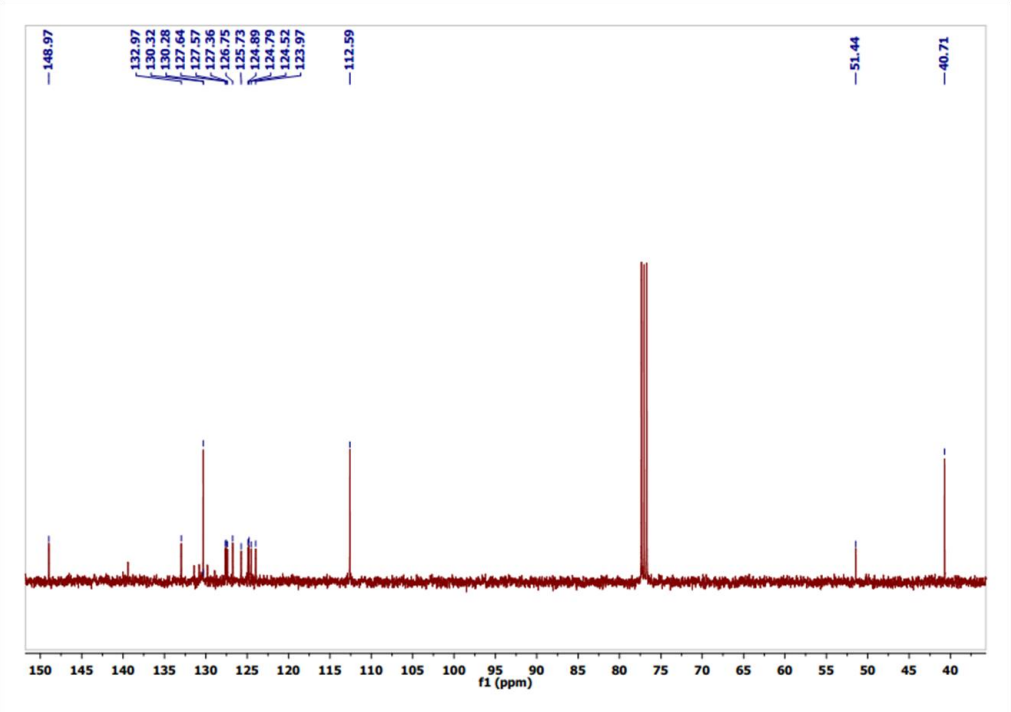


Fig.S32 ^{13}C NMR of **PyMBD** (100MHz, $CDCl_3$).

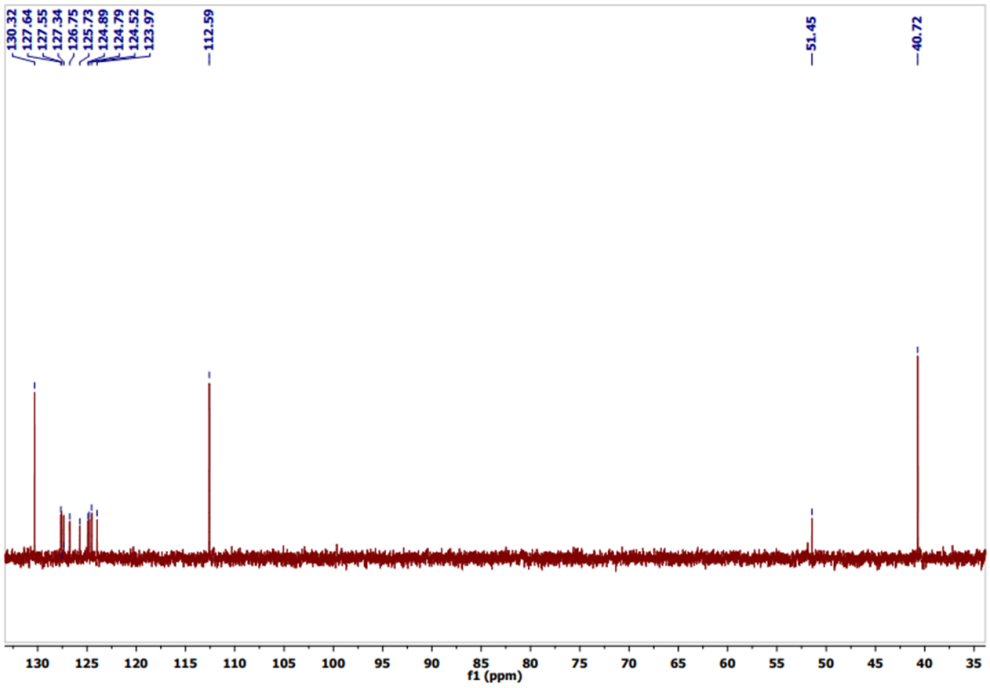


Fig.S33 DEPT-135 of **PyMBD** (100MHz, $CDCl_3$).

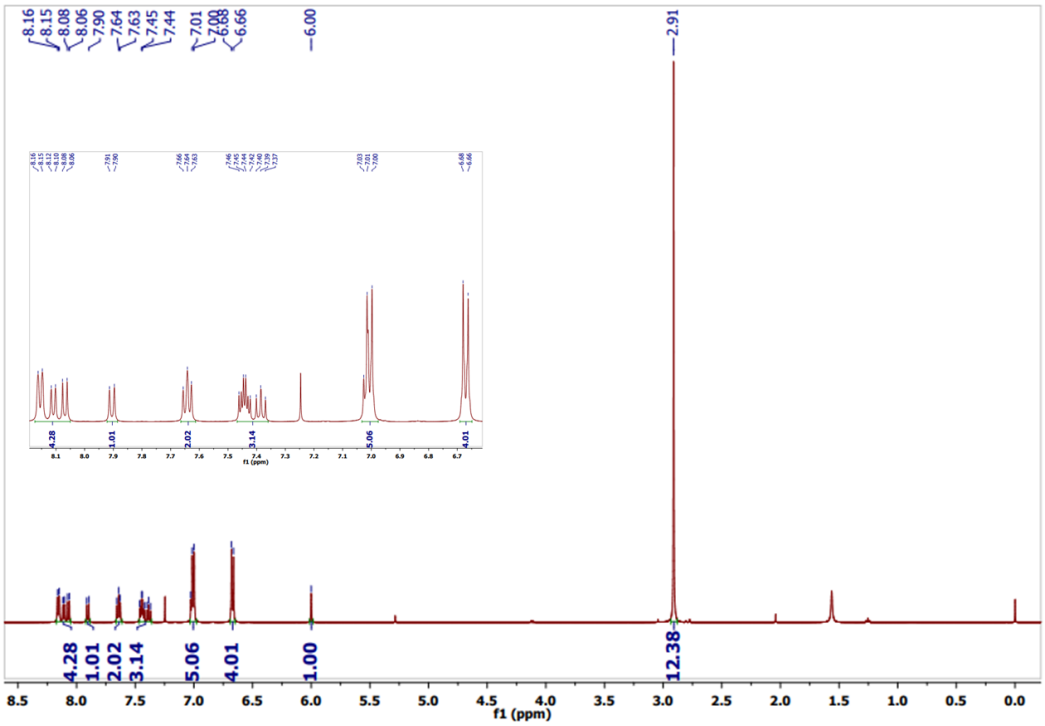


Fig.S34 ^{1}HNMR of **PrMBD** (500MHz, $CDCl_3$).

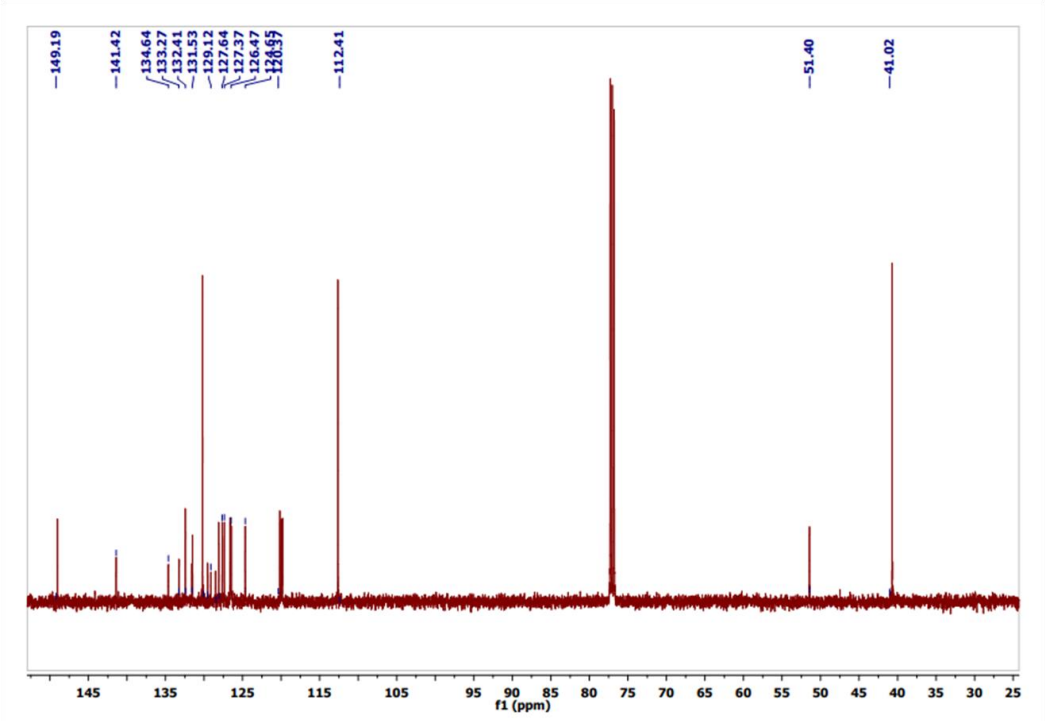


Fig.S35 ^{13}C NMR of **PrMBD** (125MHz, $CDCl_3$).

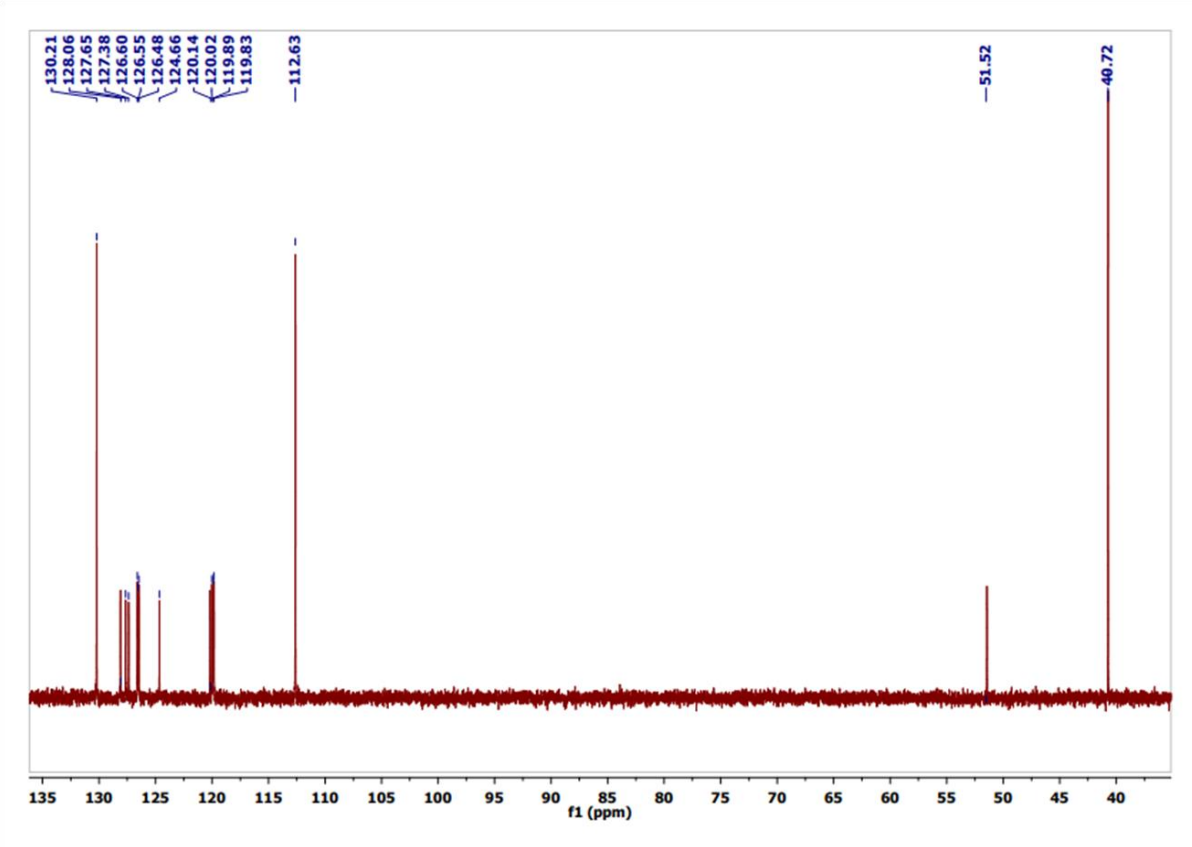


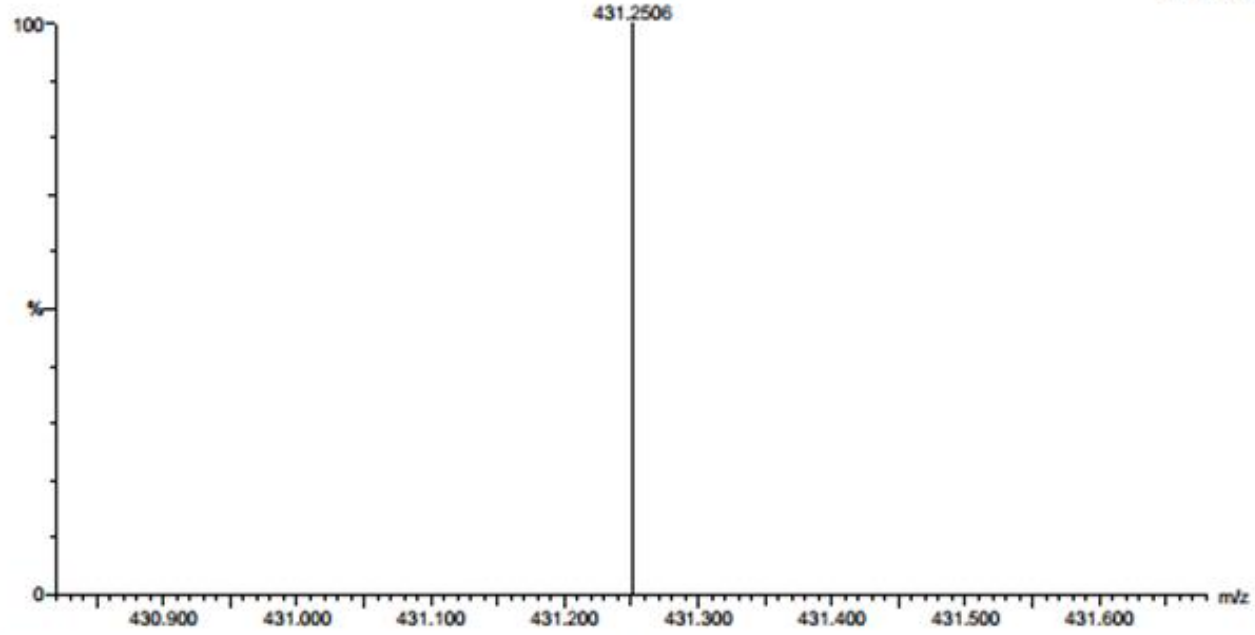
Fig.S36 DEPT-135 of **PrMBD** (125MHz, $CDCl_3$).

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-31 H: 0-31 N: 0-2

KMM-PH-BDA
08062018-02-KMM-PH-BDA 10 (0.252) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (3:19) TOF MS ES+
9.73e+004



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
431.2506	431.2487	1.9	4.4	17.5	n/a	C31 H31 N2

Fig.S37 Mass spectrum of **PhMBD.**

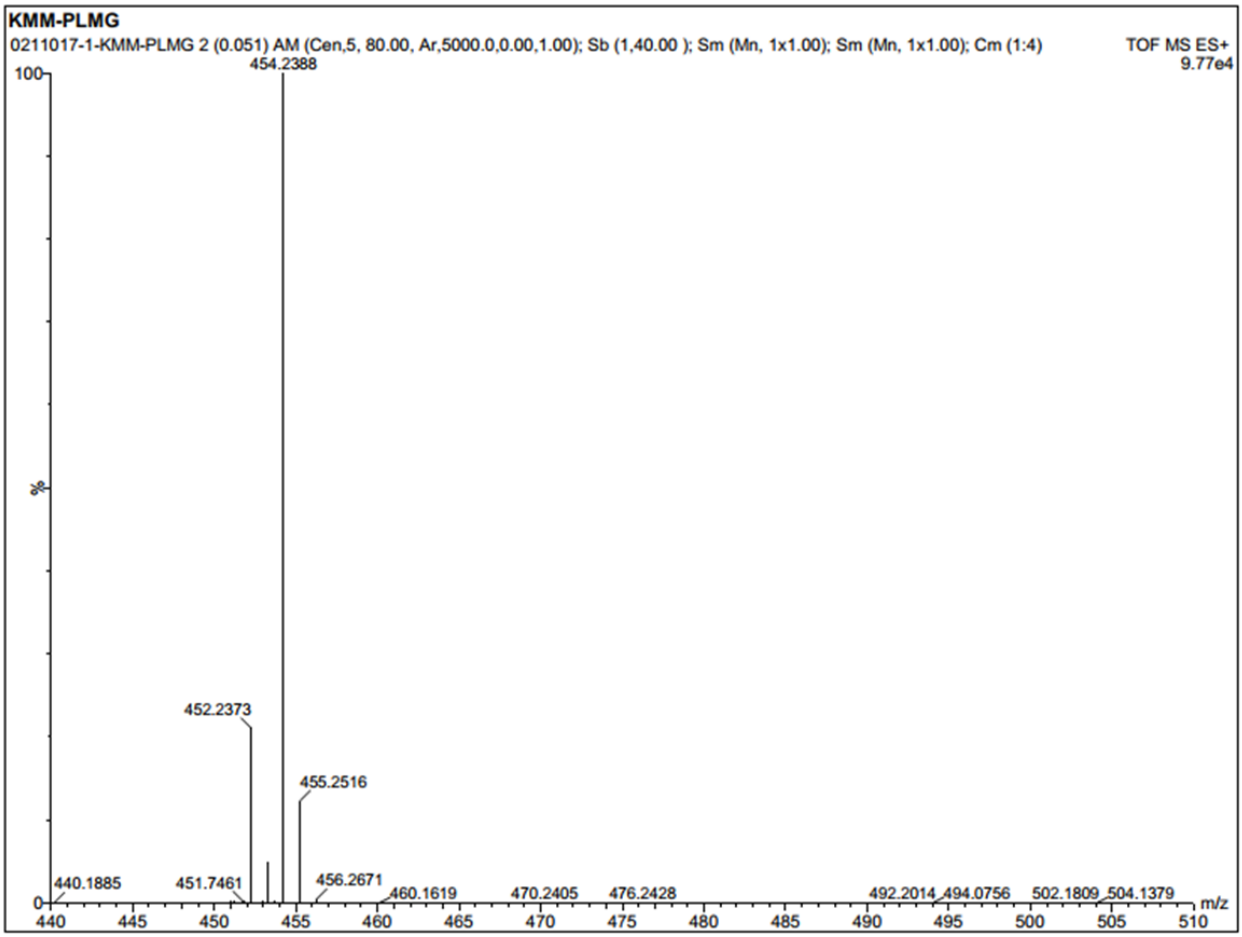
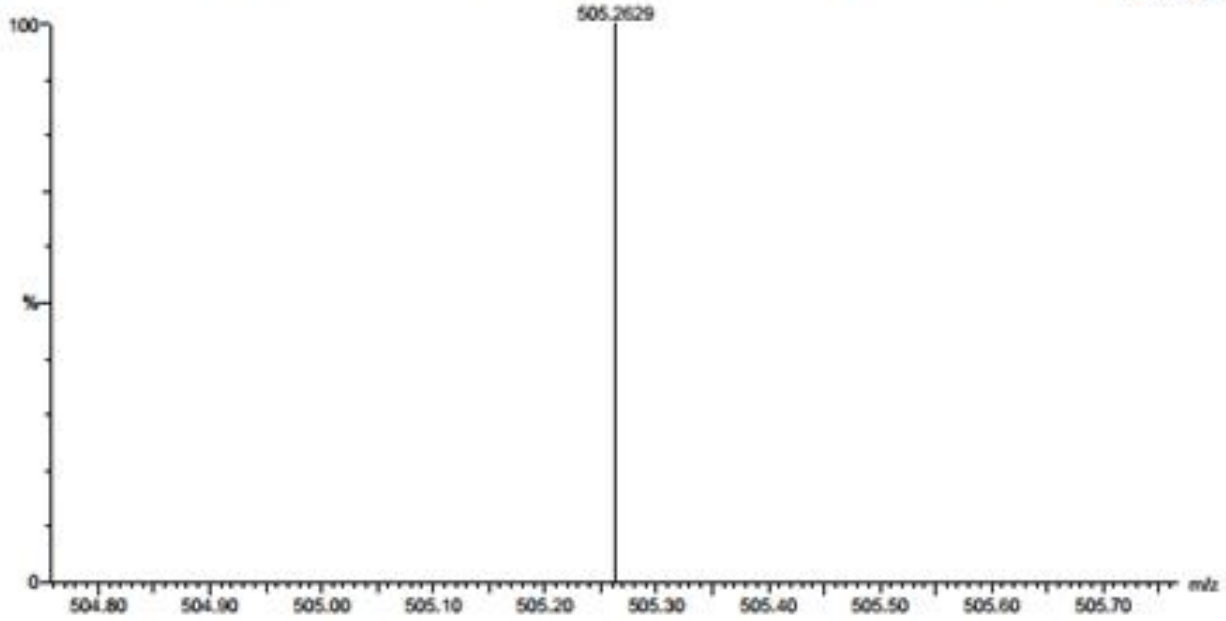


Fig.S38 Mass spectrum of **PyMBD.**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-37 H: 0-33 N: 0-2
KMM-PR-BDA
08062018-01-KMM-PR-BDA 2 (0.051) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (2:6) TOF MS ES+
4.80e+004



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
505.2629	505.2644	-1.5	-3.0	22.5	n/a	C37 H33 N2

Fig.S39 Mass spectrum of **PrMBD.**