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

Electronic Supporting Information

Hexaphenylbenzene-Based Fluorescent Aggregates for Detection of Zinc and Pyrophosphate Ions in Aqueous Media: Tunable Self-assembly Behaviour and Construction of Logic Device

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Fig. S11 DLS studies show the change in size of: (a) aggregates of derivative **7** in H_2O/EtOH (6:4, v/v), (b) in presence of Zn^{2+} ions in aggregates of **7**, (c) in addition of PPi to **7-Zn^{2+}** ensemble

Fig. S12 ^{1}H NMR spectrum of compound **3**

Fig. S13 ^{13}C NMR spectrum of compound **3**

Fig. S14 ESI-MS mass spectrum of compound **3**

Fig. S15 ^{1}H NMR spectrum of compound **5**

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Fig. S17 ESI-MS mass spectrum of compound **5**

Fig. S18 ^{1}H NMR spectrum of compound **7**

Fig. S19 ^{13}C NMR spectrum of compound **7**

Fig. S20 ESI-MS mass spectrum of compound **7**

Table S1 Comparison of probe **7** with literature reports for detection of Zn^{2+} ions.

S.No.	Publication	Sensing Media	Fluorometric response	Colorimetric response	Zinc induced modulation of Self-assembly	Detection limit	Practical applications for the construction Logic Device	Sensing ability of Zn^{2+} ions in ground water ($ZnCl_2$)	Interference with other Metal ions
1	**Present Manuscript**	**6:4 (H_2O:EtOH, v/v)**	**Not Quenched**	**Yes**	**Spherical to micro rods**	14.7 nM	**Yes**	**Yes**	**No**
2	*ACS Sens.*, 2016, **1**, 739-747	DMF/ H_2O (9:1, v/v)	Turn-on	Yes	Rod to irregular shaped	110 nM	No	No	No
3	*ACS Sens.*, 2016, **1**, 144-150	CH_3CN	Turn-on	No	No	-	No	No	Yes (Al^{3+})
4	*Dalton Trans.*, 2015, **44**, 18902-18910	CH_3OH/aqueous HEPES (9:1, v/v)	Turn-on	No	No	1.03 µM	No	No	Yes (Cu^{2+}, Al^{3+})
5	*Dalton Trans.*, 2015, **44**, 7470-7476	Tris-HCl buffer	Turn-on	No	No	2.5×10^{-5} M	No	No	Yes (Cd^{2+})
6	*New J. Chem.*, 2015, **39**, 4055-4062	HEPES/ CH_3OH (3:7)	Turn-on	No	No	76 nM	No	No	Yes (Cd^{2+})
7	***RSC Adv.***, 2015, **5**, 63634-63640	Ethanol	Turn-on	Yes	No	1 nM	No	No	No
8	*Polyhedron*, 2015, **94**, 75-82	9:1 v/v MeCN/ H_2O	Turn-on	No	No	0.13 µM	No	No	Yes (Cd^{2+})
9	*Dalton Trans.*, 2014, **43**, 1684-1690	DMF–H_2O (1 : 1)	Turn-on	No	No	µM	No	No	Yes (Cd^{2+})
10	*Dalton Trans.*, 2014, **43**, 10013-10022	DMF–H_2O (1 : 1)	Turn-on	No	No	µM	No	No	Yes (Cd^{2+})
11	*Sens. Actuators, B*, 2014, **201**, 204-212	4:1 MeOH–water	Turn-on	No	No	0.69 µM	No	-	Yes (Cu^{2+}, Ni^{2+}, Cd^{2+})
12	*Chem. Commun.*, 2013, **49**, 11430-11432	HEPES buffer	Turn-on	No	No	57 nM	No	No	Yes (Pb^{2+}, Cd^{2+})
13	*Inorg. Chem.*, 2012, **51**, 8760-8774	CH_3CN	Turn-on	No	No	2.3 pM	No	No	Yes (Cd^{2+})
15	*ACS Appl. Mater. Interfaces*, 2011, **3**, 279-286	Tris-HCl buffer	Turn-on	No	No	0.1 µM	No	-	Yes (Pb^{2+}, Cd^{2+})

Table S2 Comparison of **7-Zn^{2+}** ensemble with literature reports for detection of PPi ions.

S.No.	Publication	Sensing Media	Fluoremetric response	Colorimetric response	Pyrophosphate (PPi) induced Self-assembly	Detection limit	Practical applications for the construction Logic Device
1	**Present Manuscript**	**6:4 (H_2O:EtOH, v/v)**	**On-On**	**Yes**	**Micro rods**	74 nM	**Yes**
2	*Inorg. Chem.*, 2016, **55**, 2212-2219	In MOPS Buffer	Turn-on	Yes	No	300 nM	No
3	*ACS Omega,* 2016, **1**, 648-655	aqueous HEPES buffer	Turn-on	No	No	10 µM	No
4	*Sens. Actuators, B,* 2016, **233**, 591-598	HEPES buffer	Turn-on	Yes	No	0.11µM	No
5	***RSC Adv.***, 2015, **5**, 60096-60100	0.5% DMSO water	Turn-on	Yes	Yes	0.6 equiv.	No
6	*J. Mater. Chem. B*, 2014, **2**, 6634-6638	EtOH	ESIPT Turn-on	No	No	-	No
7	*Dalton Trans.*, 2014, **43**, 14142-14146	EtOH	Turn-on	No	No	2.7 nM	No
8	*J. Mater. Chem. B*, 2014, **2**, 3349-3354	EtOH	ESIPT Turn-on	No	No	0.2 equiv.	No
9	*Spectrochim. Acta, Part A,* 2014, **118**, 17-23	Tris–HCl buffer pH	Turn-on	No	No	2.78 µM	No
10	*Anal. Chem.*, 2012, **84**, 5117-5123	aqueous buffer solution	Turn-off	No	No	2.78 µM	No
11	*Org. Biomol. Chem.*, 2012, **10**, 5606-5612	aqueous HEPES buffer	Turn-on	Yes	No	$(2.9 \pm 0.3) \times 10^8$ M	No
12	*Org. Lett.*, 2011, **13**, 1362-1365	aqueous HEPES buffer	Turn-on	No	No	1 µM	No

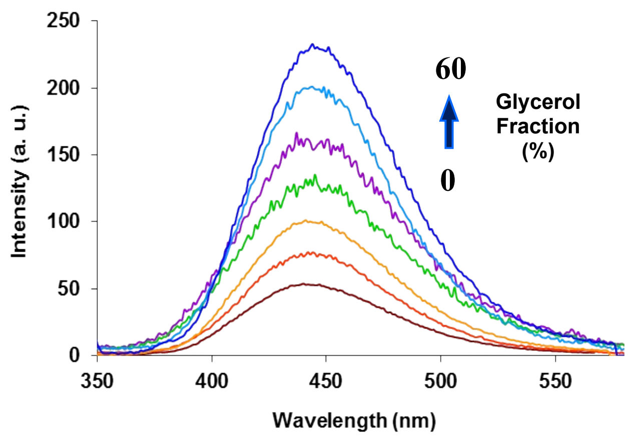


Fig. S1 Fluorescence spectra of compound **7** (5 μM) showing the variation of fluorescence intensity in Ethanol/glycerol mixture (0 to 60% volume fraction of glycerol in ethanol); λ_{ex} = 350 nm.

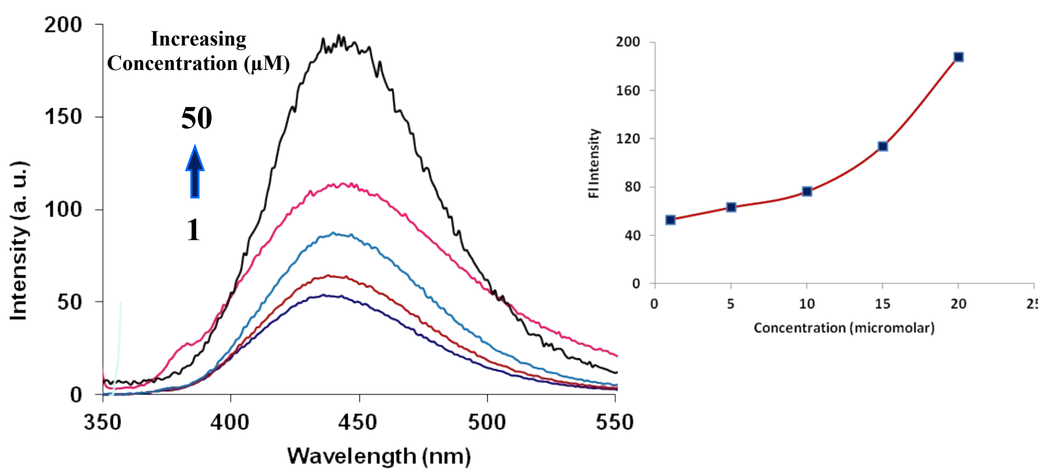


Fig. S2 Fluorescence spectra of derivative **7** in ethanol with increasing concentration from 1 to 50 μM; λ_{ex} = 350 nm. Inset showing the non-linear emission enhancement with increasing concentration.

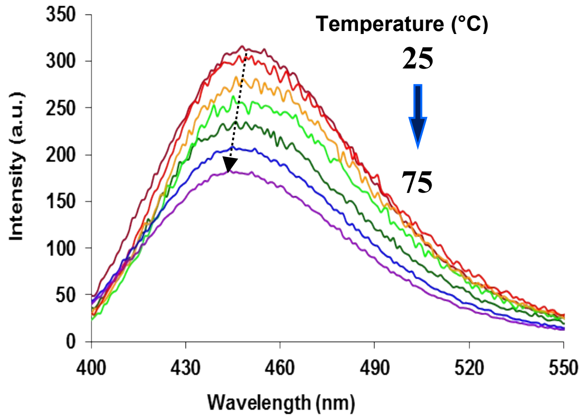


Fig. S3 Fluorescence spectra of derivative **7** (5 μM) showing the variation of fluorescence intensity with increase in temperature from 25 to 75 °C in H_2O/EtOH mixture (6:4, v/v); λ_{ex} = 350 nm.

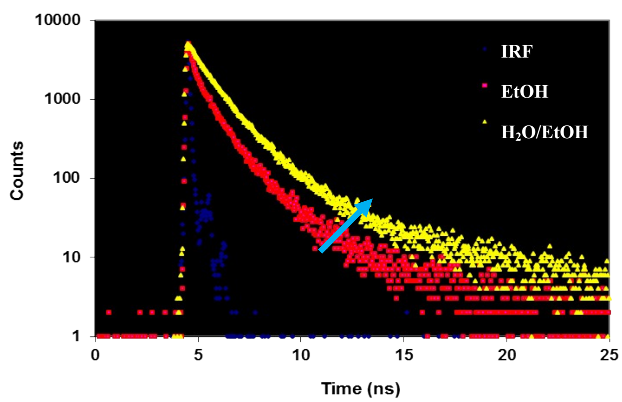
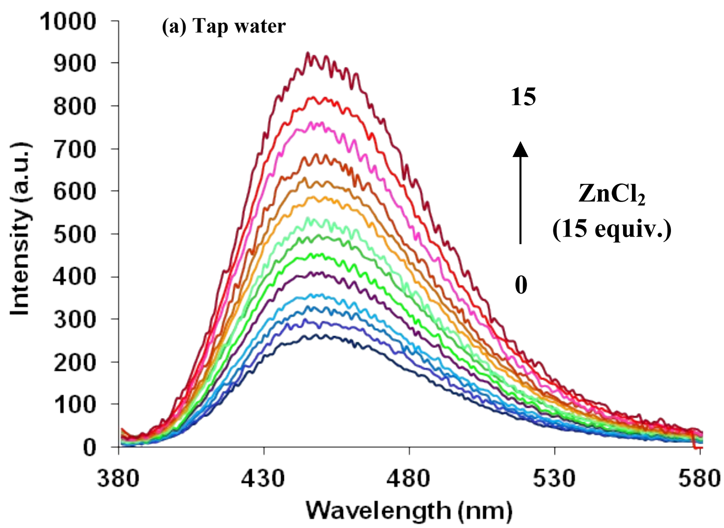


Fig. S4 Exponential fluorescence decays of derivative **7** in EtOH and H_2O/EtOH (6:4, v/v) mixture, Spectra measured at 450 nm. λ_{ex}= 377 nm.

Table S3 Fluorescence lifetime of derivative **7** in EtOH and H_2O/EtOH (6:4, v/v) mixtures.

Derivative (7)	**A_1/A_2**	**τ_1 (ns)**	**τ_2 (ns)**	**τ_{avg} (ns)**	**Φ_f**	**k_f (10^9 S^{-1})**	**k_{nr} (10^9 S^{-1})**
EtOH	100	0.638	-	0.638	0.082	0.128	1.438
(6:4, v/v), H_2O/EtOH	74.66/25.34	1.193	1.048	1.122	0.14	0.124	0.766

A_1, A_2: fractional amount of molecules in each environment, τ_1 and τ_2: biexponential life time of aggregates in 60 vol% of water in EtOH; k_f: radiative rate constant ($k_f = \Phi_f/\tau_{avg}$); k_{nr}: non-radiative rate constant (k_{nr} = (1- Φ_f)/τ_{avg}); λ_{ex}= 377 nm.



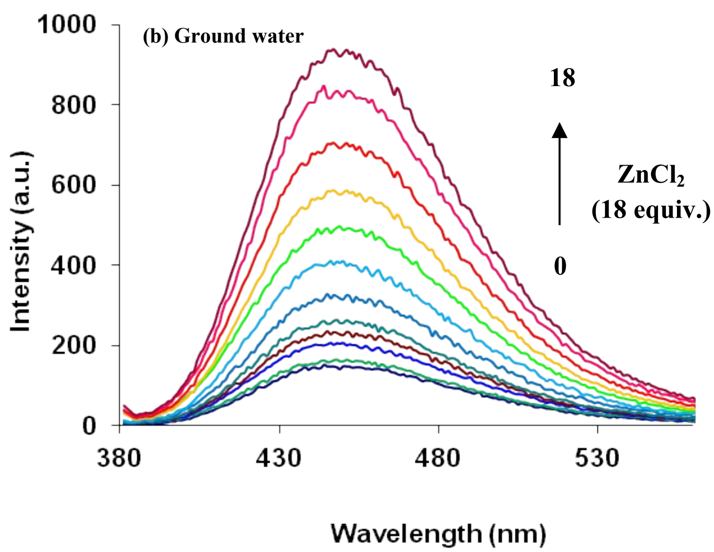
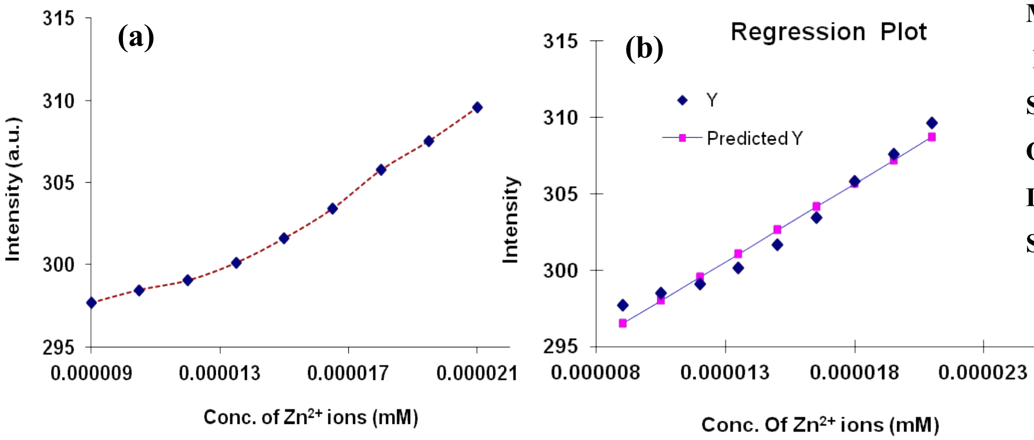


Fig. S5 Fluorescence spectra of compound **7** in H_2O/EtOH (6:4, v/v) response to $ZnCl_2$ in (a) tap water (15 equiv.) and (b) local ground water (18 equiv.), λ_{ex}= 350 nm.



Multiple R = 0.982035,

R^2 = 0.964393,

Standard deviation = 0.005,

Observation = 10,

Intercept = 287.29,

Slope = 1019333

Fig. S6 (a) Showing the fluorescence intensity of compound **7** and (b) Calibrated curve showing the fluorescence intensity of compound **7** at 450 nm as a function of Zn^{2+} ions concentration (equiv.) in H_2O/EtOH (6:4, v/v) buffered with HEPES, pH = 7.05, λ_{ex}= 350 nm.

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of receptor **7** without Zn^{2+} was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation:

DL = 3 × SD/S

Where SD is the standard deviation of the blank solution measured by 10 times; S is the slope of the calibration curve.

From the graph we get slope

S =**1019333**, and SD value is 0.005

Thus using the formula we get the Detection Limit **(DL) = 3 × 0.005/1019333 = 1.47 × 10^{-8}M = 14.7 nM.**

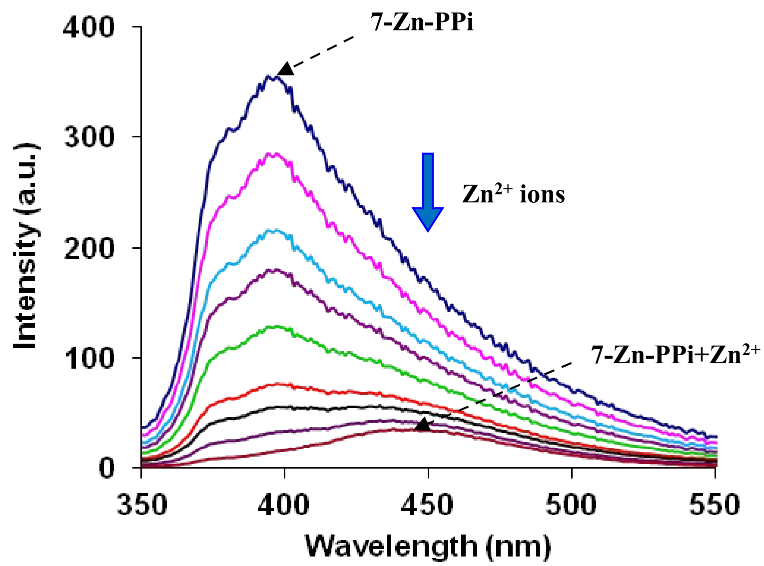


Fig. S7 Fluorescence spectra showing the quenching in emission intensity of **7-Zn-PPi** system upon further addition of Zn^{2+} ions (10 equiv.), λ_{ex}= 350 nm.

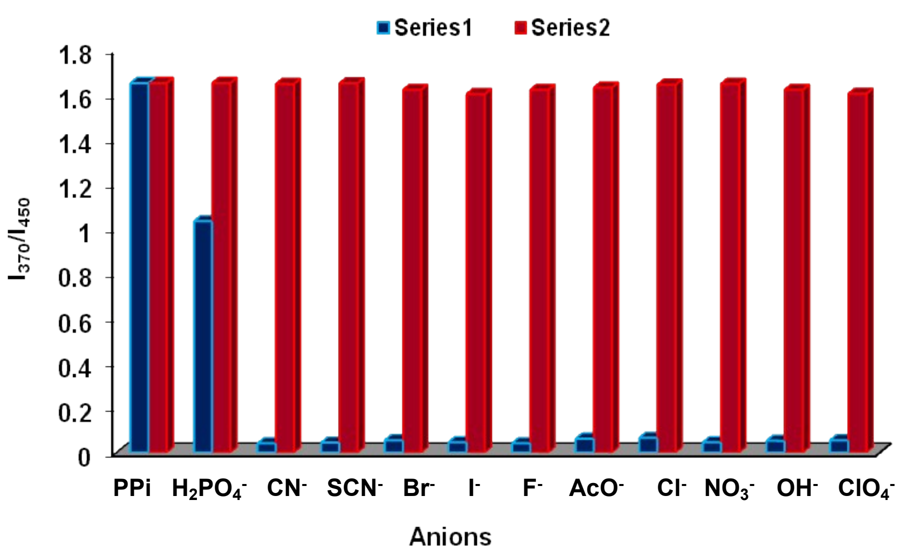


Fig. S8 Bars represent the emission intensity ratio (I_{370}/I_{450}) (I_{450} = Initial fluorescence intensity at 450 nm; I_{370} = Final fluorescence intensity at 370 nm after addition of anions). (a) Blue bars represent selectivity of **7** upon addition of different anions; (b) Red bars represent competitive selectivity of receptor **7** towards PPi ions (15 equiv.) in presence of other anions (30 equiv.).

Multiple R = 0.973106
R^2 = 0.956936,
Standard deviation = 0.006,
Observation = 9,
Intercept = 962.9946,
Slope = 242344

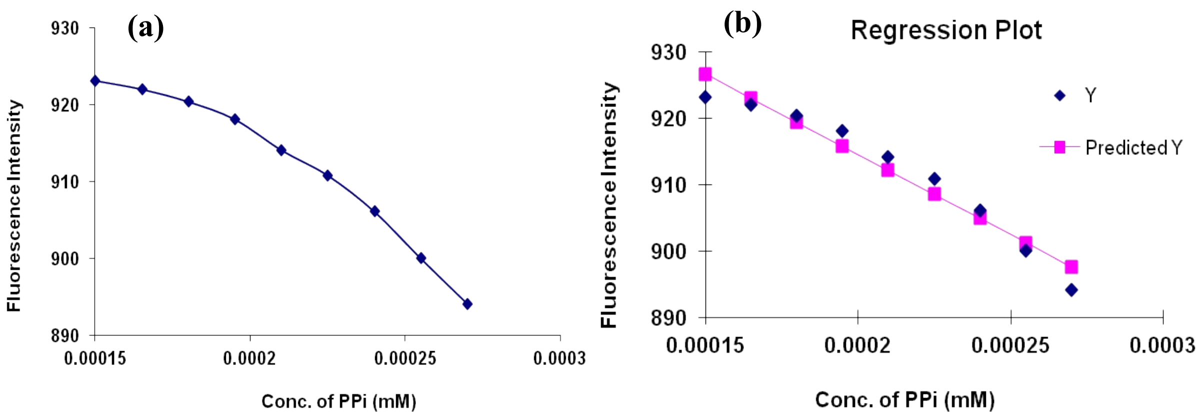


Fig. S9 (a) Showing the fluorescence intensity of **7-Zn^{+2}** ensemble and (b) Calibrated curve showing the fluorescence intensity of **7-Zn^{+2}** ensemble at 450 nm as a function of PPi ions concentration (equiv.) in H_2O/EtOH (6:4, v/v) buffered with HEPES, pH = 7.05, λ_{ex}= 350 nm.

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of receptor **7** without Zn^{2+} was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation:

DL = 3 × SD/S

Where SD is the standard deviation of the blank solution measured by 10 times; S is the slope of the calibration curve.

From the graph we get slope

S = **242344**, and SD value is 0.006

Thus using the formula we get the Detection Limit **(DL) = 3 × 0.006/242344 = 74 × 10^{-9} M = 74 nM.**

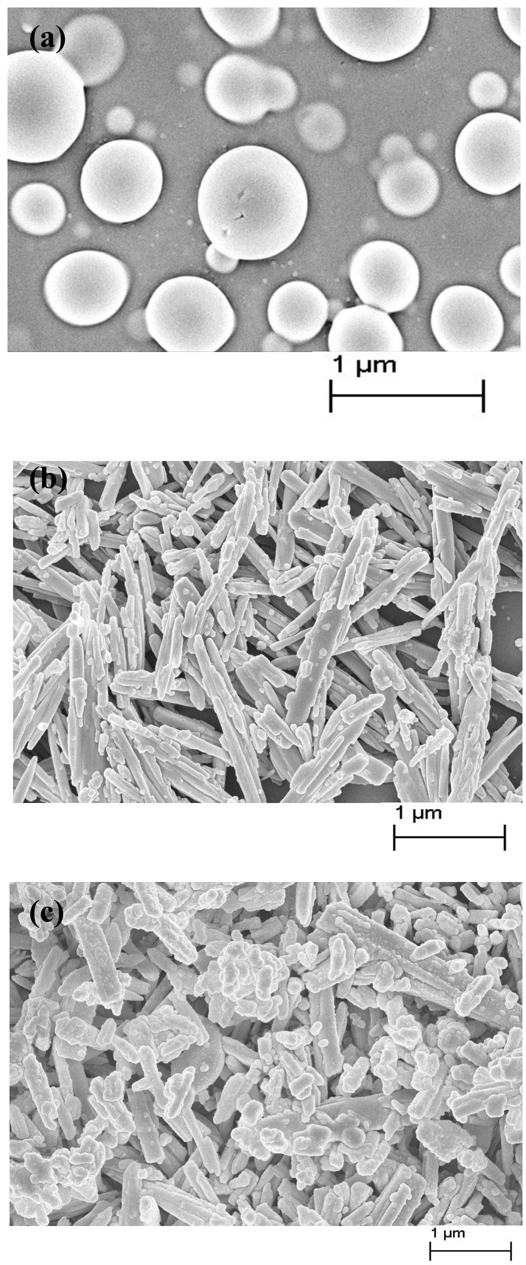


Fig. S10 SEM images show the change in morphology and size of: (a) aggregates of derivative **7** in H_2O/EtOH (6:4, v/v), (b) in presence of Zn^{2+} ions in aggregates of **7**, (c) in addition of PPi to **7-Zn^{2+}** ensemble.

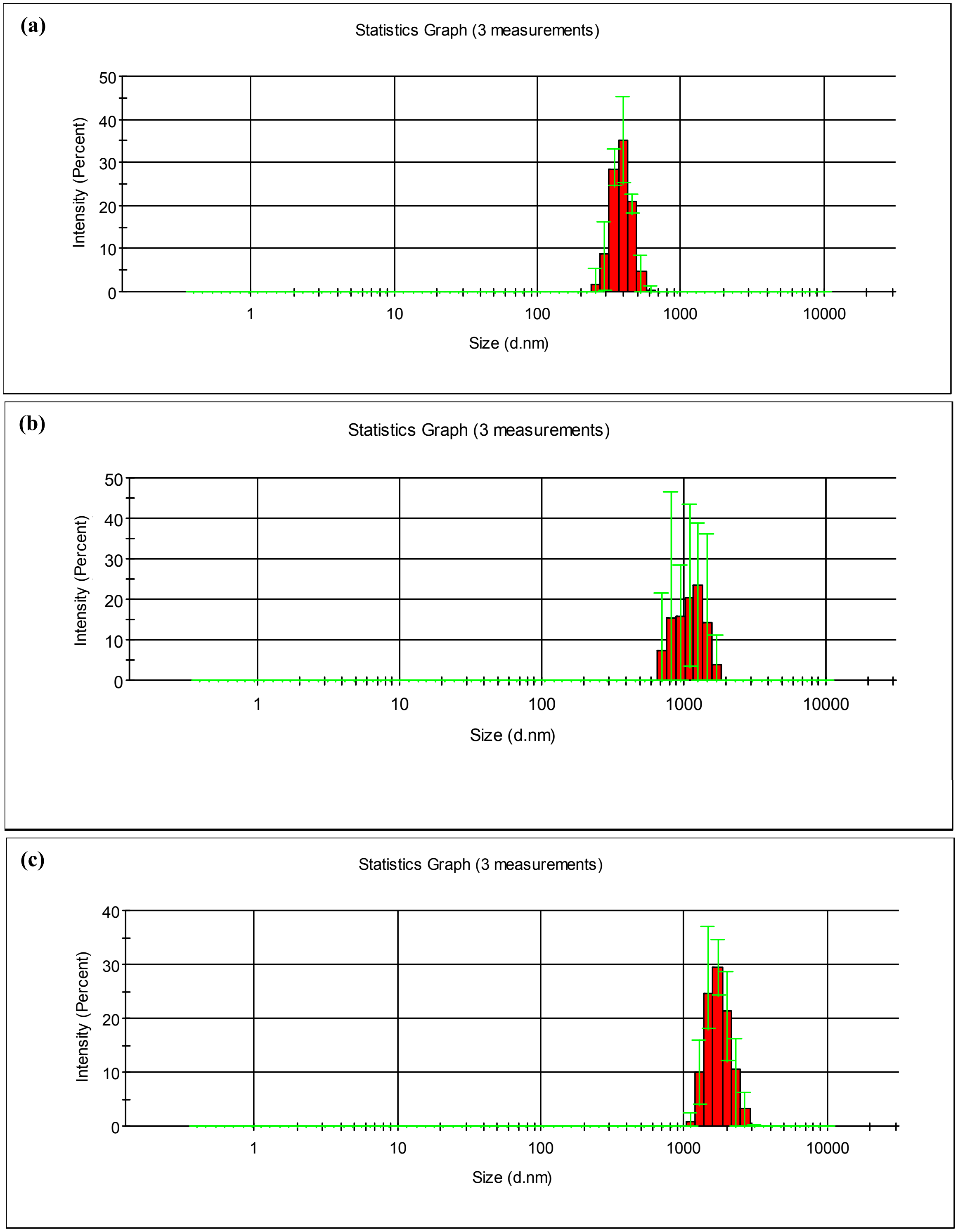


Fig. S11 DLS studies show the change in size of: (a) aggregates of derivative **7** in H_2O/EtOH (6:4, v/v), (b) in presence of Zn^{2+} ions in aggregates of **7**, (c) in addition of PPi to **7-Zn^{2+}** ensemble.

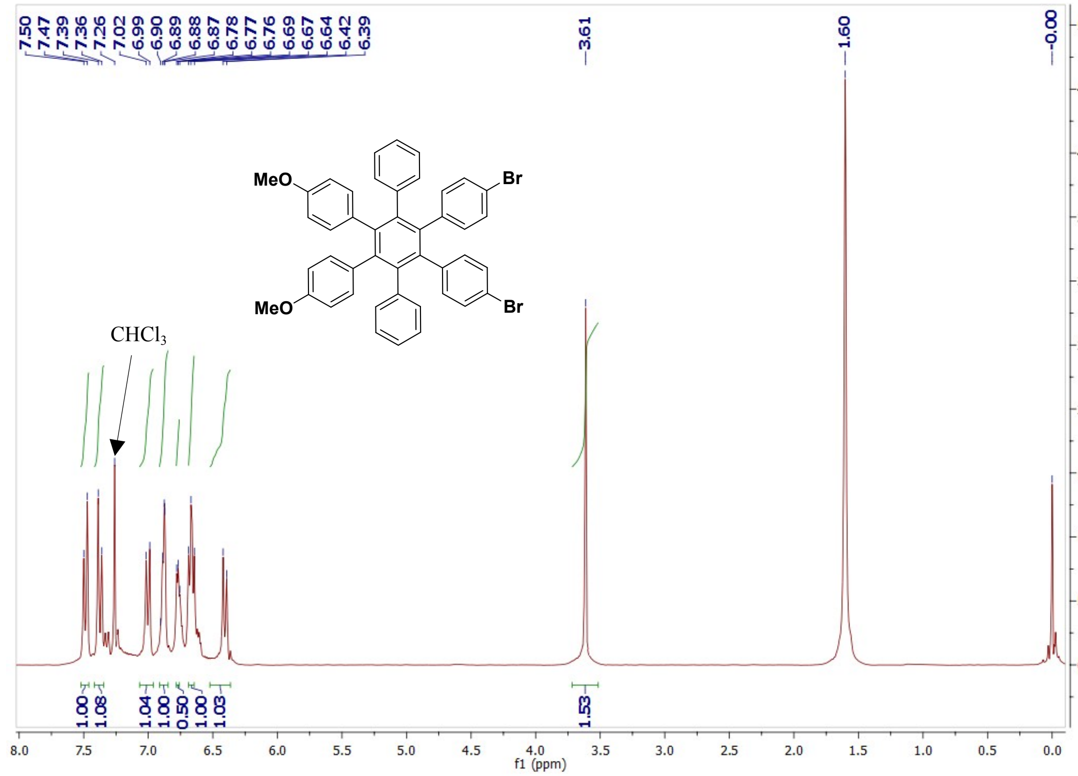


Fig. S12 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

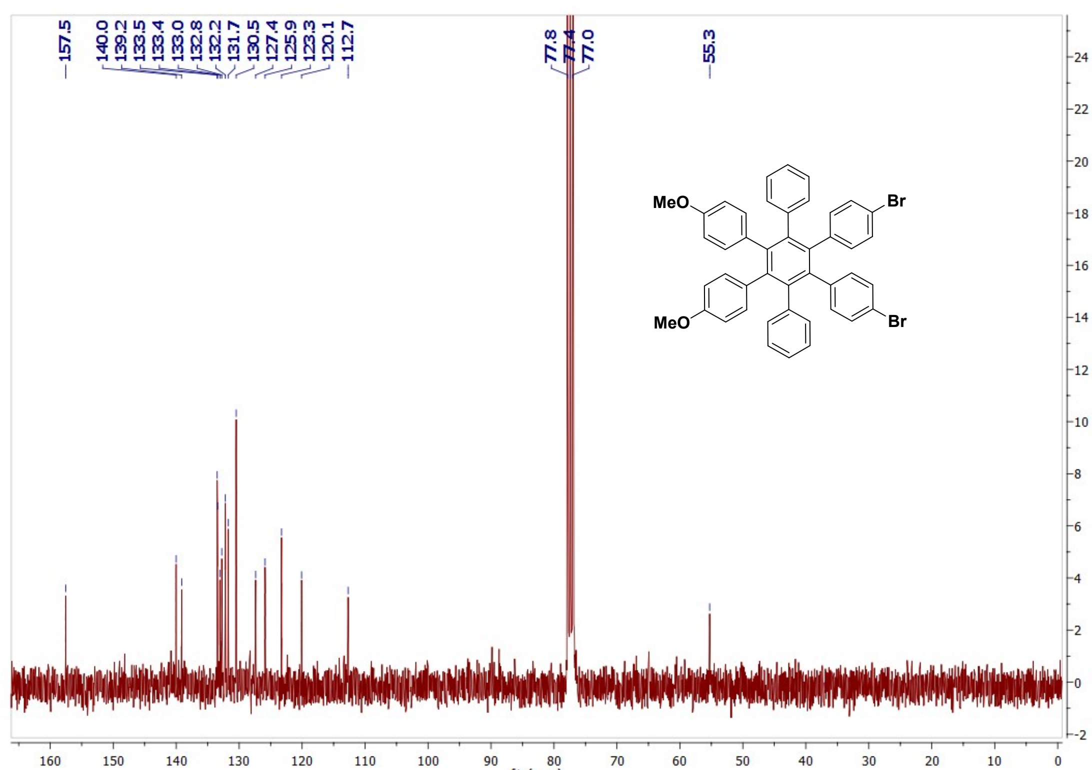


Fig. S13 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

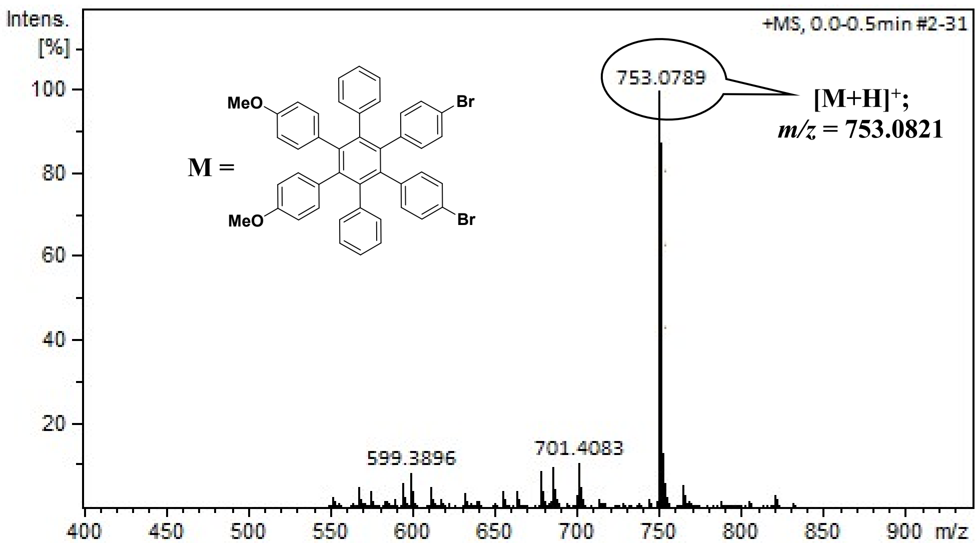


Fig. S14 ESI-MS mass spectrum of compound **3**.

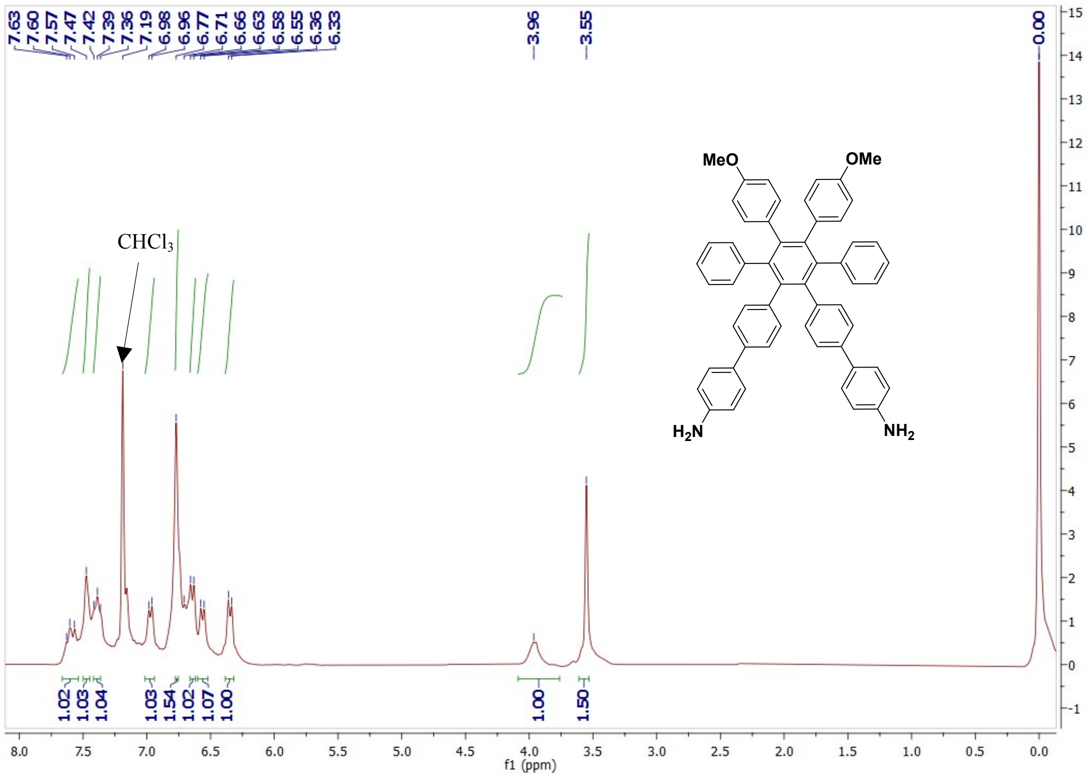


Fig. S15 ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

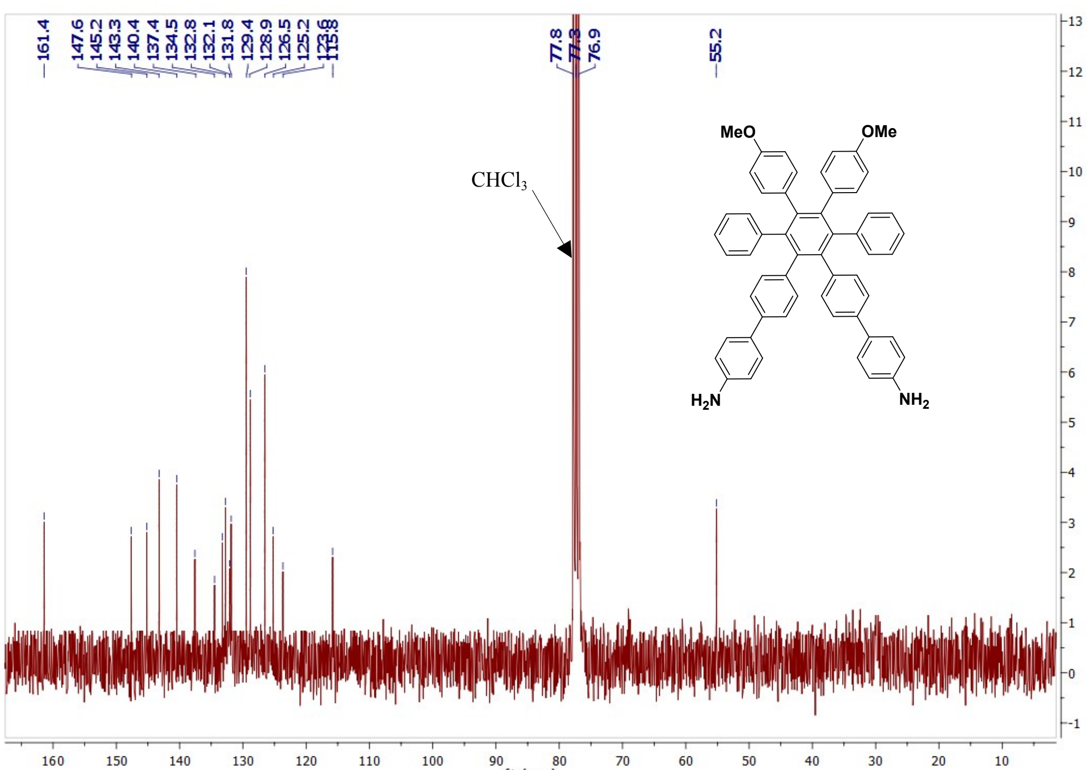


Fig. S16 ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

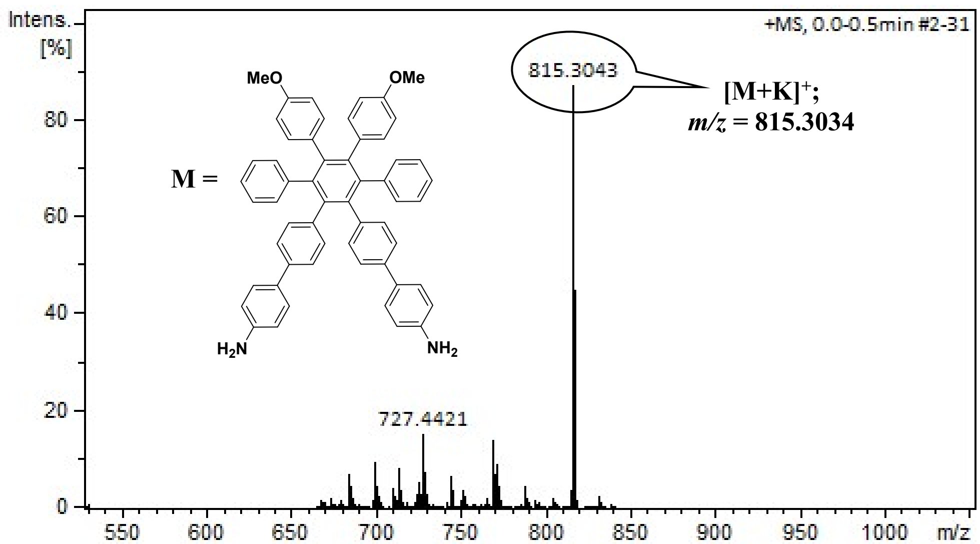


Fig. S17 ESI-MS mass spectrum of compound **5**.

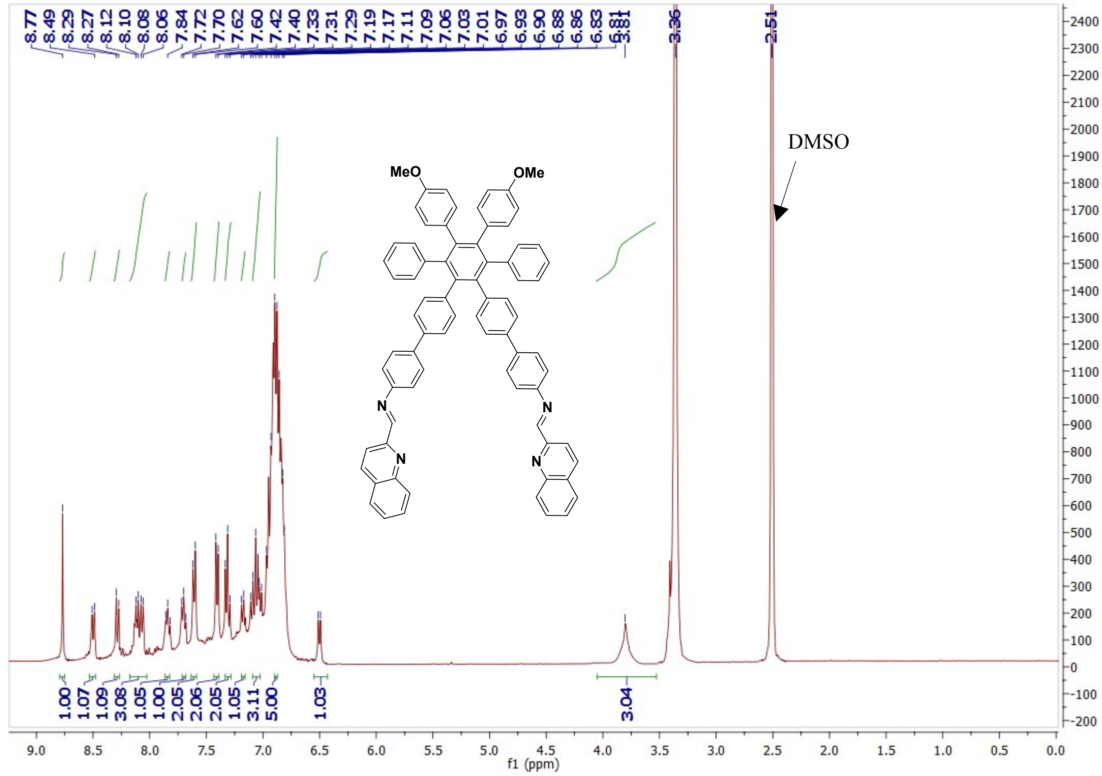


Fig. S18 ^{1}H NMR spectrum of compound **7** in DMSO-d_6.

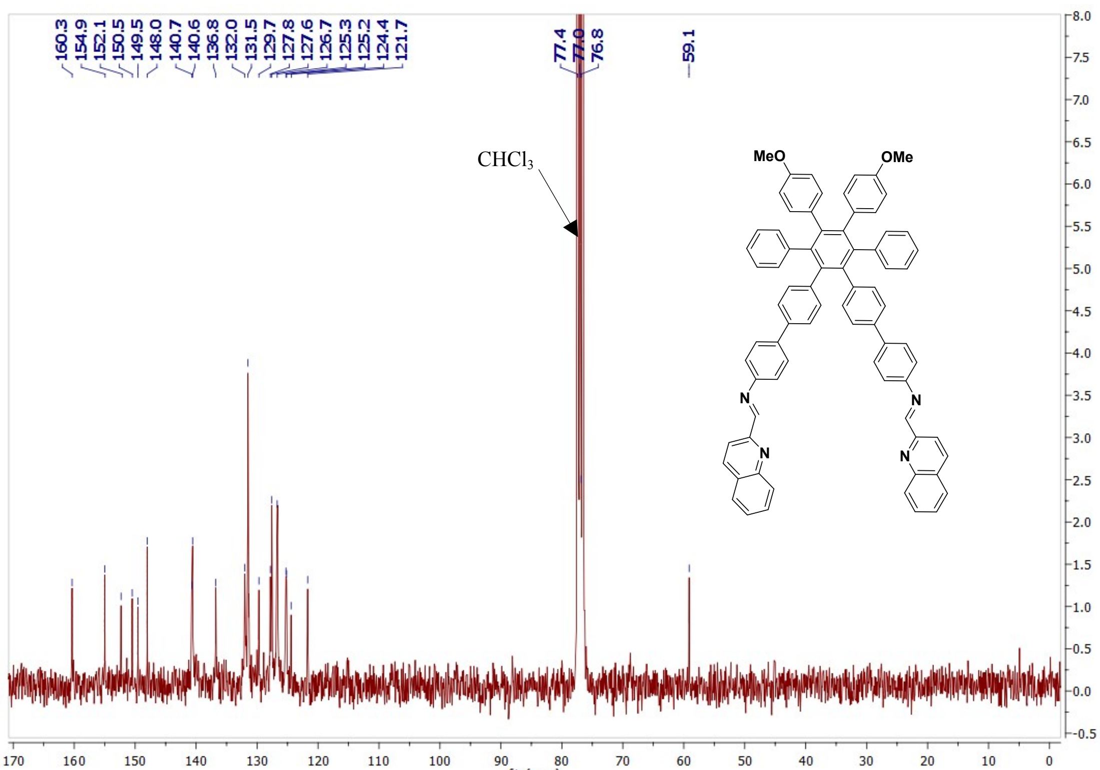


Fig. S19 ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

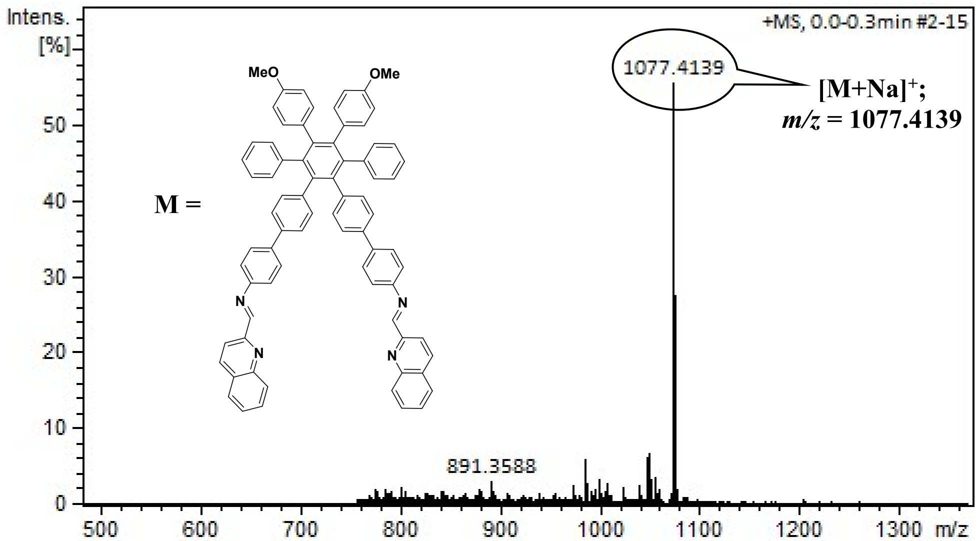


Fig. S20 ESI-MS mass spectrum of compound **7**.