

Preservation of Luminescent Properties of Zinc Complexes in the Solid State by Accumulating into Polyhedral Oligomeric Silsesquioxane

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Abstract: Multinuclear complexes have attracted great attention because of their superior properties originating from the cooperative effects between the metal ions. In this study, we synthesized polynuclear zinc complexes by chelation between the side-chains of polyhedral oligomeric silsesquioxane (POSS). From the NMR spectroscopy, high-resolution mass spectrometry and Fourier transform infrared spectroscopy (FT-IR), it was confirmed the four equivalents of zinc ions were coordinated to the single POSS molecule. Optical measurements indicated that luminescent properties can be preserved even in the solid state. The three-dimensional structure of POSS should play a significant role in suppressing concentration quenching followed by solid-state emission properties.

Introduction

Multinuclear complexes, which are complexes with multiple metal ions within a single molecule, have attracted great attention because of superior properties originating from the cooperative effects between the complexes.^{1–5} For example, it was reported that the catalytic activity of cobalt complexes was able to be dramatically enhanced by the accumulation of them in dendrimers.⁶ Besides, cyclic multinuclear complexes perform precise molecular recognition by utilizing multipoint coordination bonds of multiple metal ions.⁷ Since the unique properties of such multinuclear complexes are expressed by the shape of the molecule and the space around the complexes, the control of these properties is a significant issue.

Polyhedral oligomeric silsesquioxane (POSS) is a molecule with organic side-chains at the eight vertices of its Si–O bonded cubic structure, which has paid much attention because of structural and physical features, such as rigid three-dimensional structure and high thermal stability.^{8–26} It was reported that POSS-core dendrimers showed higher encapsulation ability than polyamidoamine dendrimers.²⁷ More recently, we have demonstrated that excited molecules can be stabilized and recruited to the formation of luminescent complexes such as excimer and exciplex.^{28,29} These properties are expected to be a platform for luminescent sensors.^{30–36} Furthermore, the efficient intramolecular interaction inside the POSS molecule is useful for the synthesis of intracomplex-type multinuclear complexes, which are prepared by chelation of metal ions to the periphery of ligands-containing dendrimers.^{37–53} Therefore, by

combining the effect of strengthening the intramolecular interactions of POSS with the electronic properties of the complex, we can expect the expression of unique synergistic functions. However, as is often the case with organic luminescent dyes, concentration quenching is often caused through non-specific intermolecular interactions by assembling into compact spaces.⁵⁴ Therefore, it is necessary to clarify the effect of accumulation of luminescent complexes on optical properties for extending further applications based on POSS.^{55–61}

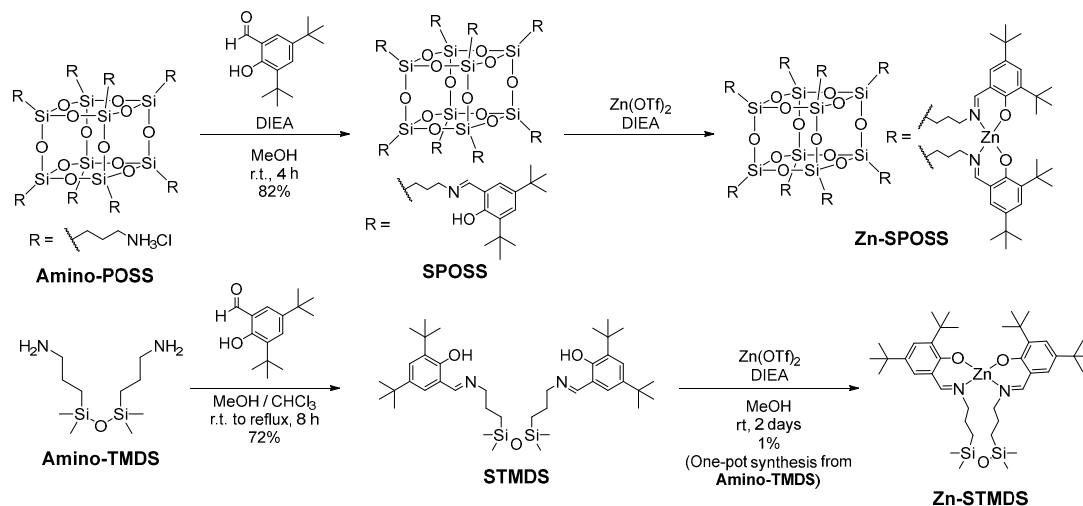
In this study, we show synthesis and optical properties of intracomplex-type polynuclear complexes using POSS as a scaffold. We constructed luminescent zinc complexes with the salicylaldehyde ligand, and the series of structural analyses and optical measurements were performed. In summary, we demonstrate that POSS is responsible for expressing emission in solid. It was shown that the steric structure of POSS plays an important role in suppressing concentration quenching followed by solid-state emission from metal complexes.

Results and Discussion

A zinc(II) complex of a tetramethyldisiloxane having salicylaldehyde ligands has been synthesized.⁶² We prepared **Zn-SPOSS** and **Zn-STMDS** according to Scheme 1. **SPOSS** was obtained through dehydrative condensation of **Amino-POSS** with 3,5-di-*tert*-butyl salicylaldehyde.^{63,64} The *tert*-butyl groups are introduced for improving the solubility of the

complexes. In the subsequent complexation reaction with zinc ions, we performed two types of reactions by changing a solvent as listed in Table S1, and the resulting compounds **Zn-SPOSS-EtOH** (entry 1) and **Zn-SPOSS-DMSO** (entry 2) were obtained with almost the same yields. **Zn-STMDS** was synthesized using 1,3-bis(3-aminopropyl)-tetramethyl disiloxane (**Amino-TMDS**) as a starting material by the same condensation and complexation reactions as **Zn-SPOSS**.⁶² From the FT-IR measurements, the coordination of zinc ions was confirmed for **Zn-SPOSS** and **Zn-STMDS** (Figure S1). In addition, the molecular weights of **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO** were measured using MALDI-TOF-MS (Figure S2). As a result, the significant peaks were obtained from both POSS derivatives at the expected mass value assigned to the compound with 4 equivalents of zinc ions. Although small dimeric peaks, which might be caused through the ionization, were observed, there were no peaks of higher molecular weight than the dimer. From these data, POSS derivatives should have the same chemical components.

Scheme 1. Syntheses of **Zn-SPOSS** and **Zn-STMDS**



The ^1H NMR spectra of **Zn-SPOSS-EtOH**, **Zn-SPOSS-DMSO**, and **SPOSS** in CDCl_3 solution are shown in Figure 1a. Regarding the imine and aromatic protons peaks of **Zn-SPOSS**, different signals were observed depending on the reaction conditions (Figure S3). In the spectrum of **Zn-SPOSS-EtOH** synthesized in the EtOH solvent at 93 °C, two peaks were observed. Meanwhile, in the spectrum of **Zn-SPOSS-DMSO** synthesized in DMSO solvent at 170 °C, the single peak which was identical with the right side of the peak in **Zn-SPOSS-EtOH** was observed. It is likely that the peak splitting can originate from the formation of isomers at the zinc complex (Figure S4) because the rotation of the alkyl substituents should be suppressed by forming a ring structure at the side-chains. In fact, these behaviors were also detected in the comparison between **STMDS** and **Zn-STMDS** (Figure 1b). To obtain further information on the structure, we performed additional analyses.

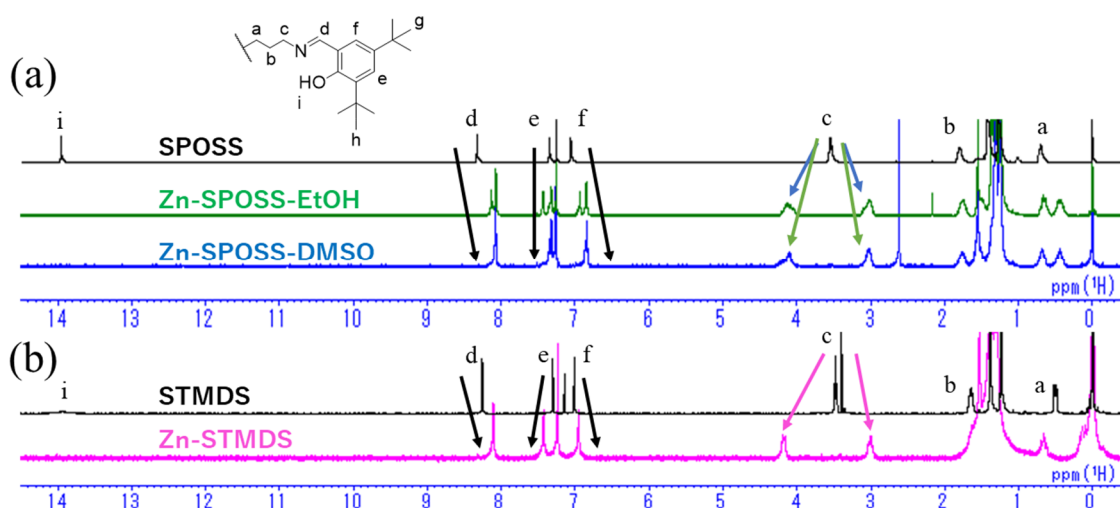


Figure 1. ^1H NMR spectra of (a) **SPOSS** (black), **Zn-SPOSS-EtOH** (green) and **Zn-SPOSS-DMSO** (blue) (b) **STMDS** (black) and **Zn-STMDS** (pink) in CDCl_3 .

Initially, to evaluate possibility whether the signal splitting should be induced by the intermolecular or intramolecular complexation, ^1H DOSY measurements were performed with **Zn-SPOSS-EtOH** which showed split peaks (Figure S5). Accordingly, diffusion coefficients were identical for each peak of the aromatic proton, clearly indicating that the signal splitting should be caused by intramolecular complexation. These results indicate that intramolecular reactions should proceed more preferentially than intermolecular reactions, and the splitting should be derived from the isomers which were chelated between different pairs of POSS vertices.

Optical measurements of **SPOSS**, **Zn-SPOSS-EtOH**, and **Zn-SPOSS-DMSO** were performed in the solution states (Table 1, Figure 2a). In the UV-vis absorption spectra, the absorption band of **SPOSS** observed at 329 nm was significantly shifted to 385 nm by the coordination of zinc ions. In the emission spectra, the emission bands were observed at around 472 nm from **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO**, indicating that luminescent zinc complexes were constructed around POSS (Figure 2b). In particular, almost the same spectra were obtained from POSS derivatives. It was reported that the optical properties of salen-type complexes were affected by the coordination structure such as the length of the side chains.⁶⁵ Taking into account on this fact, we concluded that the structural differences between **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO** should be negligible in the optical measurements in the single molecular level.

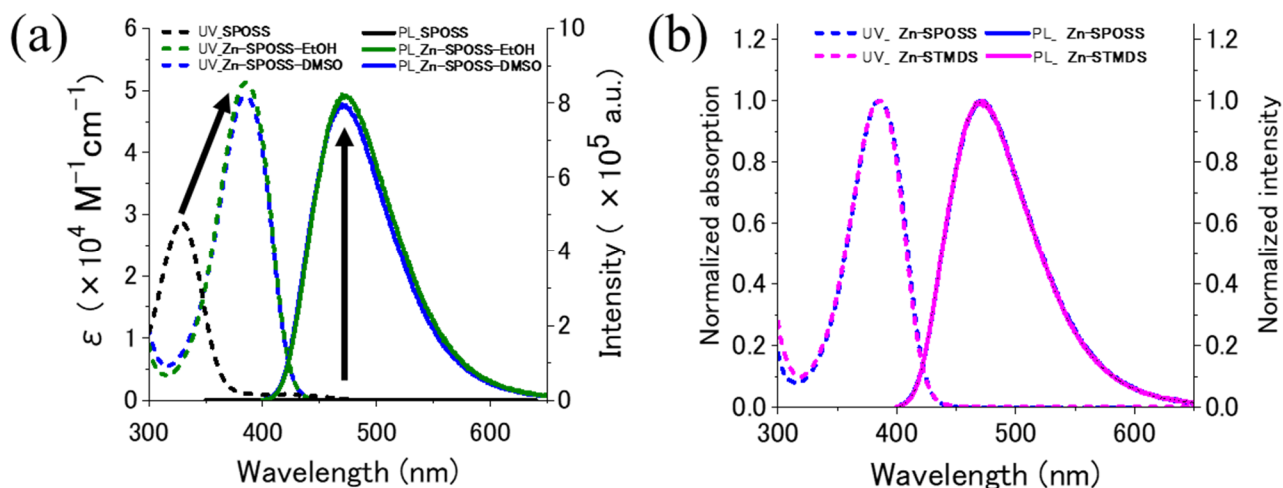


Figure 2. (a) UV-vis absorption and photoluminescence spectra of **SPOSS**, **Zn-SPOSS-EtOH**, and **Zn-SPOSS-DMSO** (1.0×10^{-5} M in CHCl_3) excited at wavelengths of absorption maxima. (b) UV-vis absorption and photoluminescence spectra of **Zn-SPOSS-DMSO** (1.0×10^{-5} M in CHCl_3) and **Zn-STMDs** (4.0×10^{-5} M in CHCl_3) excited at wavelengths of absorption maxima.

Table 1. Optical properties of **SPOSS**, **Zn-STMDs**, **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO**

Compounds	$\lambda_{\text{max,abs}}$ (nm) ^a	$\lambda_{\text{max,em}}$ (nm) ^{a,b}	ϵ ($\text{M}^{-1}\text{cm}^{-1}$) ^a	τ (ns) ^a	Φ_{PL} ^{a,c}	$\lambda_{\text{max,em}}$ (nm) ^{b,d}	Φ_{PL} ^{c,d}	$\lambda_{\text{max,em}}$ (nm) ^{b,e}	Φ_{PL} ^{c,e}
SPOSS	329	n.d. ^f	29,000	n.d. ^f	n.d. ^f	n.d. ^f	n.d. ^f	n.d. ^f	n.d. ^f
Zn-STMDs	385	472	15,000	5.6 (91%) 2.2 (9%)	0.27	471	0.15	463	0.56
Zn-SPOSS-EtOH	385	473	51,000	6.4 (92%) 1.8 (8%)	0.23	476	0.22	469	0.22
Zn-SPOSS-DMSO	385	472	51,000	6.7 (90%) 1.5 (10%)	0.23	484	0.14	469	0.23

^a 1.0×10^{-5} M; ^b Excited at $\lambda_{\text{max,abs}}$; ^c Determined as an absolute value; ^d Measured in solid; ^e 1 wt% in polystyrene; ^f Not detectable due to weak intensity.

Optical measurements were also performed in the solid states (Figure 3a, Table S2).

Zn-STMDs had the maximum emission wavelength at almost the same position as the dilute solution, and both **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO** showed red-shifts by 10 nm and 3 nm, respectively. The absolute photoluminescence quantum efficiency of **Zn-SPOSS-DMSO** was 0.14 in the solid-state, while that was 0.23 in the dilute solution. It is proposed that concentration quenching should occur due to intermolecular or intramolecular

interactions among zinc complexes. On the other hand, the quantum efficiency of **Zn-SPOSS-EtOH** was 0.22 even in the solid states, meaning that concentration quenching was efficiently suppressed. This should be attributed to the different packing structures between **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO** as supported by the different powder X-ray diffraction (PXRD) patterns (Figure S6). Further, the POSS derivatives were dispersed in the polystyrene matrix with 1 wt%, and influence of intermolecular interaction on optical properties was examined (Figure 3b, Table S3). Accordingly, all compounds showed blue-shifted emission. Interestingly, the quantum efficiencies of **Zn-SPOSS-EtOH** and **Zn-SPOSS-DMSO** in the dispersion films were 0.23 and 0.22, respectively. These data mean that especially in **Zn-SPOSS-EtOH**, the POSS core is able to prevent zinc complexes from concentration quenching and contributes to preserving luminescent properties in the condensed state. In fact, the quantum efficiency of the model compound was much higher (0.56) than those of POSS derivatives as well as that in solution. These data mean that concentration quenching cannot be avoided by cross-linking with the zinc complexes. Although the POSS unit is compact, it is assumed that formation of critical intermolecular interactions might be suppressed by three-dimensionally arranging the complexes around the cubic core.

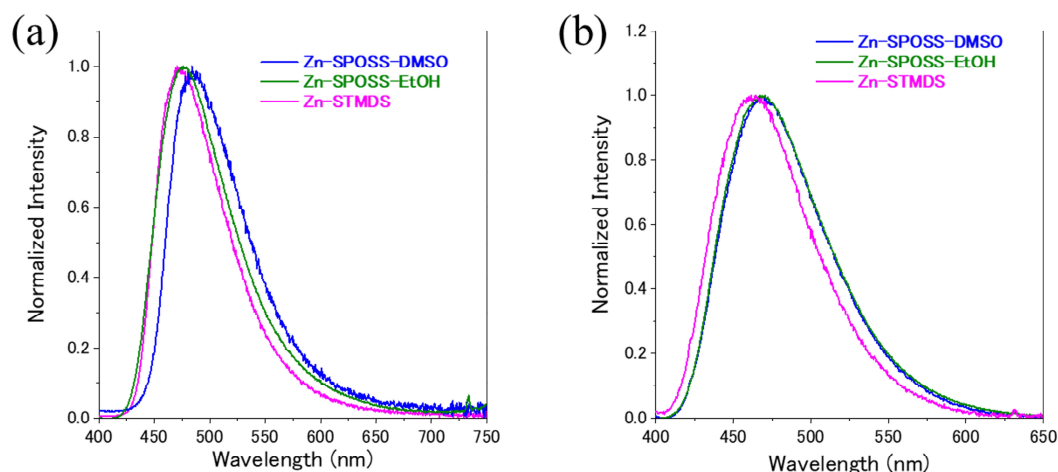


Figure 3. Photoluminescence spectra of **SPOSS**, **Zn-SPOSS-EtOH**, and **Zn-SPOSS-DMSO** (a) in the solid states and (b) in 1 wt% polystyrene dispersion films excited at wavelengths of absorption maxima.

Conclusion

Polynuclear zinc complexes were successfully synthesized by chelation between the intramolecular side-chains of POSS. From the NMR spectroscopy, high-resolution mass spectrometry, FT-IR, and optical measurements, it was confirmed the four equivalents of zinc ion were coordinated to the single POSS molecule and the desired multinuclear complex was obtained. Optical measurements indicated similar absorption and emission spectra for synthesized complexes in the solution states. In particular, it was demonstrated that emission efficiency can be preserved in the solid state by connecting to the POSS core. Our molecular design might be applicable for constructing various functional materials such as robust luminophores and fluorescent film sensors.

Acknowledgement

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References

- (1) G. I. Dzhardimalieva, I. E. Uflyand, *Dalton Trans.* **2017**, 46, 10139–10176.
- (2) E. V. Puttock, M. T. Walden, J. A. G. Williams, *Coord. Chem. Rev.* **2018**, 367, 127–162.
- (3) A. McAuley, S. Subramanian, *Coord. Chem. Rev.* **2000**, 200–202, 75–103.
- (4) B. Kar, N. Roy, S. Pete, P. Moharana, P. Paira, *Inorganica Chim. Acta* **2020**, 512, 119858.
- (5) M. Mauro, *Chem. Commun.* **2021**, 57, 5857–5870.
- (6) R. Breinbauer, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2000**, 39, 3604–3607.
- (7) T. Nakamura, Y. Kaneko, E. Nishibori, T. Nabeshima, *Nat. Commun.* **2017**, 8, 129.
- (8) D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* **2010**, 110, 2081–2173.
- (9) Z. Li, J. Kong, F. K. Wang, C. He, *J. Mater. Chem. C* **2017**, 5, 5283–5298.
- (10) H. Shi, J. Yang, M. You, Z. Li, C. He, *ACS Materials Lett.* **2020**, 2, 296–316.
- (11) K. Tanaka, Y. Chujo, *J. Mater. Chem.* **2012**, 22, 1733–1746.
- (12) Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2015**, 88, 633–643.
- (13) M. Gon, K. Tanaka, Y. Chujo, *Polym. J.* **2018**, 50, 109–126.
- (14) F. K. Wang, X. Lu, C. He, *J. Mater. Chem.* **2011**, 21, 2775–2782.
- (15) K. Naka, Y. Irie, *Polym. Int.* **2017**, 66, 187–194.
- (16) Y. Kaneko, *Chem. Rec.* **2023**, 23, e202200291.

- (17) Y. Liu, K. Koizumi, N. Takeda, M. Unno, A. Ouali, *Inorg. Chem.* **2022**, *61*, 1495–1503.
- (18) R. Kajiya, H. Wada, K. Kuroda, A. Shimojima, *Chem. Lett.* **2020**, *49*, 327–329.
- (19) S. Iwao, N. Kurono, W. Higashiguchi, T. Hayakawa, N. Ohta, K. Kamitani, S. Fujii, Y. Nakamura, T. Hirai, *Chem. Lett.* **2022**, *51*, 781–783.
- (20) H. Sakai, T.-M. Yung, T. Mure, N. Kurono, S. Fujii, Y. Nakamura, T. Hayakawa, M.-C. Li, T. Hirai, *JACS Au*, **2023**, *3*, 2698–2702.
- (21) R. Tajikawa, I. Tokuami, M. Nagao, A. Okada, H. Imoto, K. Naka, *Langmuir* **2024**, *40*, 11795–11805.
- (22) K. Kato, M. Gon, K. Tanaka, Y. Chujo, *Polymers* **2019**, *11*, 1195.
- (23) R. Nakamura, H. Narikiyo, M. Gon, K. Tanaka, Y. Chujo, *Polymers* **2019**, *11*, 1170.
- (24) D. Iizuka, M. Gon, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2022**, *95*, 743–747.
- (25) M. Gon, K. Kato, K. Tanaka, Y. Chujo, *Mater. Chem. Front.* **2019**, *3*, 1174–1180.
- (26) K. Tanaka, K. Inafuku, K. Naka, Y. Chujo, *Org. Biomol. Chem.* **2008**, *6*, 3899–3901.
- (27) H. Kozuka, K. Tanaka, Y. Chujo, *Eur. Polym. J.* **2022**, *175*, 111360.
- (28) H. Narikiyo, M. Gon, K. Tanaka, Y. Chujo, *Mater. Chem. Front.* **2018**, *2*, 1449–1455.
- (29) K. Tanaka, H. Narikiyo, T. Kato, M. Gon, Y. Chujo, *ChemPhotoChem* **2024**, e202400273. (DOI:10.1002/cptc.202400273)
- (30) M. Gon, K. Tanaka, Y. Chujo, *Chem. Asian J.* **2022**, *17*, e202200144.

- (31) D. Iizuka, M. Gon, K. Tanaka, Y. Chujo, *Chem. Commun.* **2022**, 58, 12184–12187.
- (32) H. Narikiyo, M. Gon, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2024**, 97, uoae066.
- (33) H. Narikiyo, M. Gon, K. Tanaka, Y. Chujo, *Polym. J.* **2024**, 56, 661–666.
- (34) H. Narikiyo, M. Gon, K. Tanaka, Y. Chujo, *Asian J. Org. Chem.* **2024**, e202400508.
(DOI:10.1002/ajoc.202400508)
- (35) H. Zhou, M. H. Chua, H. R. Tan, T. T. Lin, B. Z. Tang, J. Xu, *ACS Appl. Nano Mater.* **2019**, 2, 470–478.
- (36) Chanmungkalakul, S.; Ervithayasuporn, V.; Hanprasit, S.; Masik, M.; Prigyaia, N.; Kiatkamjornwong, S. *Chem. Commun.* **2017**, 53, 12108–12111.
- (37) E. Karakhanov, A. Maximov, A. Zolotukhina, *Polymers* **2022**, 14, 981.
- (38) S. Siangwata, C. Williams, N. Omosun, S. Ngubane, G. S. Smith, *Appl. Catal. A: Gen.* **2021**, 626, 118362.
- (39) J. Martinovic, A.-M. Chiorcea-Paquim, V. C. Diclescu, J. Van Wyk, E. Iwuoha, P. Baker, S. Mapolie, A.-M. Oliveira-Brett, *Electrochimica Acta* **2008**, 53, 4907–4919.
- (40) R. Malgas-Enus, S. F. Mapolie, *Polyhedron* **2012**, 47, 87–93.
- (41) J. Bu, Z. M. A. Judeh, C. B. Ching, S. Kawi, *Catal. Lett.* **2003**, 85, 183–187.
- (42) R. Malgas-Enus, S. F. Mapolie, *Inorganica Chim. Acta* **2014**, 409, 96–105.
- (43) S. F. Mapolie, J. L. van Wyk, *Inorganica Chim. Acta* **2013**, 394, 649–655.
- (44) S. V. John, N. Mayedwa, C. Ikpo, L. Y. Molefe, M. M. Ndipingwi, N. R. Dywili, J.

- Van Wyk, S. F. Mapolie, P. Baker, E. Iwuoha, *Synth. Met.* **2016**, 220, 114–122.
- (45) C. Calabrese, C. Aprile, M. Gruttadauria, F. Giacalone, *Catal. Sci. Technol.* **2020**, 10, 7415–7447.
- (46) V. Ervithayasuporn, K. Kwanplod, J. Boonmak, S. Youngme, P. Sangtrirutnugul, *J. Catal.* **2015**, 332, 62–69.
- (47) E. G. Vieira, A. G. Dal-Bó, T. E. A. Frizon, N. L. Dias Filho, *J. Organomet. Chem.* **2017**, 834, 73–82.
- (48) A. Akbari, N. Arsalani, M. Amini, E. Jabbari, *J. Mol. Catal. A: Chem.* **2016**, 414, 47–54.
- (49) H. J. Murfee, T. P. S. Thoms, J. Greaves, B. Hong, *Inorg. Chem.* **2000**, 39, 5209–5217.
- (50) L. Ropartz, R. E. Morris, D. F. Foster, D. J. Cole-Hamilton, *Chem. Commun.* **2001**, 361–362.
- (51) S. Bruña, D. Nieto, A. M. González-Vadillo, J. Perles, I. Cuadrado, *Organometallics* **2012**, 31, 3248–3258.
- (52) K. J. Haxton, D. J. Cole-Hamilton, R. E. Morris, *Dalton Trans.* **2007**, 3415–3420.
- (53) E. G. Vieira, R. O. Silva, A. G. Dal-Bó, T. E. A. Frizon, N. L. D. Filho, *New J. Chem.* **2016**, 40, 9403–9414.
- (54) S. A. Jenekhe, J. A. Osaheni, *Science* **1994**, 265, 765–768.
- (55) C. He, Y. Xiao, J. Huang, T. Lin, K. Y. Mya, X. Zhang, *J. Am. Chem. Soc.* **2004**, 126,

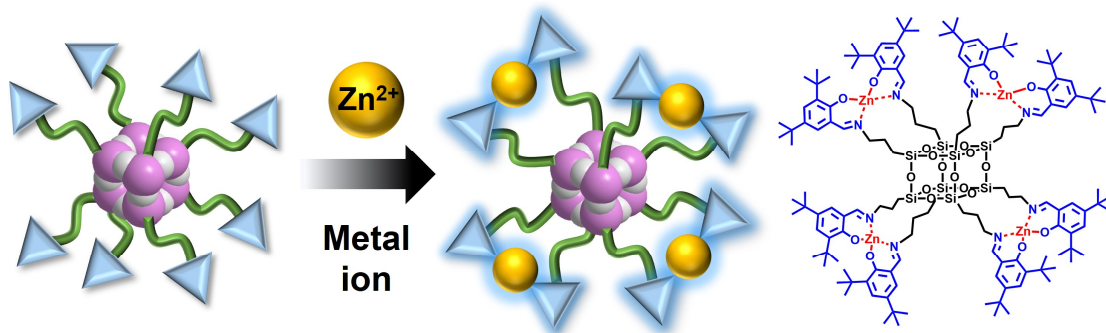
7792–7793.

- (56) M. Y. Lo, C. Zhen, M. Lauters, G. E. Jabbour, A. Sellinger, *J. Am. Chem. Soc.* **2007**, *129*, 5808–5809.
- (57) M. Gon, K. Sato, K. Tanaka, Y. Chujo, *RSC Adv.* **2016**, *6*, 78652–78660.
- (58) K. Suenaga, K. Tanaka, Y. Chujo, *Chem. Eur. J.* **2017**, *23*, 1409–1414.
- (59) K. Sato, M. Gon, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2024**, *97*, uoae040.
- (60) M. Gon, K. Sato, K. Kato, K. Tanaka, Y. Chujo, *Mater. Chem. Front.* **2019**, *3*, 314–320.
- (61) M. Gon, S. Saotome, K. Tanaka, Y. Chujo, *ACS Appl. Mater. Interfaces* **2021**, *13*, 12483–12490.
- (62) A. Vlad, M.-F. Zaltariov, S. Shova, M. Cazacu, M. Avadanei, A. Soroceanu, P. Samoila, *Polyhedron* **2016**, *115*, 76–85.
- (63) H. Imoto, S. Wada, K. Naka, *Chem. Lett.* **2016**, *45*, 1256–1258.
- (64) M. Janeta, Ł. John, J. Ejfler, T. Lis, S. Szafert, *Dalton Trans.* **2016**, *45*, 12312–12321.
- (65) V. Nishal , D. Singh , R. K. Saini , V. Tanwar , S. Kadyan , R. Srivastava , P. S. Kadyan , *Cogent Chem.* **2015**, *1*, 1079291.

Entry for the Table of Contents

Multidentate ligand

Multinuclear Metal Complex



We synthesized polynuclear zinc(II) complexes by chelation between the side-chains of cubic polyhedral oligomeric silsesquioxane (POSS). The four equivalents of zinc(II) ions were coordinated to the single POSS molecule. The luminescent properties can be preserved even in the solid state. The steric and three-dimensional structure of POSS restricted excess intermolecular interaction and should play a significant role in suppressing concentration quenching followed by solid-state emission properties.

Supporting Information

Preservation of Luminescent Properties of Zinc Complexes in the Solid State by Accumulating into Polyhedral Oligomeric Silsesquioxane

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Experimental Section

General experimental details

^1H (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100 MHz), and ^{29}Si (79 MHz) NMR spectra were recorded on JEOL JNM-EX400 or JNM-AL400 spectrometers. ^1H NMR spectra were recorded by using tetramethylsilane (TMS) as an internal standard in CDCl_3 . $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded by using residual non-deuterated solvents as an internal standard in CDCl_3 . High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher EXACTIVE for electron spray ionization (ESI) and atmospheric pressure chemical ionization (APCI), or on a Thermo Fisher Scientific OrbitrapXL spectrometers for matrix assisted laser desorption/ionization (MALDI). UV–vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. All reactions were performed under nitrogen atmosphere. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer, and samples were analyzed at room temperature. The PL lifetime measurement was recorded on a Horiba FluoroCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 292, 375 nm). An absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01 with an integral sphere. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu IRPrestige-21. Powder X-ray diffraction (PXRD) data were collected with a Rigaku SmartLab Diffractometer (sealed tube (50 kV, 40 mA); Cu K α , 1.542 Å; Bragg–Brentano geometry, a HyPix-3000 detector).

Materials

Amino-POSS was synthesized according to the literature.¹ Reagents (3-aminopropyltriethoxysilane, 3,5-di-*tert*-butylsalicylaldehyde, zinc(II) trifluoromethanesulfonate, 1,3-bis(3-aminopropyl)-tetramethyldisiloxane, *N,N*-diisopropyl ethylenediamine) (DIEA) and solvents (methanol, ethanol, dimethyl sulfoxide, and chloroform) were purchased from commercial sources and used without further purification. Triethylamine (NEt_3) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). Polystyrene (Styrene, Polymer, $n = \text{ca. } 2000$ (FUJIFILM Wako Pure Chemical Corporation) was purified by a reprecipitation method in MeOH from CHCl_3 solution. Molecular weights of the obtained polystyrene ($M_n = 81,000$ and $M_w = 210,000$, PDI = 2.6) were determined by a gel permeation chromatography (GPC) with polystyrene standards. Thin films were prepared using a spin-coating method (2000 rpm, 30 s) from chloroform solution (1 wt%, 150 μL) on a quartz substrate (0.9 cm $\times$ 5 cm).

Synthesis of SPOSS

To a MeOH (100 mL) solution of **Amino-POSS** (2.35 g, 2.00 mmol) (4.69 g, 20.0 mmol) and *N,N*-diisopropyl ethylenediamine (6.97 mL, 5.17 g, 40.0 mmol) was added a MeOH (100 mL) solution of 3,5-di-*tert*-butylsalicylaldehyde (4.69 g, 20.0 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. The precipitate was

collected and dried *in vacuo* to afford **SPOSS** as yellow solid (4.87 g, 1.86 mmol, 93%). ^1H NMR (CDCl_3 , ppm): 13.95 (s, 8H), 8.33 (s, 8H), 7.35 (d, $J = 2.4$ Hz, 8H), 7.06 (d, $J = 2.3$ Hz, 8H), 3.55 (t, $J = 6.7$ Hz, 16H), 1.84–1.77 (m, 16H), 1.43 (s, 72H), 1.28 (s, 72H), 0.73–0.69 (m, 16H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 165.9, 158.3, 139.8, 136.6, 126.6, 125.8, 117.9, 61.8, 35.0, 34.1, 31.5, 29.5, 24.5, 9.5. ^{29}Si NMR (CDCl_3 , ppm): –66.7. HRMS (MALDI) calcd. for $\text{C}_{144}\text{H}_{224}\text{N}_8\text{O}_{20}\text{Si}_8+\text{H}$ $[\text{M}+\text{H}]^+$ 2610.4984, found 2610.4935.

Synthesis of Zn-SPOSS-EtOH

To an EtOH (50 mL) solution of **SPOSS** (522 mg, 0.200 mmol) was added a MeOH (10 mL) solution of zinc(II) trifluoromethanesulfonate (0.073 g, 0.200 mmol) followed by NEt_3 (0.279 mL, 20.2 mg, 2.00 mmol) at room temperature. The reaction mixture was stirred at 93 °C for 23 h under a nitrogen atmosphere and allowed to cool at room temperature. The precipitate was collected, washed with EtOH, and dried *in vacuo* to afford a yellow solid (306 mg, 0.106 mmol, 53%). ^1H NMR (CDCl_3 , ppm): 8.15–8.06 (m, 8H), 7.45–7.31 (m, 8H), 6.97–6.82 (m, 8H), 4.16 (br, 8H), 3.00 (br, 8H), 1.74 (br, 8H), 1.50 (br, 8H), 1.37–1.21 (m, 144H) 0.67 (br, 8H), 0.43 (br, 8H). A clear $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was not obtained due to mixture of isomers. ^{29}Si NMR (CDCl_3 , ppm): –66.5. HRMS (MALDI) calcd. for $\text{C}_{144}\text{H}_{216}\text{N}_8\text{O}_{20}\text{Si}_8\text{Zn}_4+\text{H}$ $[\text{M}+\text{H}]^+$ 2858.1524, found 2858.1496.

Synthesis of Zn-SPOSS-DMSO

To a DMSO (30 mL) solution of **SPOSS** (0.104 g, 0.0400 mmol) was added a MeOH (10 mL) solution of zinc(II) trifluoromethanesulfonate (0.073 g, 0.200 mmol) followed by NEt₃ (0.056 mL, 0.0400 g, 0.0400 mmol) at 170 °C. The reaction mixture was stirred at 170 °C for 18 h and allowed to cool at room temperature. The precipitate was collected, washed with EtOH, and dried *in vacuo* to afford a yellow solid (61.2 mg, 0.0214 mmol, 53%). ¹H NMR (CDCl₃, ppm): 8.09–8.06 (m, 8H), 7.35–7.32 (m, 8H), 6.87–6.82 (m, 8H), 4.19–4.06 (m, 8H), 3.09–2.97 (m, 8H), 1.76 (br, 8H), 1.50 (br, 8H), 1.31–1.23 (m, 144H), 0.72–0.63 (m, 8H), 0.48–0.39 (m, 8H). ¹³C{¹H} NMR (CDCl₃, ppm): 172.5, 169.0, 141.3, 134.8, 129.5, 116.6, 78.9, 63.1, 35.4, 33.8, 31.3, 29.3, 25.1, 8.5. ²⁹Si NMR (CDCl₃, ppm): –66.5. HRMS (p-APCI) calcd. for C₁₄₄H₂₁₆N₈O₂₀Si₈Zn₄+H [M+H]⁺ 2858.1524, found 2858.1484.

Synthesis of STMDS

To a MeOH/CHCl₃ = 2/1 v/v (75 mL) solution of di-*tert*-butylsalicylaldehyde (2.46 g, 10.5 mmol) was added a MeOH/CHCl₃ = 2/1 v/v (75 mL) solution of 1,3-bis(3-aminopropyl)-tetramethyldisiloxane (1.24 g, 1.38 mL, 5.00 mmol). After stirred at room temperature for 2 h and 70 °C for 6 h, the reaction mixture was allowed to cool at room temperature. The solvent was removed under reduced pressure to afford a yellow oil (2.45 g, 3.60 mmol, 72%). ¹H NMR (CDCl₃, ppm): 14.00 (s, 2H), 8.33 (s, 2H), 7.37 (d, *J* = 2.4 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 2H),

3.54 (t, $J = 6.8$ Hz, 4H), 1.75–1.67 (m, 4H), 1.45 (s, 18H), 1.30 (s, 18H), 0.59–0.55 (m, 4H), 0.06 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 165.6, 158.3, 139.8, 136.7, 126.6, 125.7, 117.9, 62.6, 35.0, 34.1, 31.5, 29.4, 25.0, 15.9, 0.4. ^{29}Si NMR (CDCl_3 , ppm): 7.8. HRMS (p-APCI) calcd. for $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_3\text{Si}_2+\text{H}$ $[\text{M}+\text{H}]^+$ 681.4841, found 681.4838.

Synthesis of Zn-STMDS

To a CH_2Cl_2 (15 mL) and MeOH (15 mL) solution of 1,3-bis(3-aminopropyl)-tetramethyldisiloxane (994 mg, 1.11 mL, 4.00 mmol) was added a CH_2Cl_2 (15 mL) and MeOH (15 mL) solution of di-*tert*-butylsalicylaldehyde (1.88 g, 8.00 mmol). The reaction mixture was stirred at 70 °C for 3 h under a nitrogen atmosphere and allowed to cool at room temperature. To the reacted mixture was added a MeOH (15 mL) solution of zinc(II) trifluoromethanesulfonate (1.60 g, 4.40 mmol), and then DIEA (1.53 mL, 8.80 mmol) was added. After the reaction mixture was stirred at room temperature, the mixture was left on stand for 2 days under a nitrogen flow. The precipitate was collected by filtration, washed with cold EtOH. The collected precipitate was dissolved in MeOH and heated to 65 °C. Insoluble solids were removed by filtration and the solvent was removed under reduced pressure to afford a yellow solid (24.6 mg, 0.033 mmol, 0.82%). ^1H NMR (CDCl_3 , ppm): 8.13 (s, 2H), 7.45 (d, $J = 2.4$ Hz, 2H), 6.97 (d, $J = 2.4$ Hz, 2H), 4.21 (br, 4H), 3.06–3.00 (m, 4H), 1.40 (s, 18H), 1.32 (s, 18H), 0.72–0.64 (m, 4H), 0.10–0.01 (m, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 172.2, 168.9,

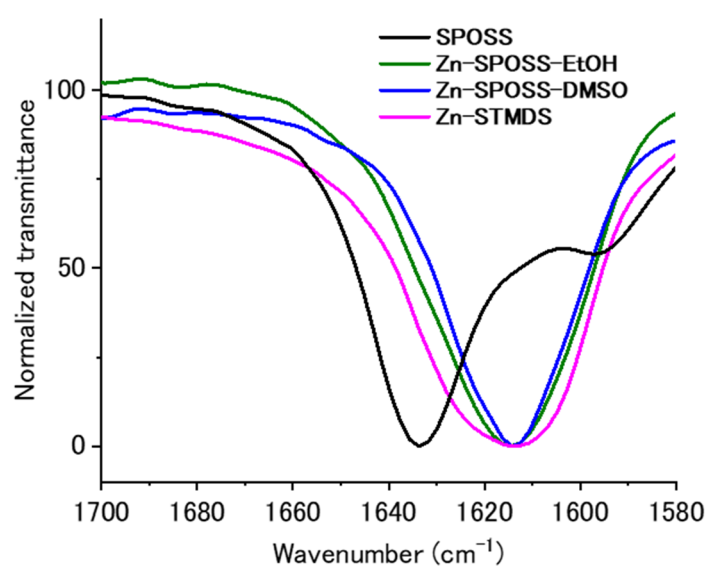
141.4, 134.8, 129.5, 129.4, 116.7, 63.7, 35.6, 33.8, 31.4, 29.4, 24.5, 15.1, 1.0, -0.4. ^{29}Si NMR

(CDCl_3 , ppm): 6.4. HRMS (p-APCI) calcd. for $\text{C}_{40}\text{H}_{66}\text{N}_2\text{O}_3\text{Si}_2\text{Zn}$ $[\text{M}]^+$ 742.3892, found

742.3882.

Table S1. Reaction conditions of complexation with zinc ions to **SPOSS**

Entry	Solvent	Set temp. (°C)		Time (h)	Yield (%)	Compound
1	EtOH/MeOH	rt	93	20	53	Zn-SPOSS-EtOH
2	DMSO/MeOH	170	170	18	53	Zn-SPOSS-DMSO

**Figure S1.** FT-IR spectra of **SPOSS**, **Zn-SPOSS-EtOH**, **Zn-SPOSS-DMSO**, and **Zn-STMDS**.

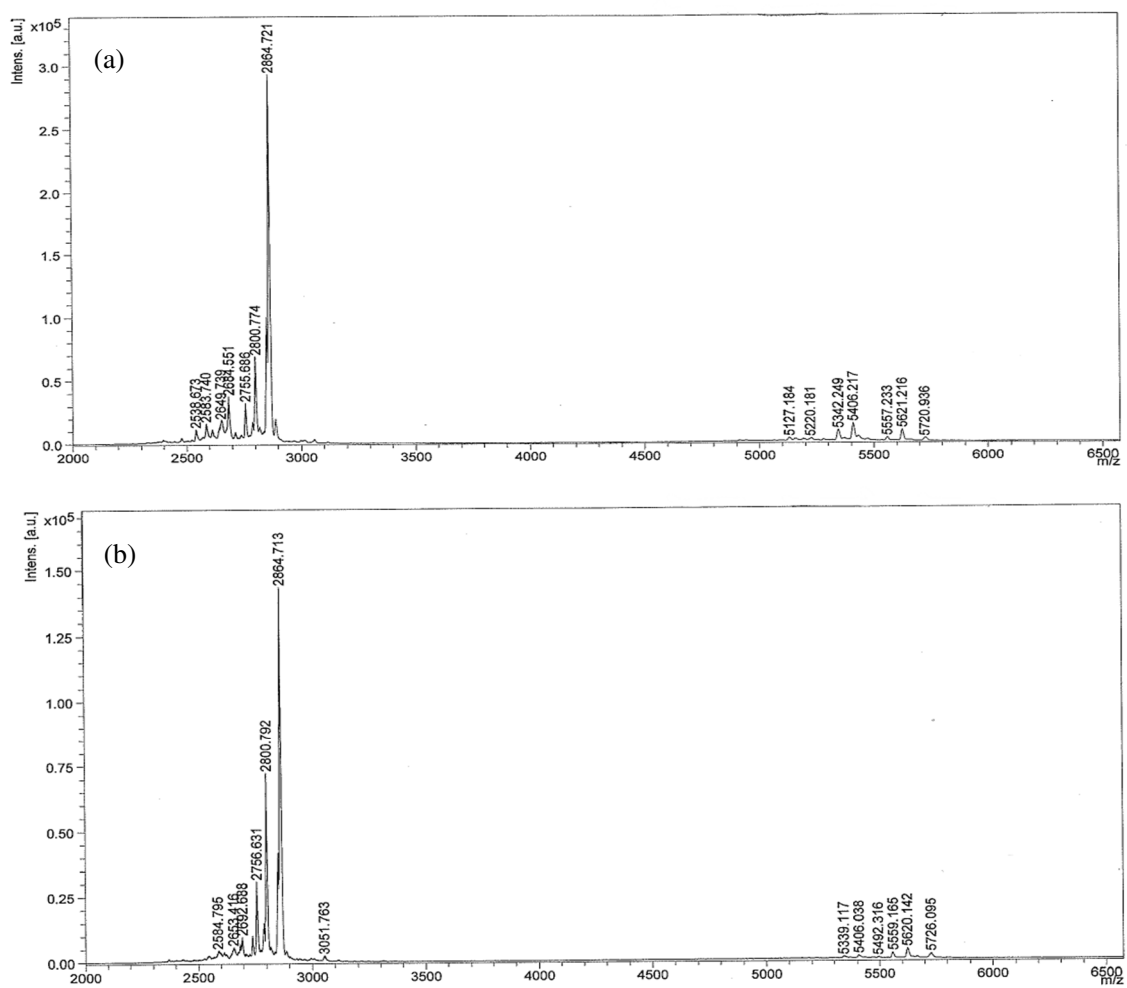


Figure S2. MALDI-TOF-MS spectra of (a) **Zn-SPOSS-EtOH** and (b) **Zn-SPOSS-DMSO**.

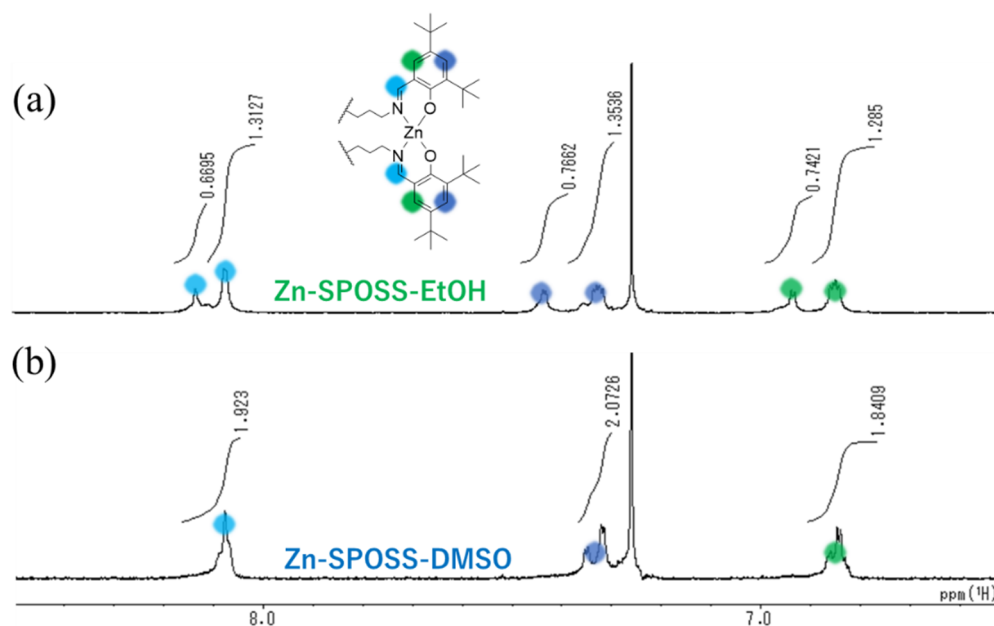


Figure S3. ^1H NMR spectra of (a) **Zn-SPOSS-EtOH** (green) and (b) **Zn-SPOSS-DMSO** (blue) in CDCl_3 in aromatic regions.

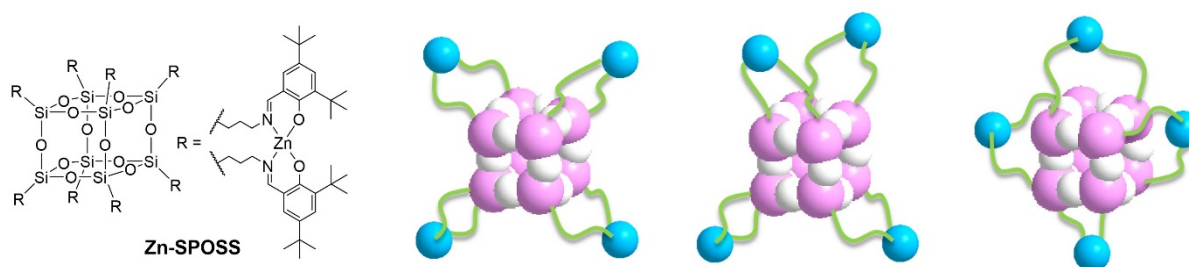


Figure S4. Representative structures of possible isomers of **Zn-SPOSS**.

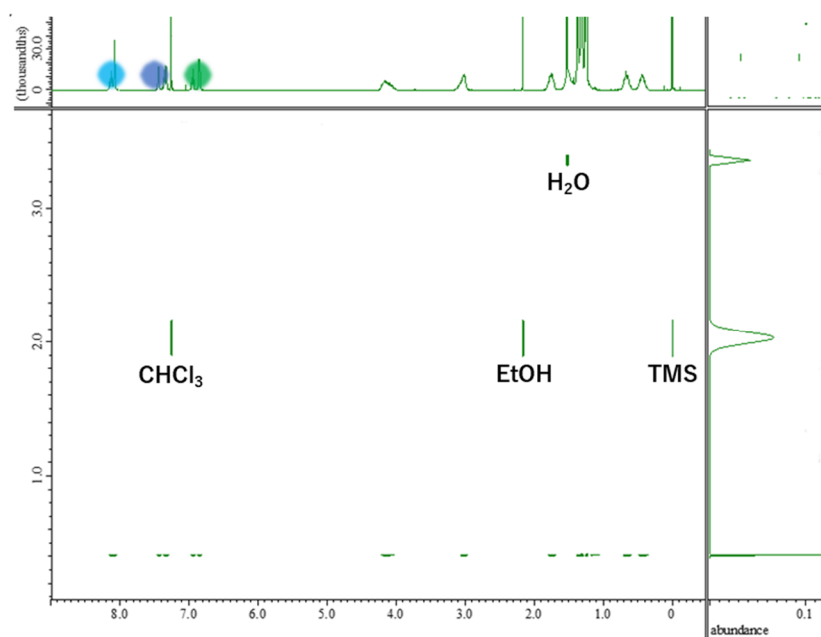


Figure S5. ^1H DOSY spectrum of **Zn-SPOSS-EtOH** (400 MHz, CDCl_3 , 303 K).

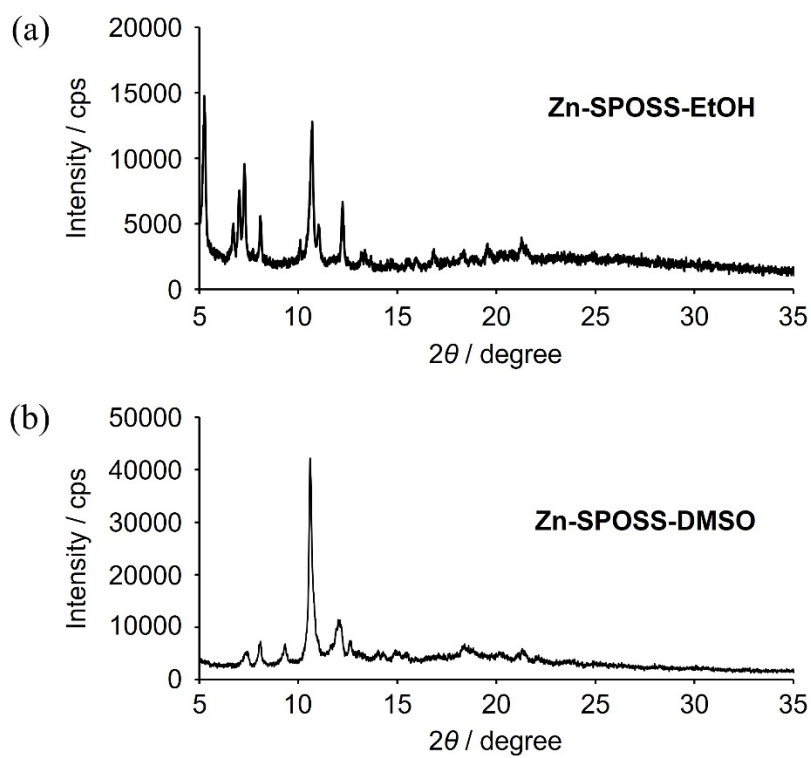


Figure S6. PXRD patterns of (a) **Zn-SPOSS-EtOH** and (b) **Zn-SPOSS-DMSO**.

Table S2. Optical properties of zinc complexes in the solid state

Sample	$\lambda_{\max}^{\text{em } a}$ /nm	τ^b /ns		$\Phi_{\text{PL}}^{a,c}$	k_r^d /s ⁻¹	k_{nr}^d /s ⁻¹
Zn-SPOSS-DMSO	484	1.8	(38%)	0.14	4.1×10^7	2.5×10^8
		4.4	(62%)			
Zn-SPOSS-EtOH	476	0.29	(20%)	0.22	4.1×10^8	6.6×10^8
		1.4	(80%)			
Zn-STMDS	471	0.93	(37%)	0.15	7.1×10^7	4.0×10^8
		2.8	(63%)			

^a Excited at $\lambda_{\max}^{\text{abs}}$. ^b PL lifetime, the numbers in parentheses indicate relative amplitude. ^c Determined as an absolute value. ^d $k_r = \Phi_{\text{PL}}/\tau_{\text{av}}$, $k_{\text{nr}} = (1 - \Phi_{\text{PL}})/\tau_{\text{av}}$, $\tau_{\text{av}} = \sum \alpha_i \tau_i$. α : relative amplitude.

Table S3. Optical properties of zinc complexes in polystyrene^a

Sample	$\lambda_{\max}^{\text{em } b}$ /nm	τ^c /ns		$\Phi_{\text{PL}}^{b,d}$	k_r^e /s ⁻¹	k_{nr}^e /s ⁻¹
Zn-SPOSS-DMSO	469	2.1	(28%)	0.23	4.1×10^7	1.4×10^8
		7	(72%)			
Zn-SPOSS-EtOH	469	2.2	(25%)	0.22	3.7×10^7	1.3×10^8
		7.1	(75%)			
Zn-STMDS	463	0.95	(9%)	0.56	8.4×10^7	6.6×10^8
		7.2	(91%)			

^a Spin coated film: in CHCl₃, 150 μ L, 2000 rpm, 30 s. ^b Excited at $\lambda_{\max}^{\text{abs}}$. ^c PL lifetime, the numbers in parentheses indicate relative amplitude. ^d Determined as an absolute value. ^e $k_r = \Phi_{\text{PL}}/\tau_{\text{av}}$, $k_{\text{nr}} = (1 - \Phi_{\text{PL}})/\tau_{\text{av}}$, $\tau_{\text{av}} = \sum \alpha_i \tau_i$. α : relative amplitude.

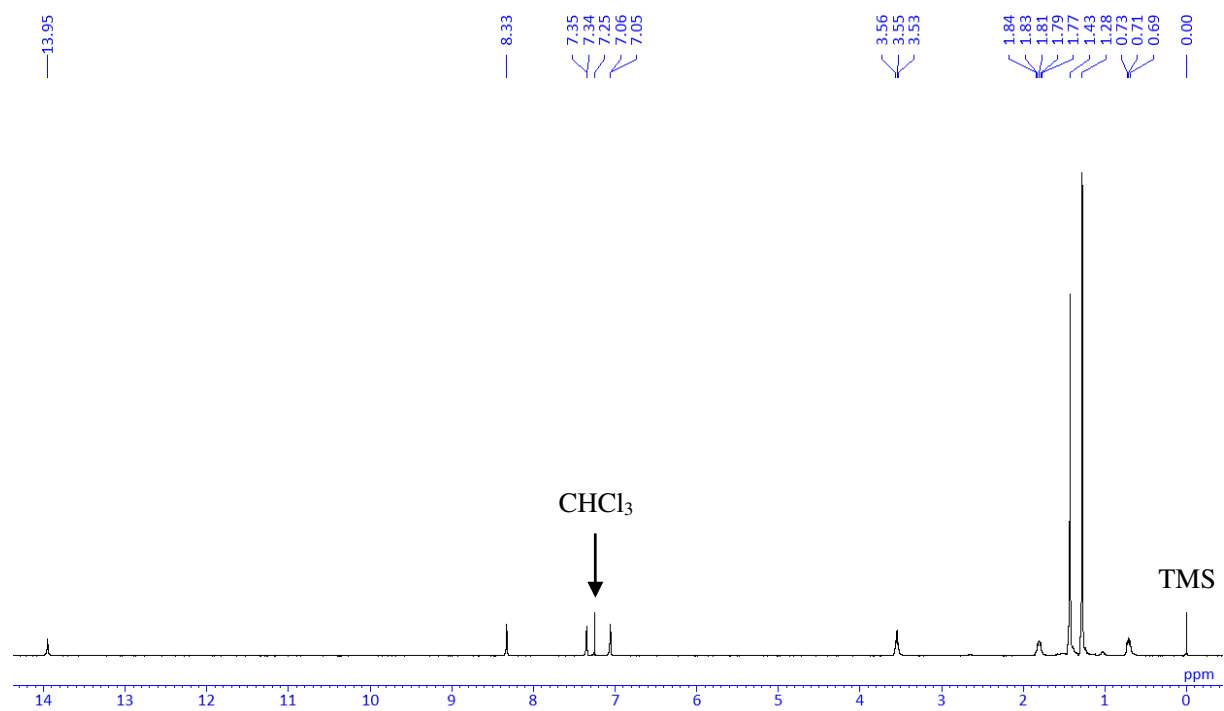


Chart S1. ¹H NMR spectrum of **SPOSS** in CDCl₃.

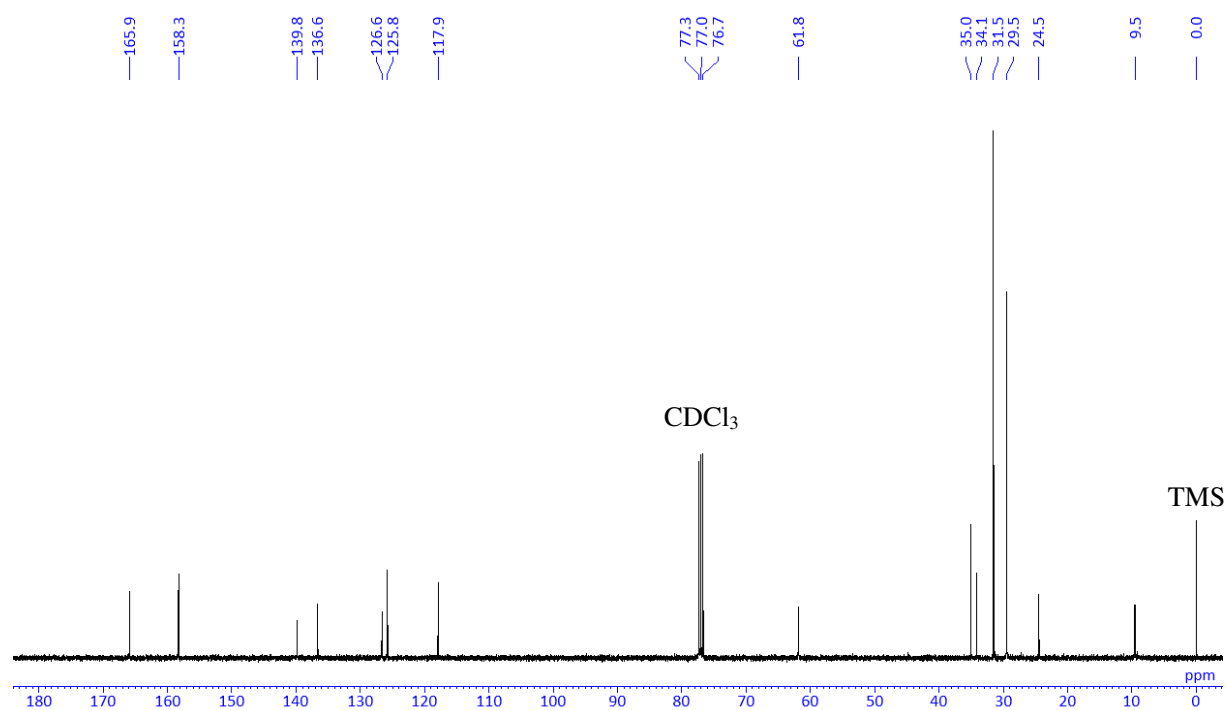


Chart S2. ¹³C{¹H} NMR spectrum of **SPOSS** in CDCl₃.

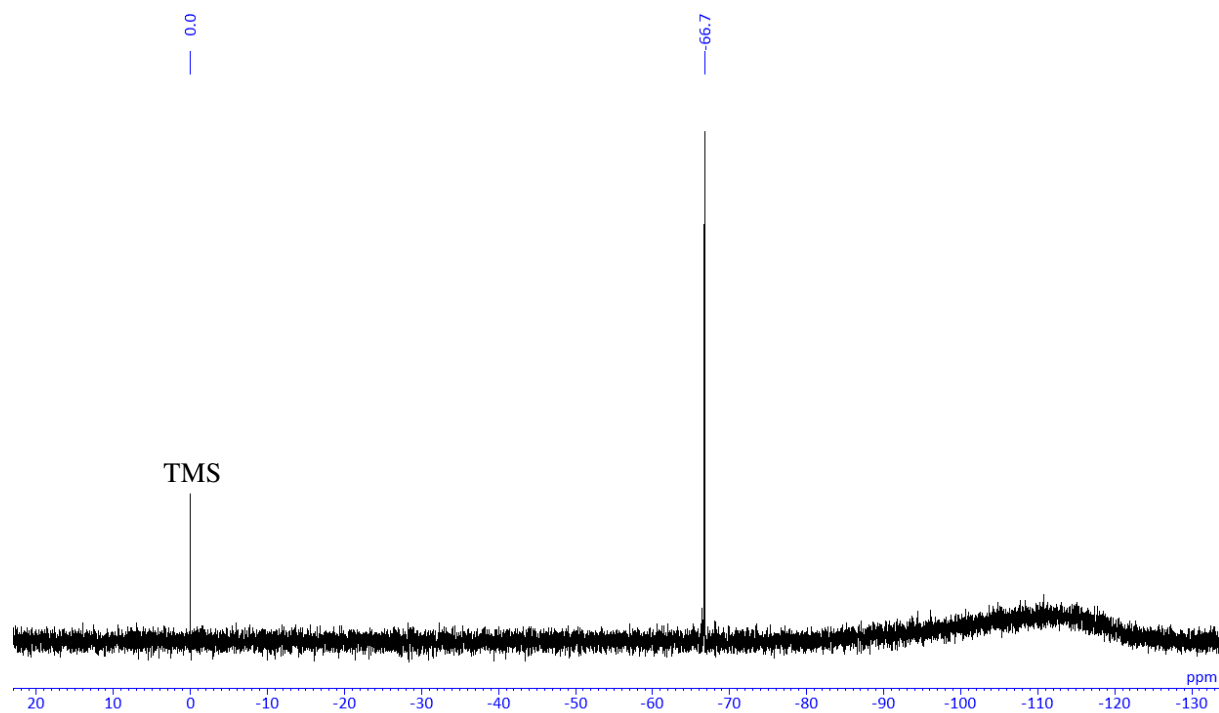


Chart S3. ^{29}Si NMR spectrum of **SPOSS** in CDCl_3 .

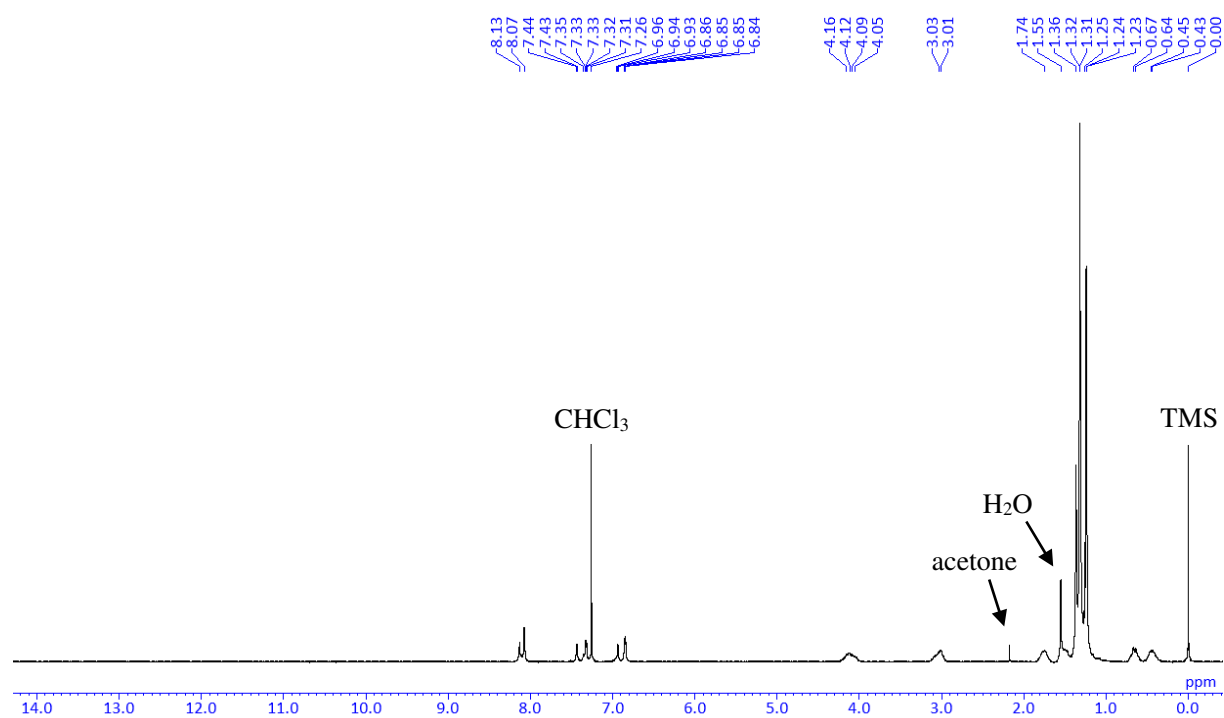


Chart S4. ^1H NMR spectrum of **Zn-SPOSS-EtOH** in CDCl_3 .

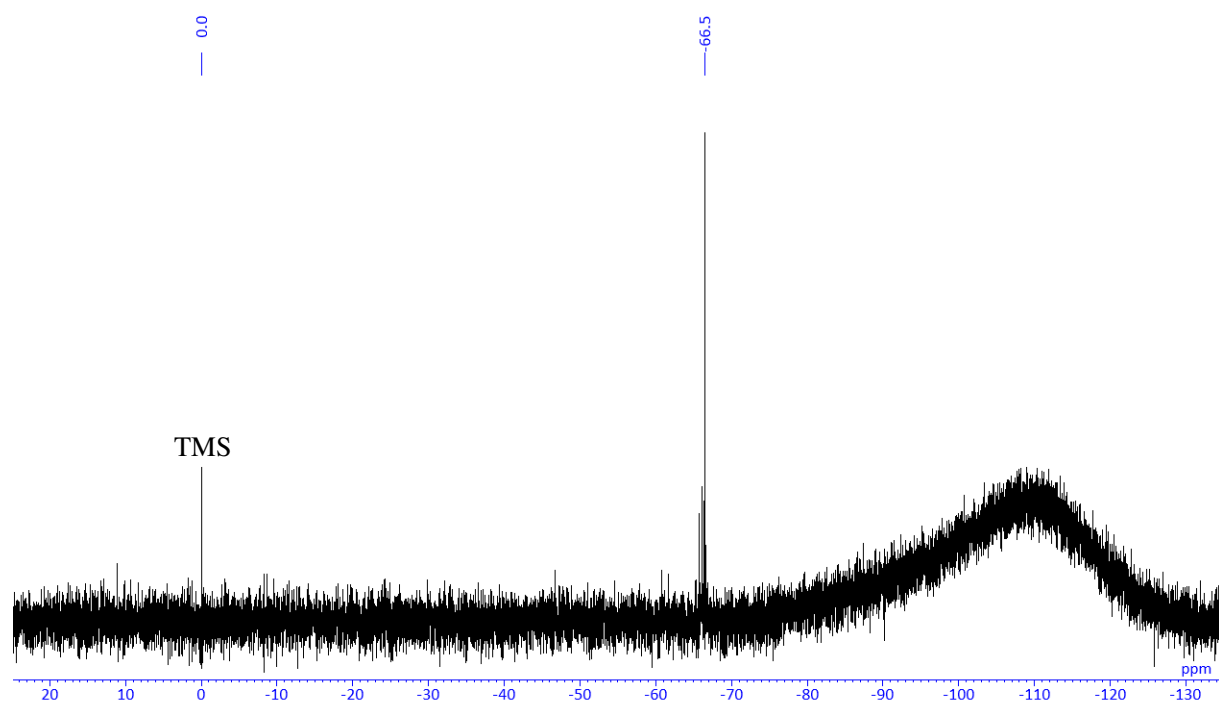


Chart S5. ^{29}Si NMR spectrum of **Zn-SPOSS-EtOH** in CDCl_3 .

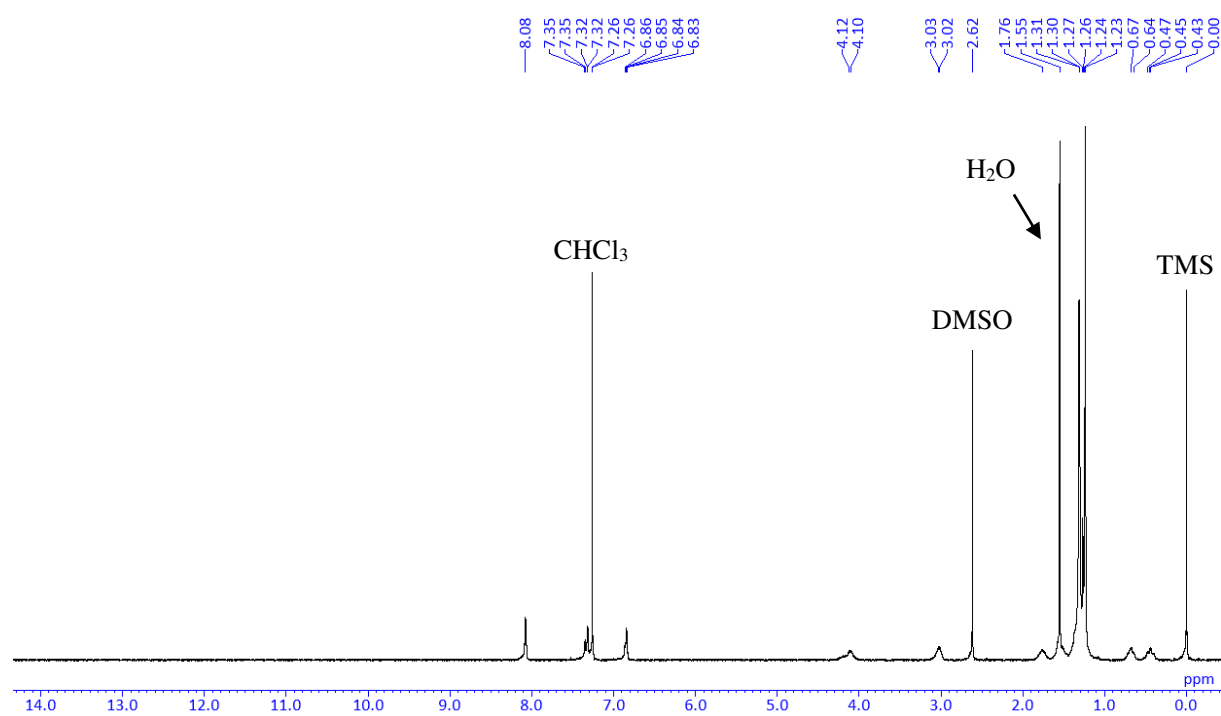


Chart S6. ^1H NMR spectrum of **Zn-SPOSS-DMSO** in CDCl_3 .

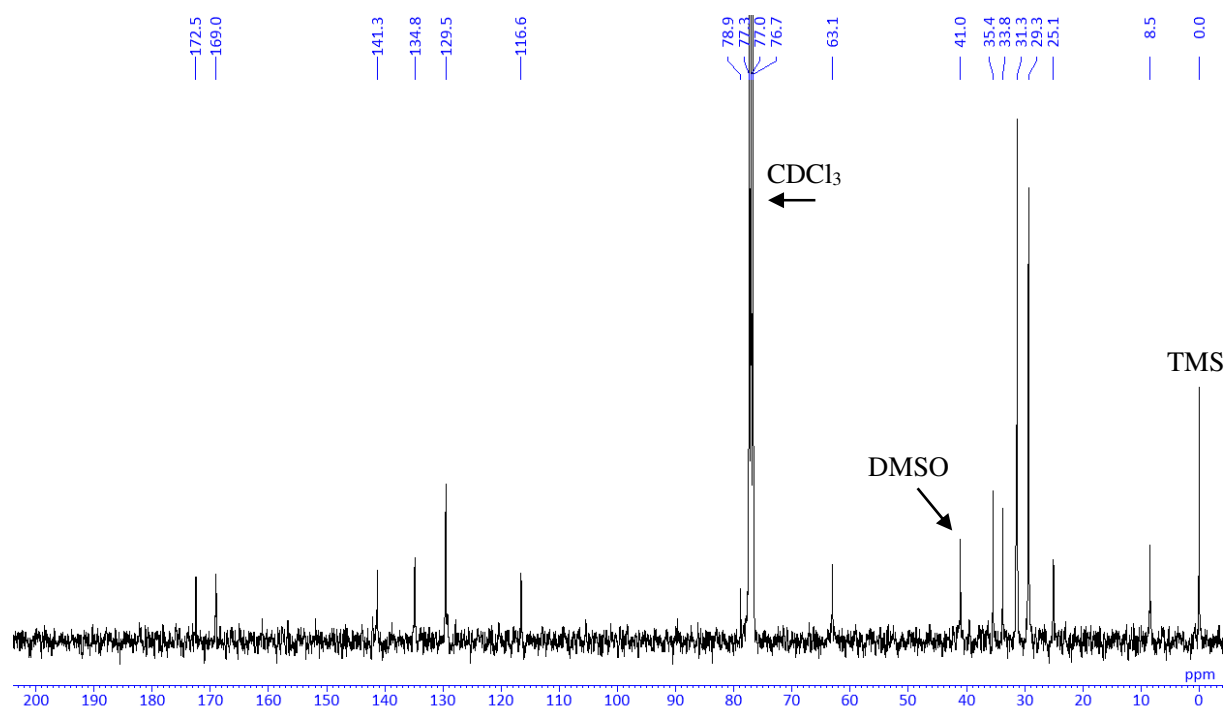


Chart S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Zn-SPOSS-DMSO** in CDCl_3 .

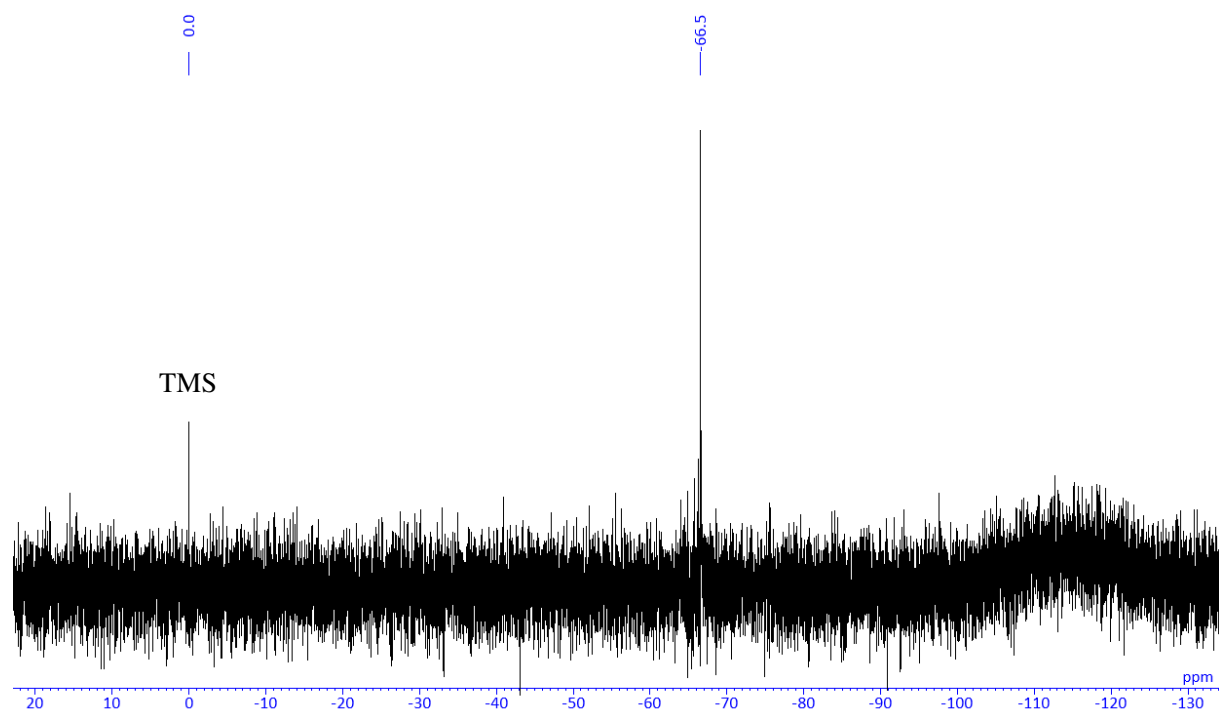


Chart S8. ^{29}Si NMR spectrum of **Zn-SPOSS-DMSO** in CDCl_3 .

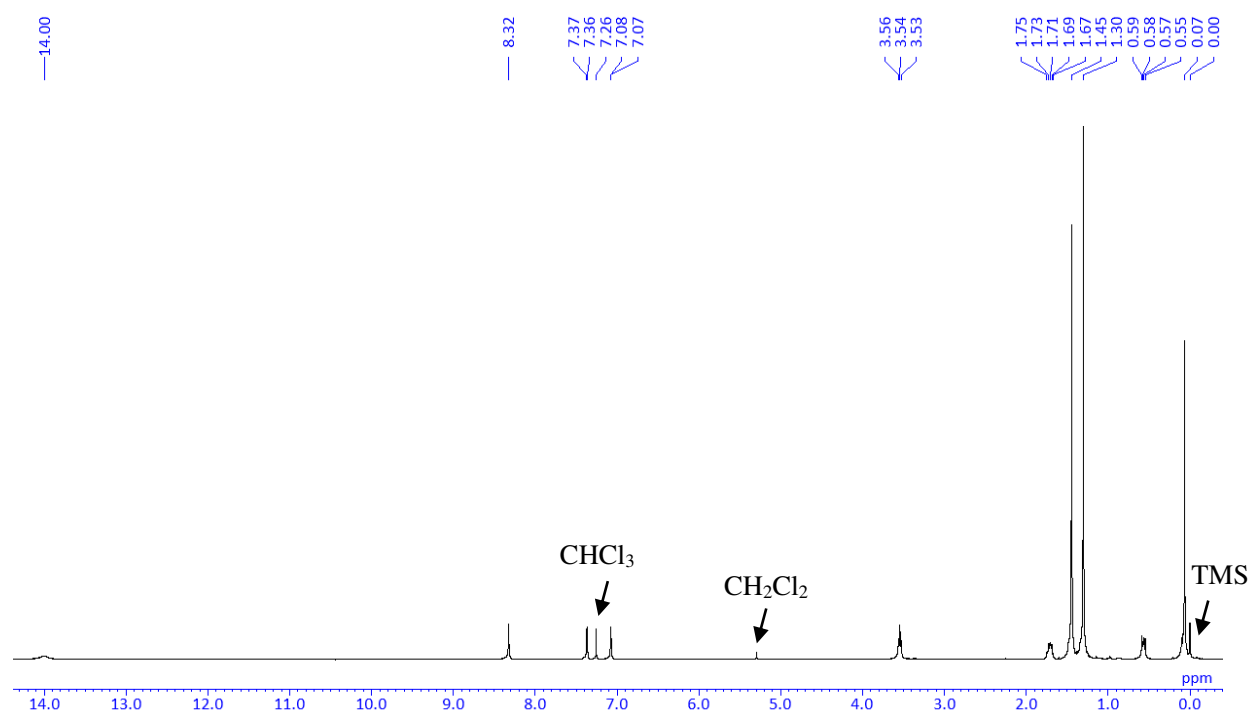


Chart S9. ¹H NMR spectrum of **STMDS** in CDCl₃.

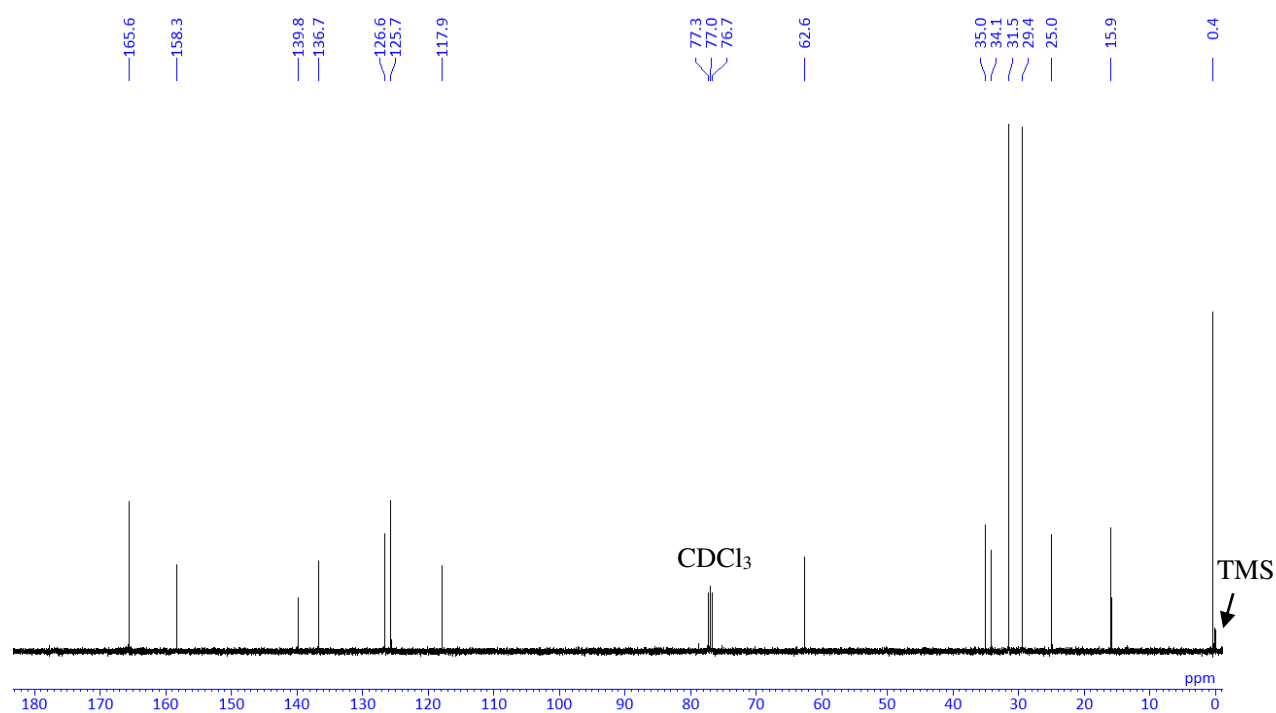


Chart S10. ¹³C{¹H} NMR spectrum of **STMDS** in CDCl₃.

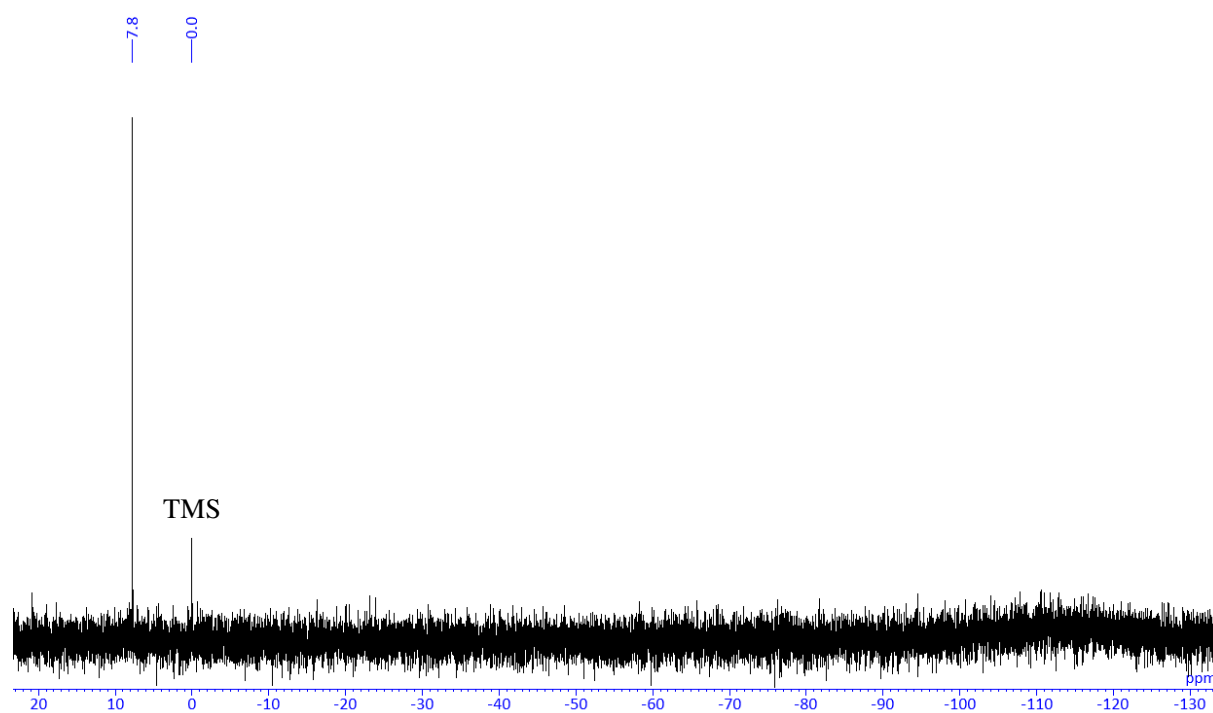


Chart S11. ^{29}Si NMR spectrum of **STMDS** in CDCl_3 .

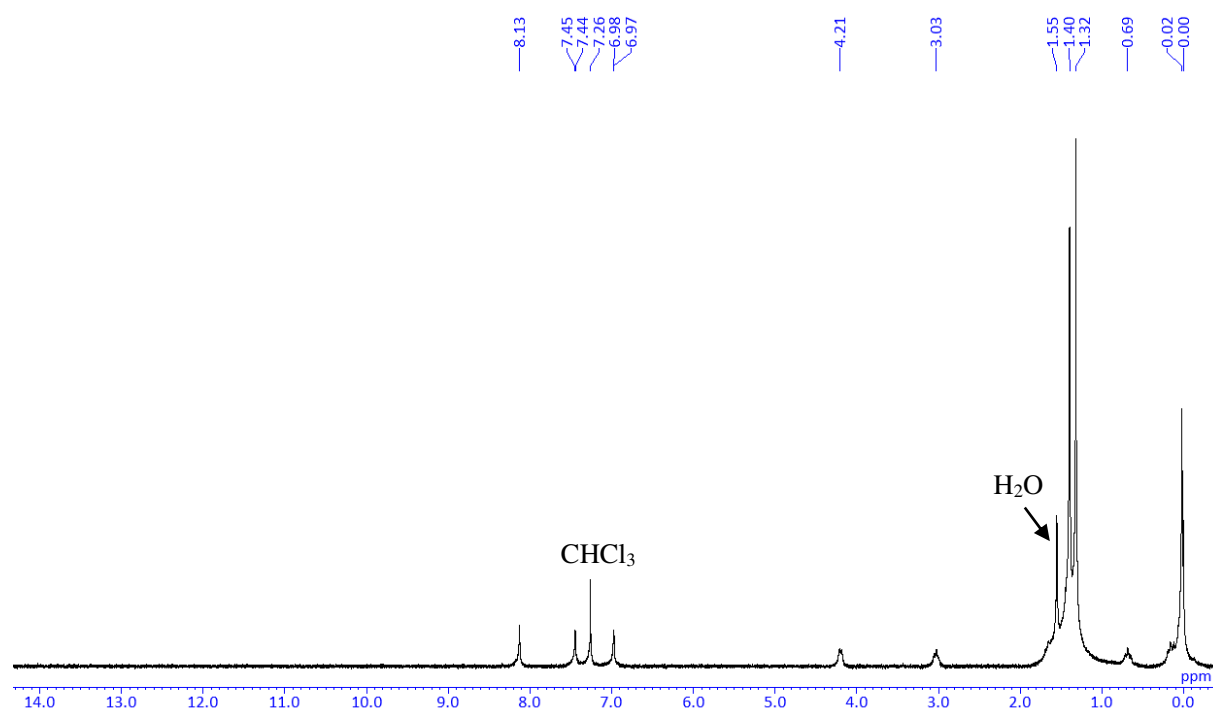


Chart S12. ^1H NMR spectrum of **Zn-STMDS** in CDCl_3 .

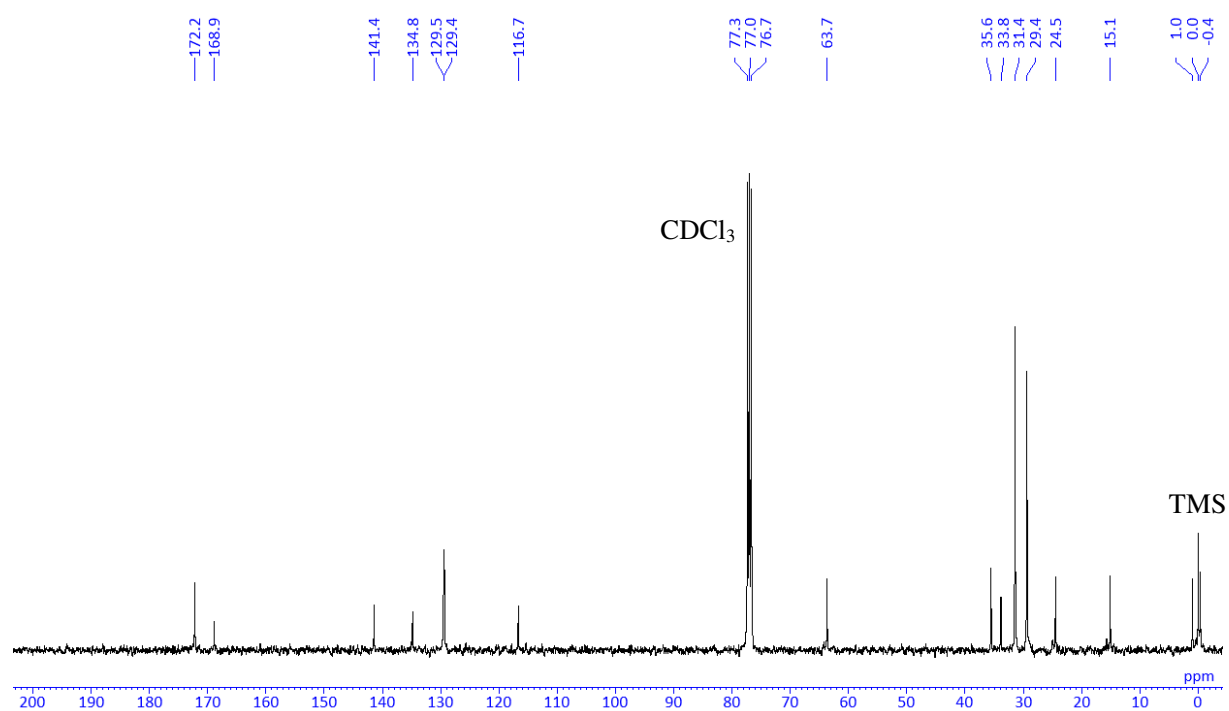


Chart S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Zn-STMDS** in CDCl_3 .

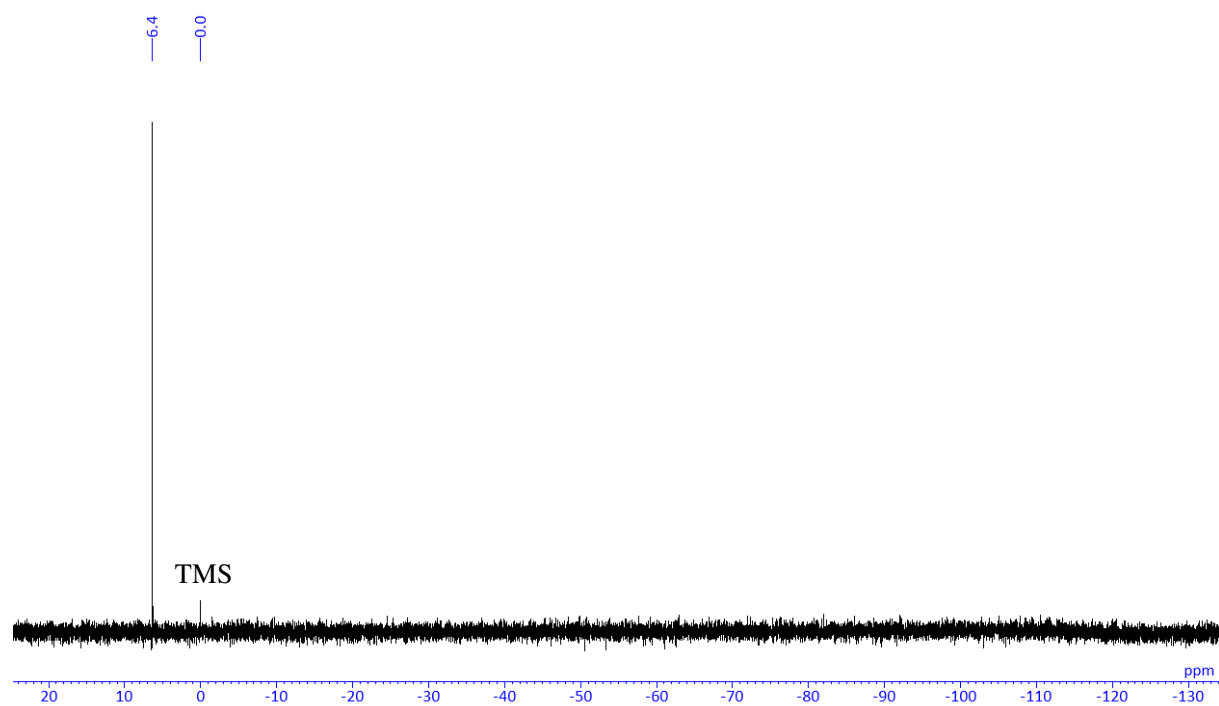


Chart S14. ^{29}Si NMR spectrum of **Zn-STMDS** in CDCl_3 .

Reference

1. K. Tanaka, K. Inafuku, S. Adachi, Y. Chujo, *Macromolecules* **2009**, *42*, 3489–3492.