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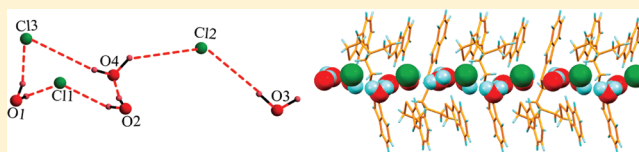
Cyclic Pentameric Puckered Hybrid Chloride–Water Cluster $[\text{Cl}_3(\text{H}_2\text{O})_4]^{3-}$ in the Hydrophobic Architecture

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S Supporting Information

ABSTRACT: A well isolated unique discrete chloride–water cluster $[\text{Cl}_3(\text{H}_2\text{O})_4]^{3-}$ having a cyclic pentamer $[\text{Cl}_2(\text{H}_2\text{O})_3]$ of half chair conformation in the metal free benzimidazole based tripodal podant purely organic hydrophobic architecture has been investigated structurally in the solid state. The bowl shape and imidazole NH of the tripodal host offer a suitable place and binding site, favoring the formation of the chloride–water cluster. The dichloride pentamer deliberately forms a heteroatomic water–cluster channel by using its tail, consisting of one chloride and one oxygen atom in the hydrophobic framework along the crystallographic *b* axis.



There has been a recent upsurge of publications regarding the theoretical¹ and experimental² aspects of water–water interactions in the water cluster both in solid and solution phase molecules because the serious attention of scientists is needed to determine its structure and characteristics. Insight into the details of the interaction could show us the nature of the water–water interaction in the atmosphere, earth, ocean, and biological systems. The detailed understanding of water molecule within the confined hydrophobic cavity remains a challenge.³ Arduous work has been done to discover the anomalous behavior of the water molecule in stabilization and functioning of biomolecules.⁴ The *in vitro* study of the water cluster will help us to understand the biological implications of a water cluster in the folding, function, and activity of proteins⁵ through hydrogen bonding and hydrophobic interactions.⁶ At the molecular level there are several types of water cluster emanated starting from dimers,⁷ trimers,⁸ tetramers,⁹ pentamers,¹⁰ hexamers,¹¹ heptamers,¹² octamers,¹³ nonamers,¹⁴ decamers,¹⁵ undecamers,¹⁶ dodecamers,¹⁷ or even greater¹⁸ in various organic environments¹⁹ and metal mediated hosts, owing to the coordination tendency of water to metal. Therefore, elucidation of the H-bonding pattern in several surroundings is important. There are a minuscule number of known cyclic water clusters containing inorganic ions such as $[(\text{NO}_3)_6(\text{H}_2\text{O})_6]^{6-}$,²⁰ $[(\text{NO}_3)_4(\text{H}_2\text{O})_6]^{4-}$,²¹ $[\text{F}_2(\text{H}_2\text{O})_6]^{2-}$,²² $[\text{Cl}(\text{H}_2\text{O})_4]^{2-}$,²³ $[\text{Cl}(\text{H}_2\text{O})_3]^{-}$,²⁴ $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$,²⁵ $[\text{Br}_2(\text{H}_2\text{O})_6]^{2-}$,²⁶ and $[\text{NH}_2(\text{H}_2\text{O})_4]^{-}$,²⁷ and up to date chloride–water clusters in a purely organic environment are very rare.^{28,16a} But immense exploration of inorganic ions in chemical and natural processes has been accepted unanimously.^{29–31} So it is very necessary to acquire knowledge about heteroatomic water chemistry to get relief from the maze and enigma of anion water clusters. Interaction between the water cluster and surrounding ions or host molecules plays a vital role in the nucleation and growth of a molecular crystal. So engrafting a water cluster in a less polar chemical environment is quintessential. Theoretical study³² of a chloride–water

cluster provides valuable information about the binding energy, solvent electrostatic stabilization energy, and coordination environment of hydrated chloride ions.

Herein, we have reported the isolated water chloride cluster $[\text{Cl}_3(\text{H}_2\text{O})_4]^{3-}$, having a cyclic pentameric unit $[\text{Cl}_2(\text{H}_2\text{O})_3]$ in a tripodal podant scaffold based flexible organic molecular framework LH_3^{3+} as counteranion. The thermal stability of the chloride water cluster was verified by TGA and DSC experiments. Additionally, the formation of the chloride water cluster in solution was also confirmed by ¹H NMR titration experiments.

The acyclic benzimidazole based tripodal podant host **L** has been prepared in good yield by modification of our recent literature procedure.³³ The chloride–water cluster has been prepared successfully by adding dropwise excess hydrochloric acid to a methanol–water (2:1) solution of **L**. Slow evaporation of this mixture gives block shaped colorless crystals within 1–2 weeks with the composition $\text{LH}_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$, as indicated by X-ray diffraction, TGA, DSC, and NMR. Single crystal X-ray diffraction analysis^{34–35} showed that the complex crystallizes in the monoclinic space group $P2_1/c$ with a $Z = 4$ asymmetric unit of the structure. A structural view of $\text{LH}_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ and an atom labeling scheme is shown in Figure 1a. The packing diagram of the complex shows the formation of a heteroatomic chloride–water cluster between the protonated hosts in a channel along the *b*-axis (Figure 1b).

The tripodal receptor is bowl shaped and has a hydrogen bond acceptor benzimidazole group exposed to the outside to form a strong hydrogen bond complex with anion or solvent molecules. After addition of acid, the imidazole nitrogen became protonated and made two imidazole nitrogen equivalents that offer suitable binding sites for those

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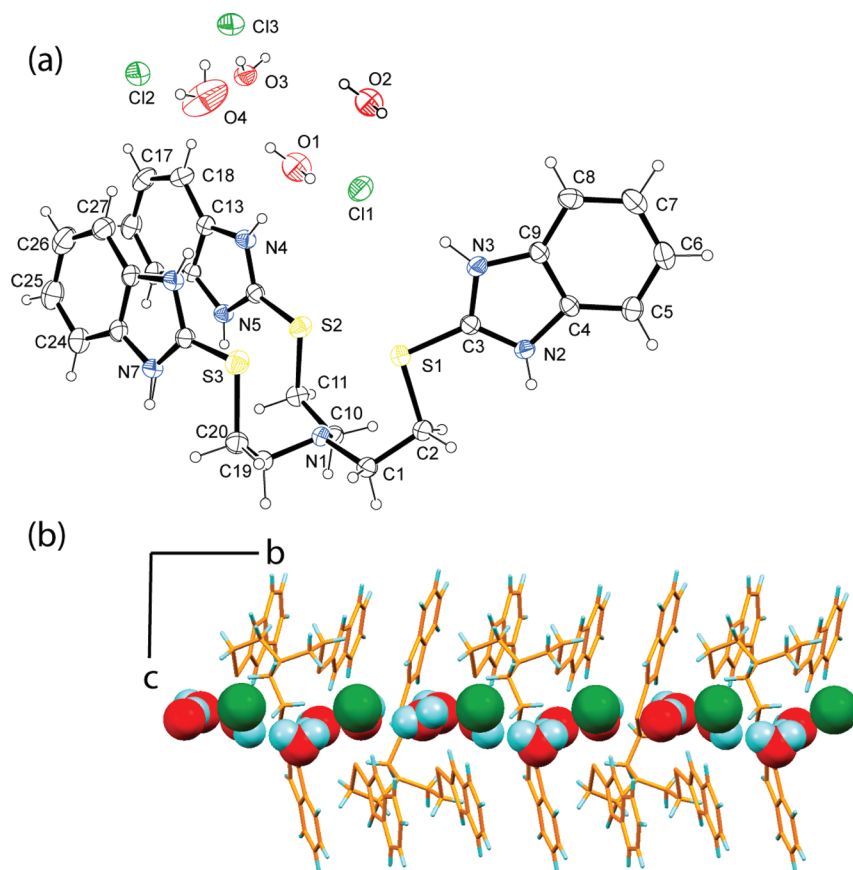


Figure 1. (a) ORTEP diagram of $\text{LH}_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ with atom labeling having a 30% thermal ellipsoid. Symmetry codes: (I) X, Y, Z identical operation. (II) $-X, \frac{1}{2} + Y, \frac{1}{2} - Z$ 2-fold screw axis; (III) $-X, -Y, -Z$ inversion center; (IV) $X, \frac{1}{2} - Y, \frac{1}{2} + Z$ glide plane. (b) Crystal packing of $\text{LH}_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ exhibiting chloride–water channels propagating through the hydrophobic channel created by the organic host.

heteroatoms. A flexible cationic tripodal receptor provides the required platform to host a chloride–water cluster. The chloride–water cluster along with a proper atom labeling scheme is shown in Figure 2a. Each pentameric cluster, consisting of two chloride and three water molecules, is connected to the next pentamer unit by the tail, having one chloride and one water molecule. The tail is a linker between two puckered heteroatomic chloride–water clusters (Figure

2b). Pentameric cluster consisting of two chloride ion and three water molecules formed cyclopentane like half chair structure. Any three atoms in the pentamer lie in the same plane, while the other two are above the plane. The chloride–water cluster is packed between two hydrophobic layers in a zigzag fashion. These clusters in the adjacent layers are arranged in an *anti*-fashion (Figure 2b).

Three different chloride anions are strongly held in the lattice through several $\text{O} \cdots \text{H} \cdots \text{Cl}$ and $\text{N} \cdots \text{H} \cdots \text{Cl}$ hydrogen bonds. As depicted in Figure 3, Cl1 is held between nearby water molecules [$\text{O1} \cdots \text{H10} \cdots \text{Cl1} = 3.183(5) \text{ \AA}$ and $\text{O2} \cdots \text{H30} \cdots \text{Cl1} = 3.150(6) \text{ \AA}$] and the imidazole $\text{N} \cdots \text{H}$ of the tripodal ligand [$\text{N3} \cdots \text{H3N} \cdots \text{Cl1} = 3.098(7) \text{ \AA}$]. Similar hydrogen bonding is observed for Cl2 also [$\text{O3} \cdots \text{H50} \cdots \text{Cl2} = 3.275(6) \text{ \AA}$, $\text{O4} \cdots \text{H80} \cdots \text{Cl2} = 3.070(1) \text{ \AA}$, and $\text{N5} \cdots \text{H5N} \cdots \text{Cl2} = 3.120(6) \text{ \AA}$]. However, Cl3 is connected to four such strong hydrogen bonds [$\text{O1} \cdots \text{H20} \cdots \text{Cl3} = 3.210(6) \text{ \AA}$, $\text{O3} \cdots \text{H60} \cdots \text{Cl3} = 3.212(6) \text{ \AA}$, $\text{O4} \cdots \text{H70} \cdots \text{Cl3} = 3.190(1) \text{ \AA}$, and $\text{N7} \cdots \text{H9N} \cdots \text{Cl3} = 3.164(6) \text{ \AA}$]. The $\text{Cl} \cdots \text{O}$ separations are smaller than those previously reported for $\text{Cl}(\text{H}_2\text{O})_4$ ²³ and $\text{Cl}_2(\text{H}_2\text{O})_6$.^{25a} The suitable bond angle distribution among different atoms in a cyclic pentamer makes any three atoms, e.g. $\text{O1} \cdots \text{Cl1} \cdots \text{O2}$, in the same plane like the half chair conformation of cyclopentane with the exception that the remaining two atoms are out of the plane. In this hybrid chloride water cluster, one oxygen atom of the pentameric unit (O4) does not interact with any imidazole $\text{N} \cdots \text{H}$ of the tripodal ligand and offers a $\text{O2} \cdots \text{H4O} \cdots \text{O4}$ strong interaction in the chloride water cluster of bond length $1.910(1) \text{ \AA}$ and bond angle $\text{O2} \cdots \text{H4O} \cdots \text{O4} 168.1(5)^\circ$. The

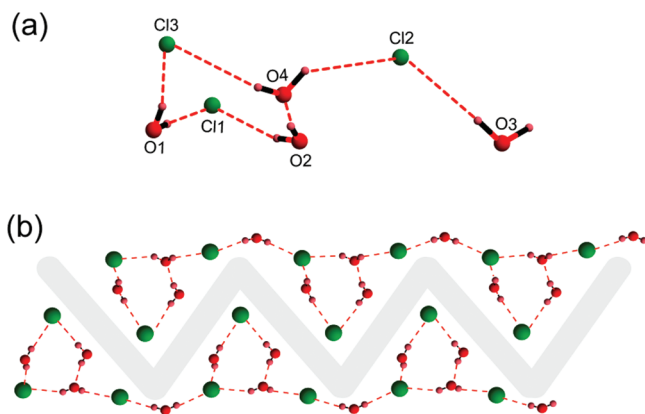


Figure 2. (a) Chloride–water pentamer $[(\text{H}_2\text{O})_3\text{Cl}_2]$ in $\text{LH}_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$, having a half chair conformation with a tail of chloride and oxygen. (b) Crystal packing of the pentameric unit along the a axis in a zigzag fashion, where the pentamer between two layers is oriented in an *anti*-fashion.

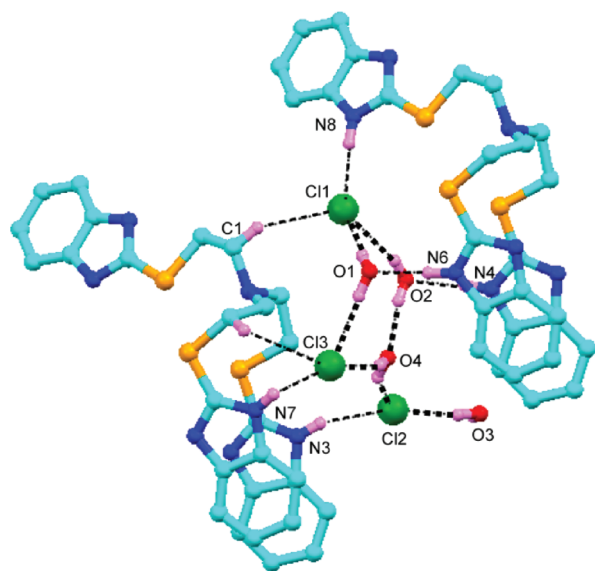


Figure 3. Coordination environments of different chloride ions in the crystal. Selected bond distances (Å) and angles (deg): Cl1...N3 = 3.098(7) and Cl1-H3N-N3 = 175.0(4), Cl1...C1 = 3.758(7), Cl...O2 = 3.150(6) and O2-Cl1-O1 = 70.5(1), O2...O4 = 2.680(1), O2...N4 = 2.712(7) and O2-H4O-O4 = 168.1(5)°, O1...N6 = 2.716(7) and O1-H6N-N6 = 174.1(4), Cl3...N7 = 3.164(6) and Cl3-H9N-N7 = 166.0(4), Cl3...C20 = 3.667(6), Cl2...N5 = 3.120(6) and Cl2-H5N-N5 = 160.0(4). Hydrogen atoms, except those participating in weak interactions, are omitted for clarity.

O...O separation is 2.68 Å stronger, which is stronger than previously reported for $\text{Cl}(\text{H}_2\text{O})_4^{23}$ and $(\text{H}_2\text{O})_5^{10}$. All the water molecules form strong hydrogen bonds with imidazole N-H and chloride anions [$\text{O1}\cdots\text{H6N-N6} = 1.848(5)$ Å, $\text{O2}\cdots\text{H4N-N4} = 1.870(5)$ Å, and $\text{O3}\cdots\text{H2N-N2} = 1.970(5)$ Å]. The bond distance between O...N is comparable with that of the known amide water pentamer.²⁷ The strength of several H-bonds is also confirmed by thermal analysis. There are three aromatic moieties in one unit offering three different π - π interactions: one is an intramolecular interaction with a distance of 3.739 Å (see Supporting Information), and another two π - π interactions are intermolecular type between adjacent moieties with a distance of 3.902 Å and 3.859 Å.

The thermal stability of the complex was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA curve shows two consecutive weight losses (see Supporting Information). The first weight loss of 8.9% (9.9%) at ~ 140 °C suggests the loss of four water molecules from the lattice. This temperature is well above 100 °C, which indicates the strong hydrogen bonding participation between the water cluster and the host molecules in the crystal lattice. After losing a crystalline water molecule, the dehydrated complex appears to be stable up to ~ 230 °C and decomposition starts after this temperature. The complete decomposition of the dehydrated complex occurs at ~ 400 °C. Both DSC and cyclic DSC curves show the exothermic peak at ~ 130 °C, corresponding to loss of a water molecule, and the endothermic peak at around 160 °C defines the melting of the dehydrated complex. Very interestingly, the cyclic DSC plot

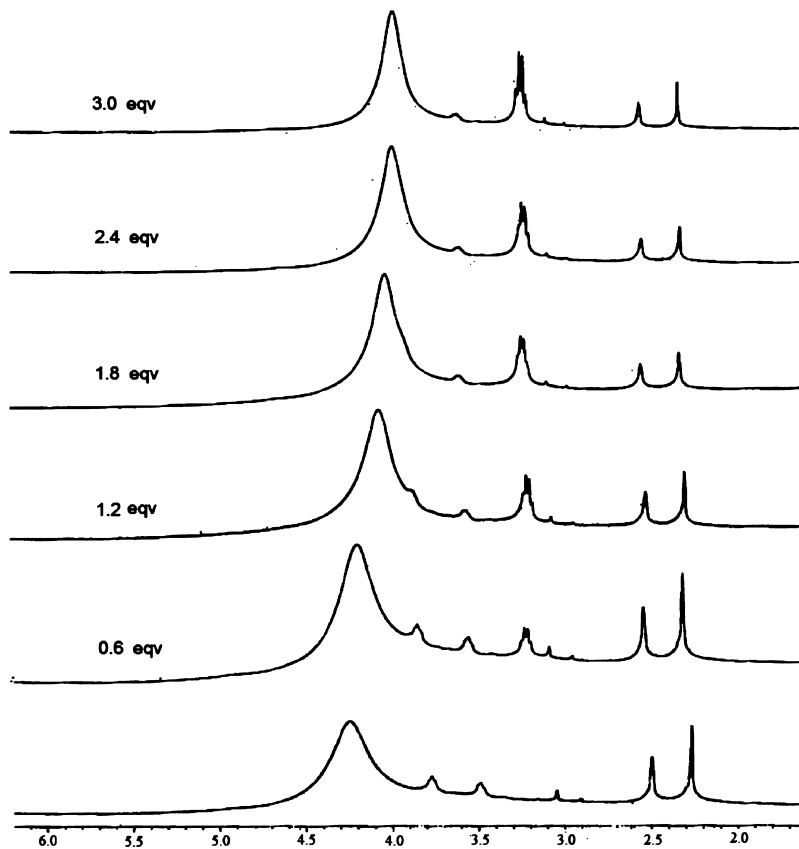


Figure 4. ^1H NMR spectra of the tosylated salt of L (2 mM) with increasing amount of TEACl (10 mM) in d_6 -DMSO showing the significant change of the water peak.

shows that with loss of temperature the melted liquid complex returned to its solid form, and this reconfirmed that the dehydrated complex is stable to 230 °C.

The vibrational stretching frequency of the O–H bond pertaining to the chloride–water cluster has been characterized by FT-IR spectroscopy (see Supporting Information). A broad peak at 3425 cm⁻¹ (refs 2e, 16a, and 19c) is attributed to the water cluster present in LH₃Cl₃·4H₂O. This peak is absent in the IR spectra of pure tripodal ligand **L**. We treated the chloride–water cluster complex with inorganic base such as NaOH and purified the product. The IR spectrum of the product was virtually superimposable with IR spectrum of **L**. The disappearance of the O–H bond after treating base clearly suggests the presence of a water cluster in the crystal lattice. After exposing the tripodal ligand in water vapor, no gain of water molecule in the crystal lattice was observed. The simulated PXRD pattern of the chloride–water cluster essentially matches with the experimental PXRD pattern. This suggests the chloride–water cluster is present in a massive amount.

In ¹H NMR spectroscopy, the ligand **L** shows a chemical shift of –NH appearing at 12.522 ppm (see Supporting Information). However, for the case of a chloride cluster there is no peak in that region; rather, it appears at 5.076 ppm (see Supporting Information) along with the water peak. To investigate the formation of the chloride–water cluster in the solution state, a ¹H NMR titration in *d*₆-DMSO at 298 K has been carried out with tetraethyl ammonium chloride (TEACl) with the tosylate salt of **L** (Figure 4), because tosylate is a bulky anion with a lower charge density and does not interfere with the binding of other strong hydrogen bond acceptor anions.³⁶ Upon gradual addition of TEACl, a significant upfield chemical shift ($\Delta\delta = 0.327$ ppm) of the water peak occurs that is continued up to 3 equiv of chloride. This is attributed to the strong H-bonding interaction between water and chloride anions, which subsequently leads to the formation of a chloride–water cluster in solution, which has already been confirmed in the solid crystal structure. Moreover, the only shift of the water peak during ¹H NMR titration precludes determination of a proper binding constant with chloride anion.

In summary, we have crystallographically characterized the novel discrete chloride–water cluster [Cl₃(H₂O)₄]³⁻, having the half chair like pentameric unit [Cl₂(H₂O)₃]. This chloride–water cluster has been trapped by a benzimidazole based tripodal hydrophobic host. Our observations underscore the conformationally flexible tripodal ligand that arranged (pre-organized) in a particular way and made a bowl shape to build up the chloride–water cluster, which subsequently formed the water cluster channel in the solid state along the crystallographic *b* axis. The formation of a chloride–water cluster in solution was also confirmed by ¹H NMR titration experiments. The thermal analysis suggests the removal of water took place at above 130 °C, which shows the H-bonding that builds the chloride–water cluster is strongly incorporated as a part of this cluster. These findings will provide new insight into the heteroatomic water cluster chemistry.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed synthesis of **L** and the chloride complex, full crystallographic data for the complex, and IR, NMR, PXRD data, and cif data of the crystal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (34) Crystallographic data and structure refinement parameters of $\text{LH}_3\text{Cl}_3\cdot 4\text{H}_2\text{O}$: FW = $\text{C}_{27}\text{H}_{38}\text{Cl}_3\text{N}_7\text{O}_4\text{S}_3$, $M = 727.20$, monoclinic, space group $P2_1/c$, $a = 9.9647(2)$ Å, $b = 11.1184(3)$ Å, $c = 31.7620(8)$ Å, $\alpha = 90.00^\circ$, $\beta = 103.5680(10)^\circ$, $\gamma = 90.00^\circ$, $V = 3420.75(14)$ Å³, $Z = 4$, $\rho(\text{cal}) = 1.412$ g/cm³, $\mu(\text{Mo K}\alpha) = 0.71073$ mm⁻¹, $T = 298(2)$ K, R_1 ; wR_2 ($I > 2\sigma(I)$) = 0.0339; 0.0497, R_1 ; $wR_2(\text{all}) = 0.0452$; 0.0508, residual electron density = 0.402/−0.354 (e/Å³), GOF = 0.921, reflection collected = 5848, independent reflection = 4763, CCDC No. = 836926.
- (35) Characterization of L and synthesized compounds: L. ¹H NMR (400 MHz, d_6 -DMSO) δ (ppm): 12.52 (s, N–H), 7.40 (m, Ar), 3.46 (t, NCH₂), 3.10 (t, SCH₂). ¹³C NMR (100 MHz, d_6 -DMSO) δ (ppm): 29.28, 52.83, 110.19, 113.24, 117.26, 121.51, 135.49, 143.75, and 150.58. FT-IR: 3049 cm⁻¹ (C–Hstr, Ar), 2961 cm⁻¹ (C–Hstr, CH₂), 2811 cm⁻¹ (C–Hstr, ν_s CH₂), 1704 cm⁻¹ (C=N) and 1617 cm⁻¹, 1435 cm⁻¹ (C=C). $\text{LH}_3\text{Cl}_3\cdot 4\text{H}_2\text{O}$. ¹H NMR (400 MHz, d_6 -DMSO) δ (ppm): 7.50 (m, Ar), 7.30 (m, Ar), 5.07 (s, N–H), 3.87 (t, NCH₂), 3.57 (t, SCH₂). ¹³C NMR (100 MHz, d_6 -DMSO) δ (ppm): 27.70, 52.00, 113.47, 124.01, 135.00, and 149.74. (FT-IR): 3425 cm⁻¹ (O–Hstr, for water cluster), 2963 cm⁻¹ (C–Hstr, CH₂), 2830 cm⁻¹ (C–Hstr, ν_s CH₂), 1624 cm⁻¹, 1524 cm⁻¹ (C=C). $\text{LH}_3\cdot\text{PTSA}_3$. ¹H NMR (400 MHz, d_6 -DMSO): 7.6 (m, Ar_{pta}), 7.40 (m, Ar_{tp}), 7.30 (s, Ar_{pta}), 7.10 (t, Ar_{pta}), 4.24 (s, N–H), 3.77 (t, NCH₂), 3.50 (t, SCH₂), 2.27 (s, CH₃_{pta}). ¹³C NMR (100 MHz, d_6 -DMSO) δ (ppm): 20.87, 28.48, 51.83, 113.47, 124.47, 125.59, 125.38, 134.27, 138.43, 144.79, and 158.17.
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