Structural and functional models for [NiFe] hydrogenase

Angamuthu, R.

2

Ligand Design, Synthetic Procedures and Experimental Methods†

Abstract. Ligand design, guide for abbreviations of short names of ligands as well as their precursors, material and experimental methods used in the synthesis and catalysis are described in this chapter.

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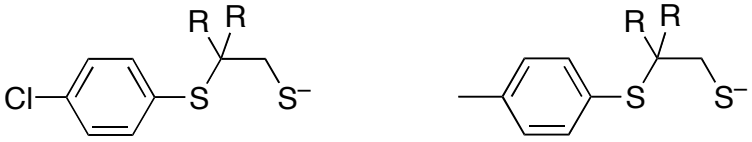
† This chapter is based on: R. Angamuthu, H. Kooijman, M. Lutz, A. L. Spek and E. Bouwman, *Dalton Trans*., **2007**, 4641-4643; R. Angamuthu, L. L. Gelauff, M. A. Siegler, A. L. Spek and E. Bouwman, *Chem. Commun*., **2009**, 2700-2702; R. Angamuthu and E. Bouwman, *Phys. Chem. Chem. Phys*., **2009**, 5578-5583, and several other unpublished reports.

2.1. Introduction

In this chapter, the synthesis of eight new bidentate and four new tetradentate ligands in combination with two other previously reported[1-4] ligands are described. In Scheme 2.1 and Scheme 2.2, the schematic structures of the ligands with their corresponding simplified code notations are shown.



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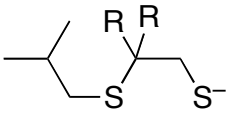
R = Me; cpsms

R = H; mpss
R = Me; mpsms



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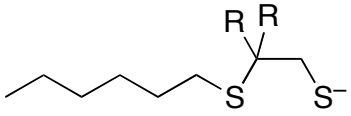
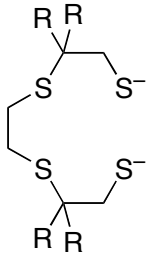


R = H; nhss
R = Me; nhsms

Scheme 2.1. Bidentate thioether-thiolate ligands used in this thesis.



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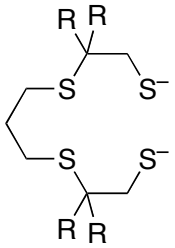
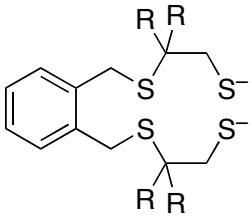


R = H; pbss
R = Me; pbsms



R = H; xbss
R = Me; xbsms

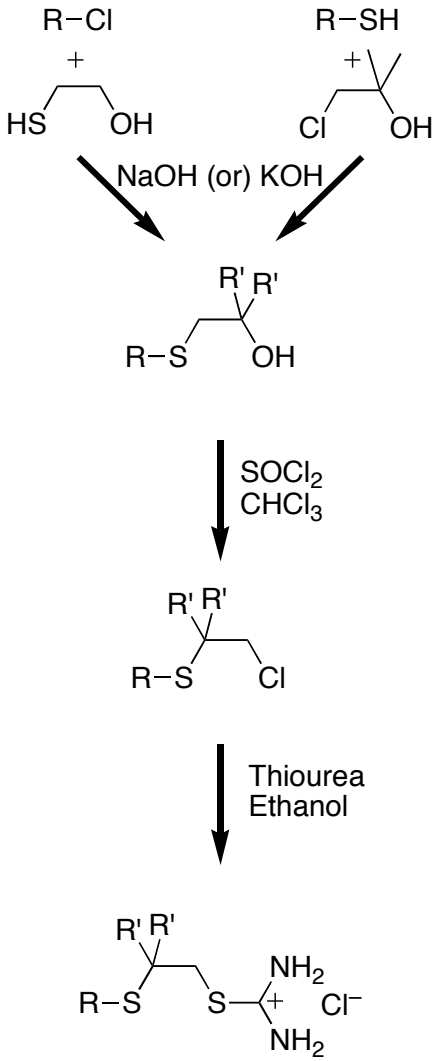
Scheme 2.2. Tetradentate dithioether-dithiolate ligands used in this thesis.

2.2. Guide for abbreviations

The first two letters in the abbreviations of the bidentate ligands representing the substituents on the thioether sulfur; **cp**, **mp**, **ib** and **nh** stand for 4-**c**hloro**p**henyl, 4-**m**ethyl**p**henyl, **i**so**b**utyl and **n**-**h**exyl, respectively. The "ss" in the abbreviations represent the two available sulfurs of the ligands and the 'm' in the "sms" stands for the dimethyl substitution. Likewise, the first letter in the abbreviations of the tetradentate ligands representing the bridge; **e**, **p** and **x** stand for **e**thyl, **p**ropyl and **x**ylyl groups. The second letter 'b' stands for 'bis' and the remaining part is the same as for the bidentate ligands.

2.3. Synthesis of Thiouronium Salt Precursors

In scheme 2.3, the general synthetic route applied to synthesize the thiouronium salt precursors of the bidentate ligands is shown. The hydroxo compounds formed in the first step of the synthesis have been made by the substitution reaction between the corresponding thiols and 1-chloro-2-methyl-2-propanol or between the corresponding chloro compounds and 2-mercaptoethanol in the presence of NaOH or KOH.



R = 4–Cl–phenyl, R' = H;	OH-cpss
R = 4–Cl–phenyl, R' = Me;	OH-cpsms
R = 4–Me–phenyl, R' = H;	OH-mpss
R = 4–Me–phenyl, R' = Me;	OH-mpsms
R = isobutyl, R' = H;	OH-ibss
R = isobutyl, R' = Me;	OH-ibsms
R = n-hexyl, R' = H;	OH-nhss
R = n-hexyl, R' = Me;	OH-nhsms
R = 4–Cl–phenyl, R' = H;	Cl-cpss
R = 4–Cl–phenyl, R' = Me;	Cl-cpsms
R = 4–Me–phenyl, R' = H;	Cl-mpss
R = 4–Me–phenyl, R' = Me;	Cl-mpsms
R = isobutyl, R' = H;	Cl-ibss
R = isobutyl, R' = Me;	Cl-ibsms
R = n-hexyl, R' = H;	Cl-nhss
R = n-hexyl, R' = Me;	Cl-nhsms
R = 4–Cl–phenyl, R' = H;	TU-cpss
R = 4–Cl–phenyl, R' = Me;	TU-cpsms
R = 4–Me–phenyl, R' = H;	TU-mpss
R = 4–Me–phenyl, R' = Me;	TU-mpsms
R = isobutyl, R' = H;	TU-ibss
R = isobutyl, R' = Me;	TU-ibsms
R = n-hexyl, R' = H;	TU-nhss
R = n-hexyl, R' = Me;	TU-nhsms

Scheme 2.3. General synthetic route applied for the synthesis of thiouronium salts.

Interestingly, during the chlorination step of the dimethyl-substituted ligands a spontaneous rearrangement takes place, by which the dimethyl groups on the α positions end up at the β positions as reported previously.[3] After the formation of the episulfonium chloride salt, the chloride ion attacks the least sterically hindered carbon,[5] thus selectively opening the ring to form the rearranged product. The chloro compounds were

reacted with thiourea to form the thiouronium salt precursors of the ligands. All the thiouronium salts reported here are crystalline powders and were found to be air-stable for many months.

2.4. Instrumental Methods

2.4.1. Analytical Techniques

Electronic absorption spectra were recorded on a Varian Cary 50 UV–Visible spectrophotometer using cuvettes of 1 cm path length. IR spectra were recorded on a Perkin-Elmer FT-IR Paragon 1000 spectrophotometer equipped with a golden gate ATR device, using the reflectance technique (4000–300 cm^{-1}, resolution 4 cm^{-1}). Elemental analyses were carried out on a Perkin-Elmer series II CHNS/O analyzer 2400. NMR spectra were recorded on a Bruker 300 DPX spectrometer. Temperature was kept constant using a variable temperature unit within the error limit of ±1 K. The software MestReNova was used for the processing of the NMR spectra.[6] Tetramethylsilane (TMS) or the solvent residual peaks were used for calibration. Mass experiments were performed on a Finnigan MAT 900 equipped with an electrospray interface. Spectra were collected by constant infusion of the sample dissolved in methanol/water or dichloromethane (with 1% HOAc). Isotopic patterns were confirmed by comparing the experimental mass spectra with the simulated mass spectra. The freely available simulating software iMass was used for the simulation of mass spectra.

2.4.2. Electrochemical Techniques

The electrochemistry measurements were performed with a computer-aided Autolab PGstat 10 potentiostat controlled by GPES4 software. A conventional three-electrode system was used, consisting of a static glassy carbon disc or platinum disc working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Extra dry N,N-dimethylformamide (99.8%, water <50 ppm, over molecular sieves) was stored under argon and used as received. Other solvents used in the electrochemical measurements were purified following conventional procedures and stored under argon. All the solutions were deaerated by purging argon for 15 minutes prior to the measurement and the electrochemical experiments were performed at room temperature under argon atmosphere.

2.4.3. Electrocatalytic Proton Reduction Experiments

Cyclic voltammetry was used to evaluate the catalytic activity of complexes in proton reduction. Additions of acids were made by syringe using stock solutions in DMF or in acetonitrile. After each addition the electrochemical solution was deaerated by

purging argon for 3 minutes prior to the next measurement to remove the dihydrogen bubbles formed on the surface of the working electrode.

2.4.4. Electrochemical Studies Using Surface-Modified Electrodes

The pyrolitic graphite electrode was abraded using P500 and P1000 SiC sandpaper and ultrasonicated in Millipore MilliQ water for 1 min. The electrode was dried in a stream of argon for 5 sec; it was then immersed once in a 2 mM solution of a selected complex in dichloromethane for 5 minutes, after which the electrode was dried in a stream of argon for 5 seconds and this surface modified electrode was immediately utilized for the electrochemical measurements. Cyclic voltammograms were measured using 0.1 M solutions of acid in acetonitrile with a Pt wire auxiliary electrode.

2.4.5. Protonation Studies Using ^{1}H NMR Spectroscopy

Protonation experiments were performed at 25±1 °C in a 5 mm NMR tube containing 0.1 mmol of a complex in 0.75 ml of deuterated solvent. Stock solutions of acids were made using 0.1 mmol of the corresponding acid in 1 ml of deuterated solvent and 125 µl from this solution was added each time. The spectra were recorded immediately after each addition of acid.

2.5. Experimental Section

2.5.1. Chemicals

All preparations were carried out in reagent-grade solvents. All chemicals used in the syntheses were obtained from Acros or Aldrich and were used without further purification unless mentioned otherwise. All synthetic manipulations were carried under argon atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were distilled using standard techniques or deoxygenated by bubbling through a stream of argon and dried over molecular sieves.

2.5.2. Safety

Although no discomforts were noticed during the usage of the thiols mentioned in the following synthetic procedures, care should be taken while using them as most of the thiols mentioned here have an extremely pungent smell and may cause skin and respiratory disorders.

2.5.3. Synthesis of the ligand precursor TU-cpss

2-(4-chlorophenylthio)ethan-1-ol (OH-cpss). 4-Chlorobenzenethiol (8.68 g, 60 mmol) and 2-chloroethanol (4.83 g, 60 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (2.4 g, 60 mmol in 10 ml H_2O) was slowly added at 0 °C. Formed NaCl was removed

by filtration after two hours of stirring at 60 °C. After evaporating the ethanol under reduced pressure, water was added and the product was extracted with chloroform (2 × 30 ml). The combined chloroform layers were dried with $MgSO_4$ and evaporated to get a colorless oil (yield: 8.46 g, 75%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 7.33 (s, 4H, phenyl ring), 4.96 (t, ^3J = 5.4 Hz, 1H, –O*H*), 3.55 (q, ^3J = 5.6 Hz, 2H, –S–CH$_2$–C*H*$_2$–OH), 3.03 (t, ^3J = 6.8 Hz, 2H, –S–C*H*$_2$–CH$_2$–OH). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 135.59 (Ph–C4), 130.07 (Ph–C1), 129.47 (Ph–C3), 128.82 (Ph–C2), 59.70 (–S–CH$_2$–*C*H$_2$–OH), 34.99 (–S–*C*H$_2$–CH$_2$–OH).

2-(4-cholorophenylthio)ethyl-1-chloride (Cl-cpss). To a solution of **OH-cpss** (8.46 g, 44.8 mmol) in 30 ml chloroform was slowly added a solution of excess $SOCl_2$ (10 g, 84 mmol) in 30 ml chloroform. After an hour of stirring the chloroform and excess thionyl chloride were evaporated under reduced pressure to yield 9.28 g of a bright yellow oil (100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.31 (d, ^3J = 6.4 Hz, 2H, phenyl ring), 7.29 (d, ^3J = 6.4 Hz, 2H, phenyl ring), 3.60 (t, 2H, ^3J = 8.3 Hz, –S–CH$_2$–C*H*$_2$–Cl). 3.19 (t, 2H, ^3J = 8.3 Hz ,–S–C*H*$_2$–CH$_2$–Cl), **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 133.08 (Ph–C4), 132.73 (Ph–C1), 131.73 (Ph–C3), 129.24 (Ph–C2), 42.03 (–S–CH$_2$–*C*H$_2$–Cl), 36.28 (–S–*C*H$_2$–CH$_2$–Cl).

2-(4-chlorophenylthio)ethyl-1-thiouronium chloride (TU-cpss). To a solution of Cl-cpss (9.28 g, 44.8 mmol) in 30 ml ethanol was added a solution of thiourea (3.04 g, 40 mmol) in 60 ml ethanol. After 3 hours of reflux the solvent was evaporated under reduced pressure, which resulted in a solid. This solid was washed with a small amount of ethanol and diethyl ether to obtain a white product in a yield of 87% based on thiourea (9.87 g). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.34 (bs, 4H, –S–C(N*H*$_2$)$_2^+$Cl$^-$), 7.35 (2d, 4H, phenyl ring), 3.42 (t, ^3J = 7.5 Hz, 2H, phenyl–S–CH$_2$–C*H*$_2$–), 3.25 (t, ^3J = 7.5 Hz, 2H, phenyl–S–C*H*$_2$–CH$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 169.59 (–S–*C*(NH$_2$)$_2^+$), 133.78 (Ph-C4), 130.56 (Ph–C1), 129.18 (Ph–C3), 131.1 (Ph–C2), 30.1 (phenyl–S–*C*H$_2$–CH$_2$–), 31.98 (phenyl–S–CH$_2$–*C*H$_2$–). **MS (ESI):** (*m/z*) calculated for $C_9H_{12}ClN_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 247.01, found 246.86.

2.5.4. Synthesis of the ligand precursor TU-cpsms

2-(4-chlorophenylthio)-1,1-dimethylethan-1-ol (OH-cpsms). 1-Chloro-2-methyl-2-propanol (6.51 g, 60 mmol) and 4-chlorobenzenethiol (8.68 g, 60 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (2.4 g, 60 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and the reaction mixture was refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under

vacuum to get a colorless oil (11.27 g, 87%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.31 (d, ^3J = 8.5 Hz, 2H, phenyl ring), 7.22 (d, ^3J = 8.5 Hz, 2H, phenyl ring), 3.06 (s, 2H, –S–CH_2–C(CH_3)$_2$–), 2.51 (s, 1H, –OH), 1.28 (s, 6H, –S–CH_2–C(CH_3)$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 135.59 (Ph-C4), 131.81 (Ph–C1), 130.43 (Ph–C3), 128.83 (Ph-C2), 70.59 (–C(CH_3)$_2$–), 48.33 (-C(CH$_3$)$_2$–), 28.50 (–CH$_2$–C(CH_3)$_2$–).

2-(4-chlorophenylthio)-2,2-dimethylethyl-1-chloride (Cl-cpsms). A solution of $SOCl_2$ (7.14 g, 60 mmol in 10 ml chloroform) was slowly added to a solution of OH-cpsms (11.27 g, 52 mmol in 30 ml chloroform) at room temperature; the mixture was stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (12.25 g, 99%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.34 (d, ^3J = 8.5 Hz, 2H, phenyl ring), 7.25 (d, ^3J = 8.5 Hz, 2H, phenyl ring), 3.34 (s, 2H, -S–C(CH_3)$_2$–CH_2–), 1.64 (s, 6H, –C(CH_3)$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 135.18 (Ph–C4), 132.44 (Ph-C1), 131.30 (Ph–C3), 129.04 (Ph–C2), 69.36 (–C(CH_3)$_2$–), 50.20 (-CH$_2$–C(CH_3)$_2$–), 31.32 (-C(CH$_3$)$_2$–).

2-(4-chlorophenylthio)-2,2-dimethylethyl-1-thiouronium chloride (TU-cpsms). A solution of thiourea (3.81 g, 50 mmol in 30 ml ethanol) was added to a solution of Cl-cpsms (12.35 g, 50 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of chloroform to this oil and standing for two hours resulted in a white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (13.54 g, 87%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.37 (s, 4H, –S–C(NH_2)$_2^+$Cl$^-$), 7.53 (d, ^3J = 8.6 Hz, 2H, phenyl ring), 7.49 (d, ^3J = 8.6 Hz, 2H, phenyl ring) 3.43 (s, 2H, –S–C(CH_3)$_2$–CH_2–), 1.29 (s, 6H, –S–C(CH_3)$_2$–CH_2–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 169.95 (–S–C(NH_2)$_2^+$Cl$^-$), 138.60 (Ph–C3), 134.89 (Ph–C4), 129.22 (Ph–C2), 128.91 (Ph–C1), 48.62 (–S–C(CH_3)$_2$–CH_2–), 42.18 (–S–C(CH_3)$_2$–CH$_2$–), 27.29 (–S–C(CH$_3$)$_2$–CH_2–). **MS (ESI):** (m/z) calculated for $C_{11}H_{16}ClN_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 275.04, found 274.84.

2.5.5. Synthesis of the ligand precursor TU-mpss

2-(4-methylphenylthio)ethan-1-ol (OH-mpss). 4-Methylbenzenethiol (7.45 g, 60 mmol) and 2-chloroethanol (4.83 g, 60 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (2.4 g, 60 mmol in 10 ml H_2O) was slowly added at 0 °C. The formed NaCl was removed by filtration after two hours of stirring at 60 °C. After evaporating the ethanol under reduced pressure, water was added to the oily residue and the product was extracted with chloroform (2 × 30 ml). The combined chloroform layers were dried with $MgSO_4$ and evaporated to get a colorless oil (yield: 7.56 g, 75%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.24 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 7.12 (d, ^3J = 8.1 Hz, 2H, phenyl

ring), 4.96 (t, ^3J = 5.3 Hz, 1H, –O*H*), 3.55 (q, ^3J = 6.6 Hz, 2H, –S–CH$_2$–C*H*$_2$–OH), 3.03 (t, ^3J = 6.9 Hz, 2H, –S–C*H*$_2$–CH$_2$–OH). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 135.18 (Ph–C1), 132.55 (Ph–C4), 129.62 (Ph–C2), 128.81 (Ph–C3), 60.01 (–S–CH$_2$–*C*H$_2$–OH), 35.61 (–S–*C*H$_2$–CH$_2$–OH).

2-(4-methylphenylthio)ethyl-1-chloride (Cl-mpss). To a solution of **OH-mpss** (7.5 g, 45 mmol) in 30 ml chloroform was slowly added a solution of excess $SOCl_2$ (10 g, 84 mmol) in 30 ml chloroform. After an hour of stirring the chloroform and excess thionyl chloride were evaporated under reduced pressure to yield 8.4 g of a bright yellow oil (100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.31 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 7.15 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 3.60 (t, ^3J = 7.6 Hz, 2H, –S–CH$_2$–C*H*$_2$–Cl), 3.19 (t, ^3J = 7.6 Hz, 2H, –S–C*H*$_2$–CH$_2$–Cl), 2.35 (s, 3H, –CH_3). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 132.73 (Ph–C1), 129.24 (Ph–C2), 131.73 (Ph–C3), 133.08 (Ph–C4), 42.03 (–S–CH$_2$–*C*H$_2$–Cl), 36.28 (–S–*C*H$_2$–CH$_2$–Cl), 22.04 (–*C*H$_3$).

2-(4-methylphenylthio)ethyl-1-thiouronium chloride (TU-mpss). To a solution of Cl-mpss (8.4 g, 44.8 mmol) in 30 ml ethanol was added a solution of thiourea (3.04 g, 40 mmol) in 60 ml ethanol. After 3 hours of reflux the solvent was evaporated under reduced pressure, which resulted in a solid. This solid was washed with a small amount of ethanol and diethyl ether to obtain a white product in a yield of 94% based on thiourea (9.87 g). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.33 (s, 4H, –S–C(N*H*$_2$)$_2^+$Cl$^-$), 7.31 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 7.17 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 3.37 (t, ^3J = 7 Hz, 2H, phenyl–S–CH$_2$–C*H*$_2$–), 3.42 (t, ^3J = 7 Hz, 2H, phenyl–S–C*H*$_2$–CH$_2$–), 2.26 (s, 3H, –CH_3). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 169.59 (–S–*C*(NH$_2$)$_2^+$Cl$^-$), 136.22 (Ph–C1), 130.70 (Ph–C4), 129.92 (Ph–C2), 129.76 (Ph–C3), 32.46 (–S–*C*H$_2$–CH$_2$–), 30.12 (–S–CH$_2$–*C*H$_2$–), 20.57 (–*C*H$_3$). MS (ESI): (*m/z*) calculated for $C_{10}H_{15}N_2S_2$ $[M\text{-}Cl]^+$ requires (monoisotopic mass) 227.07, found 226.96.

2.5.6. Synthesis of the ligand precursor TU-mpsms

2-(4-methylphenylthio)-1,1-dimethylethan-1-ol (OH-mpsms). 1-Chloro-2-methyl-2-propanol (6.51 g, 60 mmol) and 4-methylbenzenethiol (7.45 g, 60 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (2.4 g, 60 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get a colorless oil (10.72 g, 91%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.31 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 7.07 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 3.05 (s, 2H, –S–C*H*$_2$–C(CH$_3$)$_2$–), 2.51 (s, 1H, –O*H*), 2.28 (s, 3H, C*H*$_3$–phenyl–), 1.26 (s, 6H, –S–CH$_2$–C(C*H*$_3$)$_2$–). **^{13}C NMR:** δ_C

[75.47 MHz, $CDCl_3$, 298 K] 136.08 (Ph-C1), 133.23 (Ph–C4), 129.94 (Ph–C2), 129.59 (Ph–C3), 70.62 (–*C*$(CH_3)_2$–), 48.97 (–*C*H_2–C$(CH_3)_2$–), 28.48 (–C(*C*$H_3)_2$–), 20.81 (*p*-*C*H_3).

2-(4-methylphenylthio)-2,2-dimethylethyl-1-chloride (Cl-mpsms). A solution of $SOCl_2$ (7.14 g, 60 mmol in 10 ml chloroform) was slowly added to the solution of OH-mpsms (10.01 g, 51 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (10.95 g, 100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.37 (d, ^3J = 8.00 Hz, 2H, phenyl ring), 7.14 (d, ^3J = 8 Hz, 2H, phenyl ring), 3.39 (s, 2H, –S–C$(CH_3)_2$–C*H*$_2$–), 2.35 (s, 3H, C*H*$_3$–phenyl–), 1.68 (s, 6H, –C(C*H*$_3)_2$–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 136.54 (Ph–C1), 132.96 (Ph–C4), 130.61 (Ph–C2), 130.03 (Ph–C3), 69.78 (–*C*$(CH_3)_2$–), 50.66 (–*C*H_2–C$(CH_3)_2$–), 31.23 (–C(*C*$H_3)_2$–), 20.90 (*C*H_3–phenyl–).

2-(4-methylphenylthio)-2,2-dimethylethyl-1-thiouronium chloride (TU-mpsms). A solution of thiourea (3.81 g, 50 mmol in 30 ml ethanol) was added to a solution of Cl-mpsms (10.74 g, 50 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of chloroform to this oil and standing for two hours resulted white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (13.38 g, 92%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.40 (s, 4H, –S–C(N*H*$_2)_2^+Cl^-$), 7.39 (d, ^3J = 8 Hz, 2H, phenyl ring), 7.23 (d, ^3J = 8 Hz, 2H, phenyl ring) 3.33 (s, 2H, –S–C$(CH_3)_2$–C*H*$_2$–), 2.30 (s, 3H, C*H*$_3$–phenyl–), 1.26 (s, 6H, –S–C(C*H*$_3)_2$–CH_2–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 170.17 (-S-*C*$(NH_2)_2^+Cl^-$), 139.44 (Ph–C1), 136.93 (Ph–C3), 129.88 (Ph–C2), 126.52 (Ph–C4), 48.04 (–S–*C*$(CH_3)_2$–CH_2–), 42.26 (–S–C$(CH_3)_2$–*C*H_2–), 27.31 (–S–C(*C*$H_3)_2$–CH_2–), 20.83 (*C*H_3–phenyl–). **MS (ESI):** (*m/z*) calculated for $C_{12}H_{19}N_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 255.10, found 254.91.

2.5.7. Synthesis of the ligand precursor TU-ibss

2-(isobutylthio)ethan-1-ol (OH-ibss). 1-Bromo-2-methylpropane (12.33 g, 90 mmol) and 2-mercaptoethanol (7.03 g, 90 mmol) were dissolved in 60 ml ethanol. A solution of KOH (5.05 g, 90 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed KBr was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get colorless oil (11.11 g, 92%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.64 (t, ^3J = 6.1 Hz, 2H, –CH_2–S–CH_2–C*H*$_2$–), 2.78 (s, 1H, –O*H*), 2.64 (t, ^3J = 6.1 Hz, 2H, –CH_2–S–C*H*$_2$–CH_2–), 2.34 (d, ^3J = 6.9 Hz, 2H, -C*H*$_2$–S–CH_2–CH_2–), 1.73 (septet, ^3J = 6.7 Hz, 1H, $(CH_3)_2$–C*H*–), 2.34 (d, ^3J = 6.64 Hz, 6H,

($C\mathit{H}_3$)$_2$–CH–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 60.22 (–CH_2–S–CH_2–$\mathit{C}H_2$–), 40.77 (-CH_2–S–$\mathit{C}H_2$–CH_2–), 35.50 (–$\mathit{C}H_2$–S–CH_2–CH_2–), 28.52 ((CH_3)$_2$–CH–), 21.78 (($\mathit{C}H_3$)$_2$–CH–).

2-(isobutylthio)ethyl-1-chloride (Cl-ibss). A solution of $SOCl_2$ (17.85 g, 150 mmol in 50 ml chloroform) was slowly added to a solution of OH-ibss (11 g, 82 mmol in 100 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (12.27 g, 98%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.61 (t, ^3J = 7.8 Hz, 2H, –CH_2–S–CH_2–CH_2–), 2.83 (t, ^3J = 7.8 Hz, 2H, –CH_2–S–CH_2–CH_2–), 2.44 (d, ^3J = 6.9 Hz, 2H, –CH_2–S–CH_2–CH_2–), 2.34 (septet, ^3J = 6.7 Hz, 1H, (CH_3)$_2$–CH–), 1.73 (d, ^3J = 6.6 Hz, 6H, (CH_3)$_2$–CH-). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 43.06 (–CH_2–S–CH_2–$\mathit{C}H_2$–), 41.68 (–CH_2–S–$\mathit{C}H_2$–CH_2–), 34.79 (–$\mathit{C}H_2$–S–CH_2–CH_2–), 28.75 ((CH_3)$_2$–CH–), 21.89 (($\mathit{C}H_3$)$_2$–CH–).

2-(isobutylthio)ethyl-1-thiouronium chloride (TU-ibss). A solution of thiourea (6.09 g, 80 mmol in 30 ml ethanol) was added to the solution of Cl-ibss (12.21 g, 80 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of chloroform to this oil and standing for two hours resulted in a white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (15.19 g, 83%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.35 (s, 4H, –S–C(NH_2)$_2^+$$Cl^-$), 3.42 (t, ^3J = 7.6 Hz, 2H, –CH_2–S–CH_2–CH_2–), 2.73 (t, ^3J = 7.6 Hz, 2H, -CH_2–S–CH_2–CH_2–), 2.45 (d, ^3J = 6.8 Hz, 2H, –CH_2–S–CH_2–CH_2–), 1.71 (septet, ^3J = 6.7 Hz, 1H, (CH_3)$_2$–CH–), 0.91 (d, ^3J = 6.6 Hz, 6H, (CH_3)$_2$–CH–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 171.04 (–S–C(NH_2)$_2^+$$Cl^-$), 41.21 (–$CH_2$–S–$CH_2$–$\mathit{C}H_2$–), 32.05 (–$CH_2$–S–$\mathit{C}H_2$–$CH_2$–), 31.90 (-$\mathit{C}H_2$–S–$CH_2$–$CH_2$–), 29.27 (($CH_3$)$_2$–$\mathit{C}$H–), 22.96 (($\mathit{C}H_3$)$_2$–CH–). **MS (ESI):** (*m/z*) calculated for $C_7H_{17}N_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 193.08, found 192.95.

2.5.8. Synthesis of the ligand precursor TU-ibsms

2-(isobutylthio)-1,1-dimethylethan-1-ol (OH-ibsms). 2-Methyl-1-propanethiol (8.12 g, 90 mmol) and 1-chloro-2-methyl-2-propanol (9.77 g, 90 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (3.6 g, 90 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$. The solvent was evaporated and the colorless oil was dried under vacuum (10.4 g, 71%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.62 (s, 2H, –S–CH_2–C(CH_3)$_2$–OH), 2.45 (d, ^3J = 6.8 Hz, 2H, (CH_3)$_2$CH–CH_2–S–), 2.26 (s, 1H, –S–CH_2–C(CH_3)$_2$–OH), 1.75 (septet, ^3J = 6.7 Hz, 1H, (CH_3)$_2$CH–CH_2–S–), 1.23 (s, 6H, –S–CH_2–C(CH_3)$_2$–OH), 0.96 (d, ^3J = 6.7 Hz, 6H, (CH_3)$_2$CH–CH_2–S–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$,

298 K] 70.33 (–S–CH_2–*C*$(CH_3)_2$–OH), 47.63 (–S–*C*H_2–C$(CH_3)_2$–OH), 43.84 (($(CH_3)_2$CH–*C*H_2–S–), 28.97 (($(CH_3)_2$*C*H–CH_2–S–), 28.54 (–S–CH_2–C(*C*$H_3)_2$–OH), 21.88 (($(CH_3)_2$CH–CH_2–S–).

2-(isobutylthio)-2,2-dimethylethyl-1-chloride (Cl-ibsms). A solution of $SOCl_2$ (17.85 g, 150 mmol in 50 ml chloroform) was slowly added to a solution of OH-ibsms (10.22 g, 63 mmol in 100 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (11.35 g, 100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.91 (s, 2H, –S–C$(CH_3)_2$–C*H*$_2$–Cl), 2.48 (d, ^3J = 6.8 Hz, 2H, $(CH_3)_2$CH–C*H*$_2$–S–), 1.78 (septet, ^3J = 6.7 Hz, 1H, $(CH_3)_2$C*H*–CH_2–S–), 1.64 (s, 6H, –S–C(C*H*$_3)_2$–CH_2–Cl), 0.97 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3)_2$CH–CH_2–S–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 70.35 (–S–*C*$(CH_3)_2$–CH_2–Cl), 48.75 (–S–C$(CH_3)_2$–*C*H_2–Cl), 43.88 (($(CH_3)_2$CH–*C*H_2–S–), 31.28 (–S–C(*C*$H_3)_2$–CH_2–Cl), 28.81 (($(CH_3)_2$–*C*H–CH_2–S–), 21.88 (($(CH_3)_2$CH–CH_2–S–).

2-(isobutylthio)-2,2-dimethylethyl-1-thiouronium chloride (TU-ibsms). A solution of thiourea (4.57 g, 60 mmol in 60 ml ethanol) was added to the solution of Cl-ibsms (10.84 g, 60 mmol in 60 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of chloroform to this oil and standing for two hours resulted in a white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (13.27 g, 86%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.33 (s, 4H, –S–C(N*H*$_2)_2^+Cl^-$), 3.51 (t, ^3J = 7.7 Hz, 2H, –S-C$(CH_3)_2$–C*H*$_2$–), 2.42 (d, ^3J = 6.9 Hz, 2H, –C*H*$_2$–S–C$(CH_3)_2$–CH_2–), 1.51 (septet, ^3J = 6.7 Hz, 1H, $(CH_3)_2$–C*H*–), 1.31 (2H, –CH_2–S–C(C*H*$_3)_2$–CH_2–), 0.92 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3)_2$–CH–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 170.14 (–S–*C*$(NH_2)_2^+Cl^-$), 44.52 (–CH_2–S–*C*$(CH_3)_2$–CH_2–), 42.41 (-*C*H_2–S–C$(CH_3)_2$–CH_2–), 36.10 (–CH_2–S–C$(CH_3)_2$–*C*H_2–), 28.29 (($(CH_3)_2$–*C*H–), 27.57 (($(CH_3)_2$–*C*H–), 22.05 (($(CH_3)_2$–CH–). **MS (ESI):** (*m/z*) calculated for $C_9H_{21}N_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 221.11, found 220.97.

2.5.9. Synthesis of the ligand precursor TU-nhss

2-(*n*-hexylthio)ethan-1-ol (OH-nhss). 1-Hexanethiol (11.09 g, 90 mmol) and 2-chloroethanol (7.25 g, 90 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (3.6 g, 90 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get a colorless oil (11.83 g, 81%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.68 (t, ^3J = 6.1 Hz, 2H, –S–CH_2–C*H*$_2$–OH), 2.68 (t, ^3J = 6.1 Hz, 2H, -S–C*H*$_2$–CH_2–OH), 2.50 (s, 1H, –O*H*), 2.48 (t, ^3J = 7.5 Hz, 2H, CH_3–$(CH_2)_4$–C*H*$_2$–S–), 1.55 (p, ^3J = 6.7 Hz, 2H, CH_3–$(CH_2)_3$–C*H*$_2$–CH_2–S–), 1.3 (m, 6H, CH_3–(C*H*$_2)_3$–

$(CH_2)_2$–S–), 0.85 (t, ^3J = 6.6 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 60.16 (–S–CH_2–CH_2–OH), 35.09 (CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 31.56 (–S–CH_2–CH_2–OH), 31.29 (CH_3–CH_2–CH_2–$(CH_2)_3$–S–), 29.6 (CH_3–$(CH_2)_4$–CH_2–S–), 28.41 (CH_3–$(CH_2)_2$–CH_2–$(CH_2)_2$–S–), 22.42 (CH_3–CH_2–$(CH_2)_4$–S–), 13.91 (CH_3–).

2-(*n*-hexylthio)ethyl-1-chloride (Cl-nhss). A solution of $SOCl_2$ (17.85 g, 150 mmol in 30 ml chloroform) was slowly added to a solution of OH-nhss (11.69 g, 72 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (13 g, 99%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.61 (t, ^3J = 7.8 Hz, 2H, –S–CH_2–CH_2–Cl), 2.83 (t, ^3J = 7.8 Hz, 2H, –S–CH_2–CH_2–Cl), 2.54 (t, ^3J = 7.3 Hz, 2H, CH_3–$(CH_2)_4$–CH_2–S–), 1.6 (p, ^3J = 7.7 Hz, 2H, CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 1.3 (m, 6H, CH_3–(CH_2)$_3$–$(CH_2)_2$–S–), 0.88 (t, ^3J = 6.6 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 43.05 (–S–CH_2–CH_2–Cl), 34.19 (–S–CH_2–CH_2–Cl), 32.41 (CH_3–$(CH_2)_4$–CH_2–S–), 31.34 (CH_3–CH_2–CH_2–$(CH_2)_3$–S–), 29.68 (CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 28.42 (CH_3–$(CH_2)_2$–CH_2–$(CH_2)_2$–S–), 22.49 (CH_3–CH_2–$(CH_2)_4$–S–), 13.98 (CH_3–).

2-(*n*-hexylthio)ethyl-1-thiouronium chloride (TU-nhss). A solution of thiourea (5.48 g, 72 mmol in 30 ml ethanol) was added to a solution of Cl-nhss (13 g, 72 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of chloroform to this oil and standing for two hours resulted in a white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (16.08 g, 87%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.35 (s, 4H, –S–C(NH_2)$_2^+$$Cl^-$), 3.42 (t, ^3J = 7.8 Hz, 2H, –CH_2–S–C(NH_2)$_2^+$), 2.73 (t, ^3J = 7.8 Hz, 2H, –CH_2–CH_2–S–C(NH_2)$_2^+$$Cl^-$), 2.55 (t, ^3J = 7.2 Hz, 2H, CH_3–$(CH_2)_4$–CH_2–S–), 1.48 (p, ^3J = 7.4 Hz, 2H, CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 1.3 (m, 6H, CH_3–(CH_2)$_3$–$(CH_2)_2$–S–), 0.83 (t, ^3J = 6.5 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 169.8 (–S–C(NH_2)$_2^+$$Cl^-$), 30.91 (–$CH_2$–$CH_2$–S–C(N$H_2$)$_2^+$$Cl^-$), 30.83 ($CH_3$–$(CH_2)_4$–$CH_2$–S–), 30.59 ($CH_3$–$CH_2$–$CH_2$–$(CH_2)_3$–S–), 30.27 ($CH_3$–$(CH_2)_3$–$CH_2$–$CH_2$–S–), 29.01 ($CH_3$–$(CH_2)_2$–$CH_2$–$(CH_2)_2$–S–), 27.87 ($CH_3$–$CH_2$–$(CH_2)_4$–S–), 22.05 (–$CH_2$–$CH_2$–S–C(N$H_2$)$_2^+$$Cl^-$), 13.91 ($CH_3$–). **MS (ESI):** (*m/z*) calculated for $C_9H_{21}N_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 221.11, found 220.95.

2.5.10. Synthesis of the ligand precursor TU-nhsms

2-(*n*-hexylthio)-1,1-dimethylethan-1-ol (OH-nhsms). 1-Hexanethiol (11.09 g, 90 mmol) and 1-chloro-2-methyl-2-propanol (9.77 g, 90 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (3.6 g, 90 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between

water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get a colorless oil (13.37 g, 78%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.62 (s, 2H, –S–CH_2–C$(CH_3)_2$–OH), 2.53 (t, ^3J = 7.3 Hz, 2H, CH_3–$(CH_2)_4$–CH_2–S–), 2.41 (s, 1H, –O*H*), 1.55 (p, ^3J = 7.5 Hz, 2H, CH_3–$(CH_2)_3$–CH_2–CH_2–), 1.3 (m, 6H, CH_3–(CH_2)$_3$–$(CH_2)_2$–S–), 1.23 (s, 6H, –C(CH_3)$_2$–), 0.85 (t, ^3J = 6.7 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 70.25 (–*C*$(CH_3)_2$–), 64.9 (–S–*C*H_2–C$(CH_3)_2$–OH), 34.5 (CH_3–$(CH_2)_4$–*C*H_2–S–), 31.34 (CH_3–CH_2–*C*H_2–$(CH_2)_3$–S–), 29.91 (CH_3–$(CH_2)_3$–*C*H_2–CH_2–S–), 28.52 (-C(*C*H_3)$_2$–), 28.4 (CH_3–$(CH_2)_2$–*C*H_2–$(CH_2)_2$–S–), 22.46 (CH_3–*C*H_2–$(CH_2)_4$–S–), 13.94 (*C*H_3–).

2-(*n*-hexylthio)-2,2-dimethylethyl-1-chloride (Cl-nhsms). A solution of $SOCl_2$ (17.85 g, 150 mmol in 10 ml chloroform) was slowly added to a solution of OH-nhsms (13.33 g, 70 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (14.58 g, 99%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.94 (m, 2H, –S–C$(CH_3)_2$–CH_2–Cl), 2.6 (m, 2H, CH_3–$(CH_2)_4$–CH_2–S–), 1.65 (m, 6H, –S–C(CH_3)$_2$–CH_2–Cl), 1.59 (m, 2H, CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 1.3 (m, 6H, CH_3–(CH_2)$_3$–$(CH_2)_2$–S–), 0.88 (t, ^3J = 6.8 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 70.39 (–S–*C*$(CH_3)_2$–CH_2–Cl), 48.11 (–S–C$(CH_3)_2$–*C*H_2–Cl), 34.64 (CH_3–$(CH_2)_3$–*C*H_2–CH_2–S–), 31.4 (CH_3–CH_2–*C*H_2–$(CH_2)_3$–S–), 31.33 (–S–C(*C*H_3)$_2$–CH_2–Cl), 29.74 (CH_3–$(CH_2)_2$–*C*H_2–$(CH_2)_2$–S–), 28.45 (CH_3–$(CH_2)_4$–*C*H_2–S–), 22.51 (CH_3-*C*H_2-$(CH_2)_4$–S–), 14.00 (*C*H_3–).

2-(*n*-hexylthio)-2,2-dimethylethyl-1-thiouronium chloride (TU-nhsms). A solution of thiourea (5.25 g, 69 mmol in 30 ml ethanol) was added to the solution of Cl-nhsms (14.42 g, 69 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get colorless oil. Addition of chloroform to this oil and standing for two hours resulted white crystalline solid. The solid was collected by filtration and washed with chloroform before drying under vacuum (17.11 g, 87%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.34 (s, 4H, –S–C(N*H*$_2$)$_2^+$$Cl^-$), 3.52 (s, 2H, –S–C$(CH_3)_2$–C$H_2$–S–), 2.52 (t, ^3J = 7.4 Hz, 2H, CH_3–$(CH_2)_4$–CH_2–S–), 1.45 (p, ^3J = 7.5 Hz, 2H, CH_3–$(CH_2)_3$–CH_2–CH_2–S–), 1.31 (s, 6H, –S–C(CH_3)$_2$–CH_2–S–), 1.25 (m, 6H, CH_3–(CH_2)$_3$–$(CH_2)_2$–S–), 0.83 (t, ^3J = 6.6 Hz, 2H, CH_3–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 170.42 (–S–*C*(NH_2)$_2^+$$Cl^-$), 44.69 (–S–*C*$(CH_3)_2$–$CH_2$–S–), 42.43 (–S–C$(CH_3)_2$–*C*$H_2$–S–), 30.88 ($CH_3$–$(CH_2)_3$–*C*$H_2$–$CH_2$–S–), 28.96 ($CH_3$–$CH_2$–*C*$H_2$–$(CH_2)_3$–S–), 28.2 ($CH_3$–$(CH_2)_2$–*C*$H_2$–$(CH_2)_2$–S–), 27.56 (–S–C(*C*$H_3$)$_2$–$CH_2$–S–), 27.45 ($CH_3$–$(CH_2)_4$–*C*$H_2$–S–), 20.05 ($CH_3$–*C*$H_2$–$(CH_2)_4$–S–), 13.94 (*C*$H_3$-). **MS (ESI):** (*m/z*) calculated for $C_{11}H_{25}N_2S_2$ $[M–Cl]^+$ requires (monoisotopic mass) 249.15, found 248.46.

2.5.11. Synthesis of the ligand precursor TU-ebss

3,6-(dithia)octyl-1,8-dichloride (Cl-ebss): To a solution of 3,6-dithiaoctane-1,8-diol (5.47 g, 30 mmol) in 40 ml $CHCl_3$ was added drop-wise a solution of 4.35 ml $SOCl_2$ in 10 ml $CHCl_3$. The suspension was stirred for 1.5 h at room temperature. Then the chloroform and excess $SOCl_2$ were evaporated under reduced pressure to yield 6.56 g of a sticky yellowish product (100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.74 (t, 4H, –C*H*$_2$–Cl), 2.91 (t, 4H, –S–*CH*$_2$–CH$_2$–Cl), 2.77 (s, 4H, –S–C*H*$_2$–C*H*$_2$–S–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 43.9 (–*C*H$_2$–Cl), 33.3 (–S–*C*H$_2$–CH$_2$–Cl), 31.5 (–S–*C*H$_2$–*C*H$_2$–S–). **IR (neat):** 2956w, 2933w, 1435m, 1418m, 1436m, 1306w, 1231w, 1196m, 1140m, 1042w, 758ws, 699s, 677s, 420w, 370w cm^{-1}.

3,6-(dithio)octyl-1,8-dithiouronuim dichloride (TU-ebss): To a solution of Cl-ebss (5.82 g, 26.55 mmol) in 40 ml ethanol was added a solution of thiourea (3.84 g, 50.45 mmol) in 40 ml ethanol. The mixture was refluxed for one hour and the formed white precipitate was collected by filtration. The product was washed with cold ethanol and diethyl ether to yield 9.2 g of white powder (93% based on thiourea). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d$_6$, 298 K] 9.25 (s, 8H, –SC$^+$(N*H*$_2$)$_2$Cl$^-$), 3.43 (t, 4H, –C*H*$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 2.83 (m, 8H, –S–C*H*$_2$–C*H*$_2$–S– and –C*H*$_2$–CH$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d$_6$, 298 K] 170.8 (–S*C*$^+$(NH$_2$)$_2$Cl$^-$), 32.4 (–*C*H$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 31.9 (–*C*H$_2$–CH$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 31.5 (–S–*C*H$_2$–*C*H$_2$–S–). **IR (neat):** 3192m, 3050m, 1663s, 1560w, 1436m, 1227w, 1195m, 1148w, 1083w, 668s, 464s, 310w cm^{-1}. **MS (ESI):** (*m/z*) calculated for $C_8H_{18}S_4N_4$ [M–2Cl] requires (monoisotopic mass) 298.04, found 298.81.

2.5.12. Synthesis of the ligand precursor TU-ebsms

4,7-dithia-2,9-dimethyldecane-2,9-diol (OH-ebsms): To a solution of 1,2-ethanedithiol (5.65 g, 60 mmol) in 70 ml ethanol was added 1-chloro-2-methyl-2-propanol (13.03 g, 120 mmol) and NaOH (4.81 g, 120 mmol) in 45 ml water. After refluxing for two hours, the formed NaCl was removed by filtration. After evaporating the ethanol under reduced pressure, water was added and the product was extracted with chloroform. The combined chloroform layers were dried with $MgSO_4$ and evaporated to get 10.68 g of colorless oil (98 %). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.78 (m, 2H, –O*H*), 2.70 (s, 4H, –S–C*H*$_2$–C(CH$_3$)$_2$OH), 2.57 (s, 4H, –S–C*H*$_2$–C*H*$_2$–S–) 1.62 (s, 12H, –C(C*H*$_3$)$_2$OH). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 70.3 (–*C*(CH$_3$)$_2$OH), 46.4 (–S–*C*H$_2$–C(CH$_3$)$_2$OH), 34.1 (–S–*C*H$_2$–*C*H$_2$–S–), 28.3 (–(*C*H$_3$)$_2$OH).

1,8-dichloro-3,6-dithia-2,2,7,7-tetramethyloctane (Cl-ebsms): To a solution of OH-ebsms (10.68 g, 58.72 mmol) in 20 ml $CHCl_3$ was added drop-wise a solution of $SOCl_2$ (17.85 g, 150 mmol) in $CHCl_3$. The solution turned into yellow color initially and orange at the final stage of the addition of $SOCl_2$. After an hour stirring the chloroform and excess

$SOCl_2$ were evaporated under reduced pressure to yield 12.33 g of a yellow oil (100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 2.93 (s, 4H, –C*H*$_2$–Cl), 2.81 (s, 4H, –S–C*H*$_2$–C*H*$_2$–S–), 1.62 (s, 12H, -C*H*$_3$). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 70.0 (–*C*H$_2$–Cl), 48.01 (–S–CH$_2$–CH$_2$–*C*(CH$_3$)$_2$Cl), 34.3 (–S–*C*H$_2$–*C*H$_2$–S), 31.3 (–*C*H$_3$).

1,8-dithiouronium-3,6-dithia-2,2,7,7-tetramethyloctane dichloride (TU-ebsms): Thiourea (7.99 g, 105 mmol) and Cl-ebsms (12.11 g, 55.24 mmol) were dissolved in ethanol (85 ml) and refluxed for an hour. After refluxing for half an hour an off-white precipitate was formed. After cooling down to the room temperature, the formed precipitate was filtered off and washed with cold ethanol and diethyl ether and dried under vacuum to get 17.64 g of pure crystalline white solid (76% based on thiourea). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.33 (d, 8H, –SC$^+$(N*H*$_2$)$_2$Cl$^-$) 3.56 (s, 4H, –C*H*$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 2.71 (s, 4H, –S–C*H*$_2$–C*H*$_2$–S–), 1.31 (s, 12H, -C*H*$_3$). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 170.3 (-CH$_2$-S*C*$^+$(NH$_2$)$_2$), 45.5 (–*C*H$_2$–SC$^+$(NH$_2$)$_2$), 42.5 (–S–*C*(CH$_3$)$_2$–) 28 (–S–*C*H$_2$–*C*H$_2$–S–), 27.5 (–*C*H$_3$). **IR (neat):** 3023bm, 2716w, 1979w, 1634m, 1652vs, 1558w, 1538w, 1463w, 1436m, 1418m, 1382m, 13668m, 1198w, 1110w, 859w, 718s, 696s, 668s, 637s, 606s, 496w, 461m cm^{-1}. **MS (ESI):** (*m/z*) calculated for $C_{12}H_{28}S_4N_4$ [M–2HCl] requires (monoisotopic mass) 354.10, found 354.74.

2.5.13. Synthesis of H_2pbss

3,7-dithianonane-1,9-diol (OH-pbss): Propane-1,3-dithiol (1.62 g, 15 mmol) and 2-chloroethanol (2.41 g, 30 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (1.2 g, 30 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and the reaction mixture was refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get a yellow colored oil (2.53 g, 86%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.65 (q, 4H, ^3J = 5.97 Hz, –S–CH$_2$–C*H*$_2$–OH), 2.87 (s, 2H, -O*H*), 2.65 (t, 4H, ^3J = 6.12 Hz, –S-C*H*$_2$-CH$_2$-OH), 2.59 (t, 4H, ^3J = 7.05 Hz, –S–C*H*$_2$–CH$_2$–C*H*$_2$–S–), 1.81 (t, 4H, ^3J = 7.11 Hz, –S–CH$_2$–C*H*$_2$–CH$_2$–S–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 60.6 (-S–CH$_2$–*C*H$_2$–OH), 34.9 (–S–CH$_2$–*C*H$_2$–CH$_2$–S–), 30.4 (–S–*C*H$_2$–CH$_2$–OH), 29.3 (–S–*C*H$_2$–CH$_2$–*C*H$_2$–S–).

1,9-dichloro-3,7-dithianonane (Cl-pbss): A solution of $SOCl_2$ (3.57 g, 30 mmol in 10 ml chloroform) was slowly added to a solution of OH-pbss (2.53 g, 12.9 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield an orange colored oil (3.01 g, 100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 298 K] 3.75 (t, 4H, –S–CH$_2$–C*H*$_2$–Cl), 2.72 (t, 2H, –S–C*H*$_2$–CH$_2$–Cl), 2.44 (t, 4H, –S–C*H*$_2$–CH$_2$–C*H*$_2$–S–), 2.03 (t, 4H, –S–CH$_2$–C*H*$_2$–CH$_2$–

S–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 298 K] 43.0 (–S–CH_2–*C*H_2–Cl), 34.8 (–S–*C*H_2–CH_2–Cl), 31.3 (–S–*C*H_2–CH_2–*C*H_2–S–), 29.7 (–S–CH_2–*C*H_2–CH_2–S–).

1,9-dithiouronium-3,7-dithianonane dichloride (TU-pbss): A solution of thiourea (1.52 g, 20 mmol in 30 ml ethanol) was added to the solution of Cl-pbss (2.8 g, 12 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get an orange colored solid mass (3.3 g, 86%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 9.35 (s, 8H, –$SC^+(NH_2)_2$), 3.42 (t, 4H, ^3J = 6.93 Hz, –S–C*H*$_2$–CH_2–C*H*$_2$–S–), 2.76 (t, 4H, ^3J = 6.83 Hz, –C*H*$_2$–$SC^+(NH_2)_2Cl^-$), 2.63 (t, 4H, ^3J = 7.13 Hz, –C*H*$_2$–CH_2–$SC^+(NH_2)_2Cl^-$), 1.74 (t, 4H, ^3J = 7.12 Hz, –S–CH_2–C*H*$_2$–CH_2–S–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 169.8 (–S*C*$^+(NH_2)_2Cl^-$), 30.6 (–S–*C*H_2–CH_2–*C*H_2–S–), 30.2 (–*C*H_2–CH_2–$SC^+(NH_2)_2Cl^-$), 29.6 (–CH_2–*C*H_2–$SC^+(NH_2)_2Cl^-$), 29.1 (–S–CH_2–*C*H_2–CH_2–S–). **MS (ESI):** (*m/z*) calculated for $C_9H_{20}S_4N_4$ [M–2HCl] requires (monoisotopic mass) $C_{15}H_{25}S_4NiFe$ 312.06, found 312.80.

3,7-dithianonane-1,9-dithiol (H_2pbss): The synthesis was carried out using modified literature procedure.[2,3] To a solution of TU-pbss (14.9 mmol, 5.40 g) in 50 ml water was added a solution of excess NaOH (30 mmol, 1.20 g) in 20 ml water. The resulting white mixture was refluxed for 2 h. After allowing the mixture to cool down concentrated HCl was added to neutralize the product. The resulting solution was extracted twice with 50 ml CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and evaporated under vacuum to yield 1.87 g of a grey colored oil (55%). Due to the rapid oxidation in air, the successive reaction with nickel was carried out immediately and the characterization of H_2pbss was not carried out.

2.5.14. Synthesis of the ligand precursor TU-pbsms

4,8-dithia-2,10-dimethylundecane-2,10-diol (OH-pbsms): Propane-1,3-dithiol (1.62 g, 15 mmol) and 1-chloro-2-methylpropan-2-ol (3.26 g, 30 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (1.2 g, 30 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and the reaction mixture was refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get a colorless oil (2.84 g, 72%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 300 K] 2.64 (t, ^3J = 7.08 Hz, 4H, –CH_2–C*H*$_2$–S–), 2.61 (s, 4H, –S–C*H*$_2$–C$(CH_3)_2$–), 2.38 (s, 2H, –O*H*), 1.84 (p, ^3J = 7.09 Hz, 2H, –C*H*$_2$–CH_2–S–), 1.23 (s, 6H, –S–CH_2–C(C*H*$_3$)$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 300 K] 70.34 (–S–CH_2–*C*$(CH_3)_2$–), 46.40 (–S–*C*H_2–C$(CH_3)_2$–), 32.70 (–CH_2–*C*H_2–S–), 29.48 (–*C*H_2–CH_2–S–), 28.34 (–S–CH_2–*C*$(CH_3)_2$–).

1,9-dichloro-3,7-dithia-2,2,8,8-tetramethylnonane (Cl-pbsms): A solution of $SOCl_2$ (3.57 g, 30 mmol in 10 ml chloroform) was slowly added to a solution of OH-pbsms (2.84 g, 11.25 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield a bright yellow oil (3.25 g, 100%). **^{1}H NMR:** δ_H [300.13 MHz, $CDCl_3$, 300 K] 2.89 (s, 4H, –S–C(CH_3)$_2$–CH_2–), 2.68 (t, ^3J = 7.12 Hz, 4H, –CH$_2$–CH_2–S–), 1.84 (p, ^3J = 7.05 Hz, 2H, –CH_2–CH$_2$–S–), 1.60 (s, 6H, -S–C(CH_3)$_2$–CH$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, $CDCl_3$, 300 K] 70.07 (–S–*C*(CH_3)$_2$–), 47.96 (-S–C(CH_3)$_2$–*C*H$_2$–), 32.98 (–CH$_2$–*C*H$_2$–S–), 31.26 (–S–C(*C*H$_3$)$_2$–CH$_2$–), 29.44 (–*C*H$_2$–CH$_2$–S–).

1,9-dithiouronium-3,7-dithia-2,2,8,8-tetramethylnonane dichloride (TU-pbsms): A solution of thiourea (1.68 g, 22 mmol in 30 ml ethanol) was added to the solution of Cl-pbsms (3.18 g, 11 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get a colorless oil. Addition of methanol/n-hexane (1:1) to this oil and standing for a night resulted in a white crystalline solid (4.23 g, 87%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 300 K] 9.28 (s, 8H, –SC$^+$(NH_2)$_2$Cl$^-$), 3.51 (s, 4H, –S–C(CH_3)$_2$–CH_2–), 2.63 (t, ^3J = 7.32 Hz, 4H, –CH$_2$–CH_2–S–), 1.70 (p, ^3J = 7.19 Hz, 2H, –CH_2–CH$_2$–S–), 1.33 (s, 6H, –S–C(CH_3)$_2$–CH$_2$–). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 300 K] 170.17 (–S*C*$^+$ (NH$_2$)$_2$Cl$^-$), 45.05 (–S–*C*(CH_3)$_2$–CH$_2$–), 42.42 (–S–C(CH_3)$_2$–*C*H$_2$–), 29.63 (–*C*H$_2$–CH$_2$–S–), 27.56 (–S–C(*C*H$_3$)$_2$–CH$_2$–), 26.68 (–CH$_2$–*C*H$_2$–S–). **MS (ESI):** (*m/z*) calculated for $C_{13}H_{28}S_4N_4$ [M–2HCl] requires (monoisotopic mass) 368.12, found 368.87.

2.5.15. Synthesis of the ligand precursor TU-xbss

1,2-bis(4-hydroxy-2-thia-1-butyl)benzene (OH-xbss): A solution of NaOH (4.80 g, 120 mmol) in 15 ml water was added to a solution of α,α'-dichloro-*o*-xylene (10.50 g, 60 mmol) and 2-mercaptoethanol (9.38 g, 120 mmol) in 100 ml ethanol. After two hours refluxing, the formed NaCl was removed by filtration, and the solvents were evaporated under reduced pressure. Water was added and the product was extracted thrice with 50 ml $CHCl_3$. All the organic layers were combined and dried with $MgSO_4$. After evaporating the $CHCl_3$, the product was dried under vacuum to yield 14.40 g of a yellow oil (93%). **^{1}H NMR:** δ_H [300.13 MHz, DMSO-d_6, 298 K] 7.23 (m, ^3J = 3.70 Hz, 2H, phenyl ring), 7.17 (m, ^3J = 3.65 Hz, 2H, phenyl ring), 4.76 (s, 2H, –O*H*), 3.86 (s, 4H, Ph–CH_2–), 3.52 (t, ^3J = 6.83 Hz, 4H, –CH_2–OH), 2.47 (t, ^3J = 6.84 Hz, 4H, –CH_2–CH$_2$–OH). **^{13}C NMR:** δ_C [75.47 MHz, DMSO-d_6, 298 K] 136.9 (Ph–C1, Ph–C2), 130.6 (Ph–C3, Ph–C6), 127.3 (Ph–C4, Ph–C5), 61.0 (–*C*H$_2$–OH), 34.2 (Ph–CH_2–S–), 33.0 (–S–CH_2–CH$_2$–OH).

1,2-bis(4-chloro-2-thia-1-butyl)benzene (Cl-xbss): The synthesis was carried out by following a previously reported procedure.[3] Yield: 100%. **^{1}H NMR:** δ_H [75.47 MHz, DMSO-d_6, 298 K] 7.34 (m, 2H, phenyl ring), 7.26 (m, 2H, phenyl ring), 3.95 (s, 2H, Ph–

C*H*$_2$–S–), 3.70 (s, ^3J = 7.69 Hz , 4H, –C*H*$_2$–Cl), 2.78 (t, ^3J = 7.27 Hz, 4H, –S–C*H*$_2$–CH$_2$–Cl), **^{13}C NMR:** δ_C [300.13 MHz, DMSO-d$_6$, 298 K] 136.2 (Ph–C1, Ph–C2), 130.4 (Ph–C3, Ph–C6), 127.3 (Ph–C4, Ph–C5), 43.4 (–C*H*$_2$–Cl), 33.2 (–S–*C*H$_2$–CH$_2$–Cl), 32.2 (–S–CH$_2$–*C*H$_2$–Cl).

1,2-bis(4-thiouronium-2-thia-1-butyl)benzene dichloride (TU-xbss): To a suspension of Cl-xbss (15.40 g, 52.2 mmol) in 80 ml ethanol was added two equivalents of thiourea (8.04 g, 104.4 mmol). The mixture was then refluxed for two hours and the ethanol was evaporated under reduced pressure to obtain a dark oil. The oil was suspended in chloroform (60 ml) and diethyl ether (15 ml) to yield a greasy purple solid, which was filtered and washed with chloroform and ether to yield 19.66 g of a grey powder (85%). **^{1}H NMR:** δ_H [75.47 MHz, DMSO-d$_6$, 298 K] 9.33 (s, 8H, –SC$^+$(N*H*$_2$)$_2$Cl$^-$), 7.32 (m, 2H, phenyl ring), 7.22 (m, 2H, phenyl ring), 3.97 (s, 4H, Ph–C*H*$_2$–S–), 3.49 (t, ^3J = 7.67 Hz, 4H, –C*H*$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 2.71 (t, ^3J = 7.60 Hz, 4H, –C*H*$_2$–CH$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$). **^{13}C NMR:** δ_C [300.13 MHz, DMSO-d$_6$, 298 K] 169.6 (-S*C*$^+$(NH$_2$)$_2$Cl$^-$), 136.2 (Ph–C1, Ph–C2), 130.6 (Ph–C3, Ph–C6), 127.3 (Ph–C4, Ph–C5), 32.1 (-*C*H$_2$–CH$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 30.4 (–*C*H$_2$–SC$^+$(NH$_2$)$_2$Cl$^-$), 30.4 (Ph–*C*H$_2$–S–). **IR (neat):** 3013bs, 2706w, 2020w, 1652vs, 1558w, 1489w, 1417m, 1268w, 1209w, 1079w, 910w, 701s, 668s, 595s, 461s, 452s, 398m, 384w cm^{-1}. **MS (ESI):** (*m/z*) calculated for C$_{14}$H$_{22}$S$_4$N$_4$ [M–2HCl] requires (monoisotopic mass) 374.07, found 374.86.

2.6. References

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