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#### Supplementary Information

for

# **Tunable NIR-II Emitting Silver Chalcogenide Quantum Dots using**

## Thio/Selenourea Precursors: Preparation of MRI/NIR-II Multimodal

# **Imaging Agent**

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#### **1. General Information**

Materials and general considerations: Chemicals, such as toluene (95%), dimethoxy ethane, (DME,  $\geq$ 99%), diglyme ( $\geq$ 99%), tetramethylammonium hydroxide (TMAH,  $\geq$ 99%), tris(2carboxyethyl)phosphine (TCEP, 99%), tetrachloroethylene ( $\geq$ 99%), 1-octadecene (90%), triethylamine ( $\geq$ 99%), octylamine (99%), oleylamine (70%), triethylamine (99%), phenyl isothiocyanate (98%), L-cysteine ( $\geq$ 97%) and oleic acid (70%) were purchased from Sigma Aldrich and used without any further purification. Silver Nitrate (99%) was purchased from Thomas baker. Aniline (99%), N,N'-Dicyclohexylcarbodiimide, (DCC, 99%), DOTA-GA (tBu)<sub>4</sub> (99%), amino-thiophenol ( $\geq$ 99%), trifluoroacetic acid (TFA,  $\geq$ 99%), 4dimethylaminopyridine (DMAP, ≥99%), selenium powder (≥98%), 1-dodecanethiol (DDT,  $\geq$ 98%) and 1-octanethiol ( $\geq$ 98%) were purchased from TCI. Cadmium chloride ( $\geq$ 98%) and gadolinium (III) Chloride (≥98%) were purchased from Thomas Baker. All deuterated solvents were purchased from Sigma Aldrich. The silica gel 60 F<sub>254</sub> precoated plates were used to monitor the progress of the reactions using analytical thin layer chromatography (TLC) technique. The UV lamp or I<sub>2</sub> stain were used to visualize the spots. Silica gel 60–120 mesh size was employed for column chromatographic purification using a mixture of ethyl acetate and petroleum ether as the eluent for synthesizing starting materials.

#### 2. Characterization Methods

**Nuclear magnetic resonance** (**NMR**): <sup>1</sup>H, <sup>13</sup>C NMR and  $T_1$  relaxivity were recorded in Bruker ASCEND<sup>TM</sup> (400 MHz) spectrometer using either CDCl<sub>3</sub> or D<sub>2</sub>O or DMSO-d6 solvent as an internal reference. Multiplicity was indicated as follows: s (singlet), *d* (doublet), *t* (triplet), *q* (quartet), and *m* (multiplet).

**Thermogravimetric analysis (TGA):** TGA data was collected from TA Instruments, TGA Q50 Analyzer. During analysis, we programmed the system to heat at a rate of 20 °C min<sup>-1</sup> up to 600 °C. The N<sub>2</sub> gas flow was maintained at 60 mL min<sup>-1</sup> inside the heating furnace and 40 mL min<sup>-1</sup> inside the balance chamber. Two platinum pans were used; one as a reference and other one to place the sample.

**UV-Vis spectrophotometer:** The UV-Visible absorption spectra were collected using Perkin Elmer spectrophotometer (scan rate: 480 nm/s) and Agilent Technologies Cary 100 UV-vis.

The sample was dispersed either in anhydrous hexane or in anhydrous tetrachloroethylene (TCE) for measurements.

**Vis-NIR spectrofluorometer:** The PL spectra of  $Ag_2S$  QDs were collected using HORIBA Scientific spectrophotometer (Model: PTI-QM 510). The QDs were dispersed either in hexane or in TCE and the solution.

**Transmission electron microscopy** (**TEM**): TEM images were taken in JEOL-JEM-2100 Plus electron microscope. HRTEM images were obtained using 200 kV electron source. Samples were prepared by drop-casting of nanocrystal solution in hexane on a carbon coated copper grid purchased from EMS, the grids were kept overnight in a vacuum desiccator. The average particle size was measured using 400 particles. The lattice plane was obtained from lattice fringes. Image J software was used for calculation.

**Fourier Transform Infrared Spectroscopy (FTIR):** FT-IR spectra were recorded using Bruker ALPHA E, 200396.

**X-ray Diffractometer (XRD):** The purified as-prepared Ag<sub>2</sub>S QDs dispersed in hexane were drop-cast on a clean and dry glass slide. The film on glass slide was run under the PANalytical X-Ray diffractometer using Cu K $\alpha$  ( $\lambda$ = 1.54 Å) as the incident radiation (40 kV and 30 mA).

**X-ray Photoelectron Spectroscopy (XPS):** XPS samples were fabricated in glovebox on carbon coated silicon wafers to minimize charging. XPS spectra were obtained using Thermo-Scientific ESCALAB Xi<sup>+</sup> spectrometer with Al K $\alpha$  (1486.7 eV) X-ray source. For high resolution spectra constant analyser energy (CAE) of 50 eV was used and for survey spectra (CAE) of 100 eV. The XPS peaks were fitted using XPS peak 4.1 software. The Gaussian-Lorentzian (SGL) function was used to deconvolute the peaks with a fixed ratio of 80:20. The background of the spectrum was corrected using the Shirley method. The S 2p peak split into individual S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks with spin–orbit splitting of ~1.2 eV and have FWHM 1-1.2. Based on the literature report,<sup>1</sup> the three individual components were ascribed to S-H (162.9 and 164.1 eV), S-C (161.9 and 163.1 eV) and S-Ag (161.3 and 162.5 eV) peaks.

#### 3. Experimental Details

#### **General Procedures for Sulphur and Selenium Precursor Synthesis:**

Synthesis of substituted thiourea: (*Method A*). Thiourea derivatives were prepared by following previous report with slight modification.<sup>2</sup> In a typical synthesis, a solution of aniline (5.0 mmol) in toluene (10 mL) was added to a solution of phenyl isothiocyanate (5.0 mmol) in toluene (10 mL). The mixture was then allowed to stir for appropriate times. The precipitate formed was thoroughly dried under vacuum to remove toluene affording the desired precursor in very good yields.

Synthesis of substituted thiocarbamate and dithiocarbamate: (*Method B*). The thiocarbamate and dithiocarbamate derivatives were prepared by following previous report with slight modification.<sup>3</sup> A solution of thiol or phenols (5.0 mmol) in acetonitrile (10 mL) was added to a solution of phenyl isothiocyanate (5.0 mmol) in acetonitrile (10 mL). Triethylamine (5.0 mmol) was added and the reaction was stirred for 24 h at 75 °C under an inert atmosphere. The solvents were reduced under vacuum in rotatory evaporator followed by addition of *n*-hexane. The precipitates (thiocarbamate or dithiocarbamate) formed were filtered off using Buchner funnel and then washed 2-3 times with *n*-hexane. The desired product (precursor) was dried in desiccator prior to use for an experiment.

**Synthesis of selenourea:** (*Method C*). The phenyl isoselenocyanate was prepared by following previous reported method.<sup>4</sup> Similarly, to prepare selenourea derivatives previous reported protocol was followed.<sup>5</sup> Briefly, a chloroform solution (3 mL) of phenyl isoselenocyanate (3 mmol) was added to a solution of aromatic amine (3 mmol) in ethanol (EtOH, 2.5 mL). The reaction is exothermic and was allowed to cool to room temperature. Further, the mixture was stirred under reflux condition for 5-10 minutes to complete the reaction. A crystalline precipitate was then obtained after cooling to room temperature. The precipitate was filtered and dried under vacuum.

Synthesis of NIR-II emission tunable silver sulphide (Ag<sub>2</sub>S) QDs: In a double-necked round bottom flask (A), the sulphur precursor (0.2 mmol) was dissolved in dimethoxymethane (1 mL) and kept for degassing under vacuum for 30 minutes at room temperature. After 30 minutes, the reaction was kept under N<sub>2</sub> atmosphere. The mixture of silver nitrate (0.034 g, 0.2 mmol), 1-octadecene (3.5 mL) and 1-dodecanethiol (DDT, 0.5 mL) in another 50 mL three-necked round bottom flask (B) were degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 °C for 15 min until a pale-yellow solution was obtained. Next, the temperature of the reaction mixture was increased to 150  $^{\circ}$ C under N<sub>2</sub> atmosphere. The cold precursor solution of flask A was swiftly injected to the hot solution of flask B and the reaction mixture was stirred until it turned black from red colour at different times depending upon the nature of the substituents attached to the precursors. Then, the reaction mixture was quickly quenched in a cold ice bath.

Synthesis of NIR-II emission tunable silver selenide ( $Ag_2Se$ ) QDs: In a double-necked round bottom flask (A), the substituted selenourea precursor (0.2 mmol) was dissolved in dimethoxymethane (1 mL) and kept for degassing under vacuum for 30 minutes at room temperature. After 30 minutes, the reaction was kept under N<sub>2</sub> atmosphere. The mixture of silver nitrate (0.034 g, 0.2 mmol), 1-octadecene (3.5 mL), 1-dodecanethiol (0.5 mL) taken in another 50 mL three-necked round bottom flask (B) were degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 °C for 15 min until a paleyellow solution was obtained. Next, the temperature of this reaction mixture was increased to 150 °C under N<sub>2</sub> atmosphere. The cold precursor solution of flask A was swiftly injected to the hot solution of flask B and the reaction mixture was stirred until it turned black from red colour at different times depending upon the nature of precursors. The reaction mixture was then quickly quenched in a cold ice bath.

**Purification of QDs:** To the as-prepared QDs, 4 mL of ethanol/methanol and 1 mL of hexane were added followed by centrifugation at 6000 rpm for 15 min for two times. The supernatant was then discarded. Next, 1 mL of toluene was added again to the precipitate and centrifuged at 6000 rpm for 5 minutes for 2 times. Finally, to purify further, the obtained QDs were dispersed in 1 mL hexane/TCE and centrifuged at 3000 rpm for one time.

Synthesis of CdS QDs using oleic acid: In a two-necked round bottom flask (A), substituted thiourea precursor (1-(4-methoxyphenyl)-3-phenylthiourea (3c), 0.2 mmol) was dissolved in dimethoxy ethane (1 mL) and was kept for degassing under vacuum for 30 minutes at room temperature. After 30 minutes, it was kept under N<sub>2</sub> atmosphere. The mixture of cadmium chloride (CdCl<sub>2</sub>, 0.028 g, 0.2 mmol), 1-octadecene (3.5 mL) and oleic acid (1 mL) taken in another 50 mL three-necked round bottom flask (B) were degassed under vacuum at room temperature for 30 min, followed by degassing under vacuum at 120 °C for 15 min and kept under N<sub>2</sub> atmosphere. The cold precursor solution of flask A was swiftly injected to the hot solution of flask B and the reaction mixture was quenched by immediate cooling in ice-bath. Similarly, the CdS QDs was prepared by using another thiourea precursor 1-(4-nitrophenyl)-3-

phenylthiourea (**3e**) to compare the UV-vis absorbance of the as-prepared CdS QDs obtained from **3c**.

**Phase transfer of Ag<sub>2</sub>S QDs:** The purified precipitate of Ag<sub>2</sub>S QDs (0.102g) was dispersed in a 2 mL of chloroform. Simultaneously, 0.45 mg of *L*-cysteine was dissolved in 2 mL of Millipore water by dropwise addition of tetramethyl ammonium hydroxide and the pH of the system was maintained at the range of ~9.<sup>6</sup> These two solutions were mixed and the corresponding biphasic mixtures were stirred vigorously for 2 h at 14000 rpm at room temperature. The phase transferred Ag<sub>2</sub>S QDs in water were washed three times with pure Millipore water using micro spin-X filter (0.22 µm) and further the QDs were dispersed in 1.5 mL of water.

Synthesis of gadolinium complex (Gd-L) as MRI contrast agent and functionalization with colloidal  $Ag_2S$  QDs: The synthesis gadolinium complex (Gd-L) and its subsequent chelation with colloidal  $Ag_2S$  QDs was accomplished by following a reported method published by one of us.<sup>7</sup>

**I.** Synthesis of functionalized DOTA-GA ('Bu)<sub>4</sub> with 4-aminothiophenol (10): (*Method D*). The mixture of DOTA-GA ('Bu)<sub>4</sub> (0.57 mmol, 0.4 g) and 4-aminothiophenol (1.14 mmol, 0.14 g) were taken in 15 mL of DCM as a solvent. To this mixture, N, N'-dicyclohexylcarbodiimide (DCC, 0.57 mmol, 0.12 g) and 4-dimethylaminopyridine (DMAP, 0.06 mmol, 0.007g) were further added and stirred for 24 h at room temperature. The progress of the reaction was monitored with TLC and the product was purified with column chromatography delivering a white solid product (10) in 78% yield.

**II. Deprotection of BOC group in compound 10:** (*Method E*). The solution of **10** (130 mg, 0.172 mmol) in TFA (3 mL) and DCM (1.5 mL) was stirred at room temperature for 18 h. The solvents were removed under vacuum. The residue was repeatedly (3x) dissolved in DCM and the solvent removed in vacuo. After solvents were evaporated to dryness, the solid was again washed three times with dichloromethane followed by three times with diethyl ether producing a brown solid product (**11**) in 65 % yield.

**III. Synthesis of gadolinium complex (Gd-L):** 0.076 mmol of deprotected product (**11**) was dissolved in water (2 mL) and the pH was adjusted to 5.5 by adding small aliquots of 1.0 M of NaOH. Then, GdCl<sub>3</sub>.6H<sub>2</sub>O (0.076 mmol) was dissolved in water (1 mL) maintaining the pH at 5.5. The two solutions were combined and the pH was readjusted to 5.5 followed by stirring for 30 min. The solvent was removed under vacuum to give a hydroscopic white powder (**Gd-L**) which was further purified on a sephadex G25 resin to remove inorganic salts. The complex was afforded after solvent was removed as a white hydroscopic solid in 69% yield (Gd).

**IV. Complexation of the ligands (Gd-L) with QDs:** To the mixture of tris-(2-carboxyethyl) phosphine hydrochloride (TCEP, 0.25 mL) and QDs (**QD1** and **QD2**), degassed water (2 mL) was added, pH was adjusted between 9 to 10.5 using 0.5 M tetramethylammonium hydroxide (0.8 mL) and stirred vigorously for 24 h in the dark. The products (**Gd-QD1** and **Gd-QD2**) were obtained by spin filtration through centrifugation. Further, the obtained **Gd-QD1** and **Gd-QD2** were subjected to NMR studies for relaxivity measurements. The absence of free Gd was confirmed by xylenol orange test.<sup>8</sup> The pH of the Gd-capped QDs were adjusted for relaxivity measurements at 7.4.

#### **Relaxivity measurements**

The suspension of **Gd-QD1** and **Gd-QD2** were loaded in a 1 mm diameter capillary tube and the top face of capillary tube was sealed by parafilm. The capillary tube was then placed in NMR tube in D<sub>2</sub>O environment. The  $1/T_1$  measurements were performed on a Bruker Avance III (400 MHz). The efficiency of a contrast agent can be measured in terms of water relaxivity,  $r_1$  (expressed in units of mM<sup>-1</sup>s<sup>-1</sup> per Gd complex) and is field- and temperature-dependent. We know<sup>9</sup>,

$$\frac{1}{T_{1(obs)}} = \frac{1}{T_{1(H2O)}} + \frac{1}{T_{1(para)}}$$

Where  $T_1(\text{obs})$  is the observed longitudinal relaxation time in seconds and  $T_1(\text{H}_2\text{O})$  and  $T_1(\text{para})$  are respectively diamagnetic (in absence of paramagnetic ions) and paramagnetic water relaxation contribution<sup>9</sup>

Furthermore,  $\frac{1}{T_{1(obs)}} = \frac{1}{T_{1(H2O)}} + r_1[M]$ 

Where [M] is the molar concentration of the paramagnetic substance, which can be calculated from the NMR shift of water proton in the presence of the paramagnetic substance. The overall concentration of Gd ions was calculated using Evan's formula.<sup>10</sup>

$$[M] = \frac{3 \times \Delta \delta}{4\pi \times \chi_M \, 10^3}$$

Where,  $\Delta \delta$  is the difference in chemical shift (ppm) between the shifted resonance of the solvent in the presence of paramagnetic material and the pure solvent.  $\chi_M$  is magnetic (molar) susceptibility which is estimated using Curie equation<sup>11</sup>  $\mu_{eff} = 2.83 \sqrt{(\chi_M \times T)}$  where,  $\mu_{eff}$  is magnetic moment (for Gd<sup>3+</sup>,  $\mu_{eff} = 7.94$ )<sup>12,13</sup> and T is the temperature. To calculate relaxivity per **QD** the concentration of QD is required. We determined the concentration of CQDs i.e., [**QD**] using Lambert-Beer's law,  $A = \varepsilon [QD] l$  where A is absorbance (determined from UV-Vis spectroscopy) and  $\epsilon$  molar extinction coefficient of Ag<sub>2</sub>S CQDs.

#### Determination of Optical constants of Ag<sub>2</sub>S using DFT:

Monoclinic Ag<sub>2</sub>S exhibits anisotropic nature and hence their refractive index and dielectric values are different for X and Z directions (Table S1). The optical constants of Ag<sub>2</sub>S have been determined from the first principles calculation based on full potential linearized augmented plane wave (FP-LAPW) method.<sup>14</sup> The monoclinic phase (space group P2<sub>1</sub>/m) with optimized lattice parameters of a = 4.22 Å, b = 7.56 Å, c = 4.24 Å and  $\beta = 110.55^{\circ}$  has been considered. The effect of exchange correlation of electrons are treated with Perdew-Burke-Ernzerhof generalised gradient approximations (PBE-GGA)<sup>15</sup> and modified Becke-Johnson (mBJ) potential is included to match the energy band gap with experimental report. Ag<sub>2</sub>S is an indirect energy band gap semiconductor with gap value (1.12 eV) consistent to experimental data (1.1 eV).<sup>16</sup> The frequency dependent complex dielectric constant  $\varepsilon(\omega)$  describes the optical response of a materials against photon radiation and can be expressed as  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ , where  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  are real and imaginary parts, respectively. The refractive index and the extinction coefficient along the three independent directions of an anisotropic monoclinic symmetric unit cell of bulk sample are further estimated from the complex dielectric constants using following relations.

$$k = \frac{\left(-\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}}}{\sqrt{2}}$$



Figure S1: Optical constants of monoclinic Ag<sub>2</sub>S (X and Z directions)

Table S1: Optical constants of monoclinic Ag<sub>2</sub>S (X and Z directions); Note, I = imaginary and R = real parts of dielectric constants ( $\varepsilon_1$  and  $\varepsilon_2$ ) and refractive indexes (n and k).

Energy	ε <sub>1</sub> (R) Χ	ε <sub>2</sub> (I) Χ	n (R) X	k(I) X	ε <sub>1</sub> (R) Ζ	ε <sub>2</sub> (I) Ζ	n (R) Z	k(I) Z
(eV)								
1.37418	3.54E+00	1.76E-01	1.25E+01	1.25E+00	3.43E+00	1.27E-01	1.18E+01	8.75E-01
1.40139	3.55E+00	1.90E-01	1.26E+01	1.35E+00	3.45E+00	1.37E-01	1.19E+01	9.45E-01
1.4286	3.56E+00	2.02E-01	1.26E+01	1.44E+00	3.46E+00	1.46E-01	1.20E+01	1.01E+00
1.45581	3.57E+00	2.12E-01	1.27E+01	1.51E+00	3.48E+00	1.54E-01	1.21E+01	1.07E+00
1.48302	3.59E+00	2.20E-01	1.28E+01	1.58E+00	3.50E+00	1.63E-01	1.22E+01	1.14E+00
1.51023	3.60E+00	2.28E-01	1.29E+01	1.64E+00	3.52E+00	1.72E-01	1.24E+01	1.21E+00
1.53744	3.62E+00	2.36E-01	1.30E+01	1.71E+00	3.55E+00	1.82E-01	1.25E+01	1.29E+00
1.56466	3.64E+00	2.45E-01	1.32E+01	1.78E+00	3.57E+00	1.95E-01	1.27E+01	1.39E+00
1.59187	3.66E+00	2.55E-01	1.34E+01	1.87E+00	3.60E+00	2.10E-01	1.29E+01	1.51E+00
1.61908	3.69E+00	2.69E-01	1.35E+01	1.98E+00	3.63E+00	2.28E-01	1.31E+01	1.65E+00
1.64629	3.72E+00	2.85E-01	1.37E+01	2.12E+00	3.66E+00	2.50E-01	1.33E+01	1.83E+00
1.6735	3.74E+00	3.04E-01	1.39E+01	2.27E+00	3.68E+00	2.75E-01	1.35E+01	2.03E+00
1.70071	3.77E+00	3.25E-01	1.41E+01	2.45E+00	3.71E+00	3.03E-01	1.37E+01	2.25E+00
1.72792	3.80E+00	3.49E-01	1.43E+01	2.65E+00	3.74E+00	3.33E-01	1.39E+01	2.49E+00

1.75513	3.83E+00	3.75E-01	1.45E+01	2.87E+00	3.76E+00	3.66E-01	1.40E+01	2.75E+00
1.78235	3.86E+00	4.05E-01	1.47E+01	3.12E+00	3.79E+00	4.01E-01	1.42E+01	3.04E+00
1.80956	3.88E+00	4.38E-01	1.49E+01	3.41E+00	3.81E+00	4.39E-01	1.43E+01	3.35E+00
1.83677	3.91E+00	4.76E-01	1.51E+01	3.73E+00	3.83E+00	4.80E-01	1.44E+01	3.68E+00
1.86398	3.94E+00	5.19E-01	1.52E+01	4.09E+00	3.85E+00	5.24E-01	1.45E+01	4.03E+00
1.89119	3.96E+00	5.65E-01	1.54E+01	4.48E+00	3.87E+00	5.71E-01	1.46E+01	4.42E+00
1.9184	3.98E+00	6.14E-01	1.55E+01	4.89E+00	3.88E+00	6.21E-01	1.46E+01	4.81E+00
1.94561	3.99E+00	6.65E-01	1.55E+01	5.31E+00	3.88E+00	6.71E-01	1.46E+01	5.22E+00
1.97283	4.00E+00	7.15E-01	1.55E+01	5.73E+00	3.89E+00	7.22E-01	1.46E+01	5.61E+00
2.00004	4.01E+00	7.65E-01	1.55E+01	6.14E+00	3.88E+00	7.70E-01	1.45E+01	5.98E+00
2.02725	4.02E+00	8.15E-01	1.55E+01	6.55E+00	3.88E+00	8.16E-01	1.44E+01	6.33E+00
2.05446	4.02E+00	8.64E-01	1.54E+01	6.95E+00	3.87E+00	8.59E-01	1.42E+01	6.65E+00
2.08167	4.02E+00	9.13E-01	1.53E+01	7.34E+00	3.86E+00	8.99E-01	1.41E+01	6.94E+00
2.10888	4.02E+00	9.64E-01	1.52E+01	7.75E+00	3.86E+00	9.38E-01	1.40E+01	7.23E+00
2.13609	4.02E+00	1.02E+00	1.51E+01	8.17E+00	3.85E+00	9.77E-01	1.39E+01	7.53E+00
2.16331	4.02E+00	1.07E+00	1.50E+01	8.60E+00	3.85E+00	1.02E+00	1.38E+01	7.83E+00
2.19052	4.01E+00	1.13E+00	1.48E+01	9.04E+00	3.84E+00	1.06E+00	1.36E+01	8.15E+00
2.21773	3.99E+00	1.18E+00	1.45E+01	9.45E+00	3.83E+00	1.11E+00	1.35E+01	8.48E+00
2.24494	3.97E+00	1.24E+00	1.42E+01	9.83E+00	3.82E+00	1.15E+00	1.33E+01	8.81E+00
2.27215	3.95E+00	1.29E+00	1.39E+01	1.02E+01	3.80E+00	1.20E+00	1.30E+01	9.13E+00
2.29936	3.92E+00	1.33E+00	1.36E+01	1.05E+01	3.78E+00	1.24E+00	1.28E+01	9.41E+00
2.32657	3.89E+00	1.38E+00	1.33E+01	1.07E+01	3.76E+00	1.29E+00	1.25E+01	9.66E+00
2.35379	3.87E+00	1.41E+00	1.30E+01	1.09E+01	3.73E+00	1.32E+00	1.22E+01	9.88E+00
2.381	3.84E+00	1.45E+00	1.26E+01	1.11E+01	3.70E+00	1.36E+00	1.19E+01	1.01E+01
2.40821	3.81E+00	1.49E+00	1.23E+01	1.13E+01	3.68E+00	1.39E+00	1.16E+01	1.02E+01
2.43542	3.78E+00	1.52E+00	1.20E+01	1.15E+01	3.65E+00	1.42E+00	1.13E+01	1.04E+01
2.46263	3.76E+00	1.55E+00	1.17E+01	1.16E+01	3.63E+00	1.45E+00	1.11E+01	1.05E+01
2.48984	3.73E+00	1.58E+00	1.14E+01	1.18E+01	3.61E+00	1.47E+00	1.08E+01	1.06E+01
2.51705	3.71E+00	1.61E+00	1.12E+01	1.19E+01	3.59E+00	1.50E+00	1.06E+01	1.08E+01
2.54427	3.69E+00	1.64E+00	1.09E+01	1.21E+01	3.57E+00	1.53E+00	1.04E+01	1.09E+01
2.57148	3.67E+00	1.67E+00	1.07E+01	1.22E+01	3.55E+00	1.56E+00	1.01E+01	1.11E+01
2.59869	3.64E+00	1.70E+00	1.04E+01	1.24E+01	3.53E+00	1.59E+00	9.89E+00	1.12E+01
2.6259	3.62E+00	1.73E+00	1.01E+01	1.25E+01	3.50E+00	1.63E+00	9.63E+00	1.14E+01

2.65311	3.60E+00	1.77E+00	9.85E+00	1.27E+01	3.48E+00	1.66E+00	9.36E+00	1.16E+01
2.68032	3.58E+00	1.80E+00	9.55E+00	1.29E+01	3.46E+00	1.70E+00	9.07E+00	1.17E+01
2.70753	3.55E+00	1.84E+00	9.22E+00	1.31E+01	3.43E+00	1.74E+00	8.74E+00	1.19E+01
2.73475	3.52E+00	1.88E+00	8.87E+00	1.32E+01	3.40E+00	1.78E+00	8.37E+00	1.21E+01
2.76196	3.49E+00	1.92E+00	8.48E+00	1.34E+01	3.36E+00	1.82E+00	7.97E+00	1.22E+01
2.78917	3.45E+00	1.96E+00	8.08E+00	1.35E+01	3.31E+00	1.85E+00	7.53E+00	1.23E+01
2.81638	3.41E+00	2.00E+00	7.64E+00	1.37E+01	3.26E+00	1.89E+00	7.06E+00	1.23E+01
2.84359	3.37E+00	2.04E+00	7.16E+00	1.38E+01	3.20E+00	1.92E+00	6.59E+00	1.23E+01
2.8708	3.31E+00	2.08E+00	6.65E+00	1.38E+01	3.14E+00	1.94E+00	6.13E+00	1.22E+01
2.89801	3.25E+00	2.11E+00	6.12E+00	1.38E+01	3.08E+00	1.95E+00	5.71E+00	1.20E+01
2.92522	3.19E+00	2.14E+00	5.61E+00	1.37E+01	3.03E+00	1.96E+00	5.34E+00	1.18E+01
2.95244	3.13E+00	2.16E+00	5.11E+00	1.35E+01	2.97E+00	1.96E+00	5.01E+00	1.16E+01
2.97965	3.06E+00	2.17E+00	4.66E+00	1.33E+01	2.92E+00	1.95E+00	4.72E+00	1.14E+01
3.00686	2.99E+00	2.17E+00	4.24E+00	1.30E+01	2.87E+00	1.95E+00	4.45E+00	1.12E+01
3.03407	2.93E+00	2.17E+00	3.89E+00	1.27E+01	2.82E+00	1.94E+00	4.20E+00	1.10E+01
3.06128	2.87E+00	2.16E+00	3.59E+00	1.24E+01	2.78E+00	1.93E+00	3.98E+00	1.08E+01
3.08849	2.82E+00	2.15E+00	3.35E+00	1.21E+01	2.73E+00	1.92E+00	3.78E+00	1.05E+01
3.1157	2.77E+00	2.13E+00	3.15E+00	1.18E+01	2.69E+00	1.91E+00	3.61E+00	1.03E+01
3.14292	2.73E+00	2.11E+00	2.99E+00	1.15E+01	2.65E+00	1.89E+00	3.47E+00	1.00E+01
3.17013	2.69E+00	2.09E+00	2.86E+00	1.13E+01	2.62E+00	1.87E+00	3.36E+00	9.77E+00
3.19734	2.66E+00	2.08E+00	2.75E+00	1.10E+01	2.59E+00	1.85E+00	3.28E+00	9.54E+00
3.22455	2.63E+00	2.06E+00	2.64E+00	1.08E+01	2.56E+00	1.82E+00	3.22E+00	9.33E+00
3.25176	2.59E+00	2.05E+00	2.52E+00	1.06E+01	2.53E+00	1.80E+00	3.17E+00	9.14E+00
3.27897	2.56E+00	2.04E+00	2.41E+00	1.04E+01	2.51E+00	1.78E+00	3.13E+00	8.97E+00
3.30618	2.53E+00	2.03E+00	2.28E+00	1.03E+01	2.49E+00	1.77E+00	3.09E+00	8.80E+00
3.3334	2.49E+00	2.01E+00	2.16E+00	1.00E+01	2.47E+00	1.75E+00	3.05E+00	8.64E+00
3.36061	2.46E+00	2.00E+00	2.06E+00	9.82E+00	2.45E+00	1.73E+00	3.02E+00	8.49E+00
3.38782	2.43E+00	1.98E+00	1.98E+00	9.60E+00	2.43E+00	1.71E+00	2.99E+00	8.34E+00
3.41503	2.40E+00	1.96E+00	1.92E+00	9.37E+00	2.42E+00	1.70E+00	2.97E+00	8.20E+00
3.44224	2.37E+00	1.93E+00	1.87E+00	9.15E+00	2.40E+00	1.68E+00	2.94E+00	8.05E+00
3.46945	2.34E+00	1.91E+00	1.85E+00	8.93E+00	2.38E+00	1.66E+00	2.93E+00	7.90E+00
3.49666	2.32E+00	1.88E+00	1.84E+00	8.71E+00	2.37E+00	1.64E+00	2.93E+00	7.75E+00
3.52388	2.30E+00	1.85E+00	1.85E+00	8.51E+00	2.35E+00	1.61E+00	2.94E+00	7.60E+00

3.55109	2.28E+00	1.82E+00	1.88E+00	8.32E+00	2.34E+00	1.59E+00	2.97E+00	7.45E+00
3.5783	2.27E+00	1.79E+00	1.93E+00	8.14E+00	2.34E+00	1.56E+00	3.01E+00	7.31E+00
3.60551	2.26E+00	1.77E+00	1.99E+00	7.98E+00	2.33E+00	1.54E+00	3.08E+00	7.19E+00
3.63272	2.25E+00	1.74E+00	2.06E+00	7.83E+00	2.34E+00	1.52E+00	3.15E+00	7.08E+00
3.65993	2.25E+00	1.71E+00	2.14E+00	7.71E+00	2.34E+00	1.50E+00	3.24E+00	7.00E+00
3.68714	2.25E+00	1.69E+00	2.22E+00	7.61E+00	2.35E+00	1.48E+00	3.32E+00	6.94E+00
3.71436	2.26E+00	1.67E+00	2.30E+00	7.53E+00	2.36E+00	1.46E+00	3.41E+00	6.90E+00
3.74157	2.26E+00	1.65E+00	2.38E+00	7.47E+00	2.36E+00	1.45E+00	3.48E+00	6.87E+00
3.76878	2.26E+00	1.64E+00	2.44E+00	7.43E+00	2.37E+00	1.44E+00	3.55E+00	6.86E+00
3.79599	2.27E+00	1.63E+00	2.49E+00	7.39E+00	2.38E+00	1.44E+00	3.60E+00	6.85E+00
3.8232	2.27E+00	1.62E+00	2.53E+00	7.36E+00	2.39E+00	1.43E+00	3.65E+00	6.85E+00
3.85041	2.27E+00	1.61E+00	2.55E+00	7.33E+00	2.40E+00	1.43E+00	3.69E+00	6.85E+00
3.87762	2.27E+00	1.61E+00	2.57E+00	7.29E+00	2.40E+00	1.43E+00	3.73E+00	6.85E+00
3.90484	2.27E+00	1.60E+00	2.60E+00	7.23E+00	2.41E+00	1.42E+00	3.77E+00	6.85E+00
3.93205	2.27E+00	1.58E+00	2.64E+00	7.17E+00	2.41E+00	1.42E+00	3.81E+00	6.85E+00
3.95926	2.27E+00	1.57E+00	2.70E+00	7.12E+00	2.42E+00	1.42E+00	3.86E+00	6.86E+00
3.98647	2.28E+00	1.56E+00	2.78E+00	7.09E+00	2.43E+00	1.42E+00	3.91E+00	6.89E+00
4.01368	2.29E+00	1.55E+00	2.86E+00	7.08E+00	2.44E+00	1.42E+00	3.96E+00	6.93E+00
4.04089	2.30E+00	1.54E+00	2.93E+00	7.10E+00	2.45E+00	1.42E+00	4.00E+00	6.98E+00
4.0681	2.32E+00	1.54E+00	2.99E+00	7.13E+00	2.46E+00	1.43E+00	4.02E+00	7.04E+00
4.09531	2.33E+00	1.54E+00	3.04E+00	7.18E+00	2.47E+00	1.44E+00	4.03E+00	7.11E+00
4.12253	2.34E+00	1.55E+00	3.07E+00	7.24E+00	2.48E+00	1.45E+00	4.03E+00	7.17E+00
4.14974	2.34E+00	1.56E+00	3.08E+00	7.29E+00	2.48E+00	1.46E+00	4.02E+00	7.23E+00

# Determination of molar extinction coefficient ( $\epsilon$ ) of Ag<sub>2</sub>S CQDs

The molar extinction coefficient (expressed as M<sup>-1</sup>cm<sup>-1</sup>) is related to absorption cross section (expressed in cm<sup>2</sup>) and Avogadro's number (N),

$$\epsilon = \frac{\sigma_{QD} \times N}{2303}$$

The absorption cross section was determined using Ricard equation,<sup>17</sup>

Where,

$$\omega = \text{angular frequency} \qquad \sigma_{QD} = \frac{\omega}{n_s c} (\frac{4}{3}\pi R^3) |f(\omega)|^2 2n_{QD} k_{QD}$$

 $n_s =$  refractive index of solvent matrix

 $n_{QD}$  = real part of refractive index of quantum dots

 $k_{QD}$  = imaginary part of refractive index of quantum dots and  $f(\omega)$  is Local field factor which is calculated using the following equation,

$$f(\omega) = \frac{3\varepsilon_s}{\varepsilon_{QD} + 2\varepsilon_s}$$

Where,  $\varepsilon_s is$  diectric constant of solvent and  $\varepsilon_{QD} is$  dielectric constant of Ag<sub>2</sub>S. We used optical constants (bulk dielectric constants and the refractive index) for monoclinic Ag<sub>2</sub>S with a band gap of 1.08 eV calculated using DFT (above). The concentration of Ag<sub>2</sub>S CQDs were determined at high photon energy (~450 nm), where molar extinction coefficient is independent of the size of CQDs.<sup>18</sup> We used molar extinction coefficient of 1.73  $\times$  10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup> (considering optical constants in X-direction) calculated using Ricard equation.

#### Calculation of quantum yield (QY):

Fluorescence quantum yield was determined by comparison of the integrated fluorescence intensity of QDs in organic solvent (TCE) and water against standard dye IR-140. Plot of the integrated fluorescence spectrum of Ag<sub>2</sub>S in water and TCE with five different concentrations were measured. Linear fits were used to calculate quantum yield by comparing the slopes to reference IR-140 ( $\Phi_f = 0.167$ , ethanol). The relative quantum yield of an unknown sample was determined by comparing the emission and absorption of the sample with that of the NCs of known quantum yield using the equation:

$$QY_{S} = QY_{R} \times \frac{I_{S} \times A_{R} \times n_{S}^{2}}{I_{R} \times A_{S} \times n_{R}^{2}}$$

Where, *I* is the integrated PL intensity, *n* is the refractive index, and A is the absorbance (at the excitation wavelength). Subscripts *R* and *S* stands for reference and sample respectively. The measurements were performed with  $Ag_2S$  CQDs at five different concentrations and the average value was reported.

4. Characterization of colloidal QDs, precursors and functionalized QDs



**Figure S2**. (a) Photoluminescence (PL) spectrum recorded for the attempted synthesis of  $Ag_2S$  QDs using oleic acid as capping ligand. No PL emission was detected (excitation: 800 nm). The colloidal stability was also poor, as shown in figure (b).



**Figure S3**. (a) Photoluminescence (PL) spectrum recorded for the attempted synthesis of  $Ag_2S$  QDs using oleic acid/oleyl amine as capping ligands. No PL emission was detected (excitation: 600 or 800 nm). The colloidal stability was poor, as shown in figure (b) the particles settled at the bottom of the vial.



**Figure S4**. (a) Photoluminescence (PL) spectra recorded for the synthesis of  $Ag_2S$  QDs after the reaction of DDT at 120 °C, 130 °C and 150 °C showing no characteristic emission peak of  $Ag_2S$  QDs; (b) Photographs of the concentrated aliquots taken from the reaction mixture of  $Ag_2S$  QDs at 120 °C, 130 °C and 150 °C after 1h.



**Figure S5**. (a) XRD spectrum of as-prepared Ag<sub>2</sub>S QDs obtained from only DDT at 200 °C; (b) Photoluminescence (PL) spectra recorded for the synthesis of Ag<sub>2</sub>S QDs using DDT at 200 °C at various interval of time.



**Figure S6**. (a) Thermogravimetric analysis (TGA) and its corresponding derivative of weight loss curves of precursor (**3c**) indicating the initial decomposition temperature of 145 °C; (b) thermogravimetric analysis (TGA) and its corresponding derivative of weight loss curves of precursor (**3e**) indicating the initial decomposition temperature of 150 °C.



**Figure S7**. FTIR spectra of dodecanethiol (DDT, black colour) and DDT-capped  $Ag_2S$  QDs (red colour) showing distinct shift of C-H stretching frequency confirming the surface passivation of  $Ag_2S$  QDs by DDT.



**Figure S8**. The reaction of Ag(I) with **3b** at different temperatures. The red shift of the PL emission (due to the increase in size of the nanocrystals) is observed on increasing the injection temperature from 120  $^{\circ}$ C to 150  $^{\circ}$ C.



Figure S9. Temporal evolution of PL emission peak of Ag<sub>2</sub>S QDs prepared from **3a** at 150 °C.



**Figure S10**. Electronic effect on CdS: The observed size/absorbance tunability of CdS CQDs (following our approach) is opposite to that observed for Ag<sub>2</sub>S CQDs.



**Figure S11**. XPS spectra of Ag<sub>2</sub>S QDs: (a) the whole survey; (b) C 1s calibrated at 284.8 eV; (c) Ag 3d core level spectrum; (d) S 2p binding energies.



Figure S12. Deconvoluted XPS spectrum of  $Ag_2S$  QDs: S 2p core-level spectrum showing three different chemical environments corresponding to S-Ag (Ag<sub>2</sub>S), S-C (ligand) and S-H (ligand).



**Figure S13**. XPS spectra of Ag<sub>2</sub>Se QDs: (a) the whole survey analysis; (b) Ag 3d core level spectrum and (c) Se 3d spectrum.



**Figure S14**. (a) Structure of gadolinium (Gd<sup>3+</sup>) based MRI contrast agent (Gd-L); (b) <sup>1</sup>HNMR spectrum of Gd-L demonstrating the exchange of water protons between bound and bulk water of surrounding; <sup>1</sup>HNMR spectrum of (c) Gd-QD2 demonstrating the exchange of water protons between bound and bulk water of surrounding.

## 5. Relaxivity studies of Gd-L:



Figure S15. Relaxivity plot of Gd-L at four different concentrations.



Figure S16. Plot of 1/T<sub>1</sub> versus different concentrations of Gd-L.

#### 6. Spectral Data:

**1,3-Diphenylthiourea (3a).** 1,3-diphenylthiourea was prepared according to the general procedure (*Method A*) by reacting solutions of aniline (**2a**, 0.55 g, 5.0 mmol) in (10 mL) toluene and phenylisothiocyanate (**1**, 0.07 g, 5 mmol) in toluene (10 mL) to afford **3a** in 82% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.77 (s, 2H), 7.48 (d, 4H, *J*= 7.6 Hz), 7.32 (t, 4H, *J*=7.6 Hz), 7.11 (t, 2H, *J*=7.4 Hz).<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) 179.6, 139.4, 128.4, 124.3, 123.6.

**1-Phenyl-3**-*p*-tolylthiourea (3b). 1-phenyl-3-*p*-tolylthioureawas prepared according to the general procedure (Method A) by reacting solutions of *p*-toluidine (2b, 0.54 g, 5.0 mmol) in toluene (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in toluene (10 mL) to

afford **3b** in 80% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.70 (s, 2H), 7.50 (d, 2H, *J*=7.7 Hz), 7.37–7.30 (m, 4H), 7.15–7.10 (m, 3H), 2.28 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) 179.6, 139.5, 136.7, 133.6, 128.3, 124.3, 123.8, 123.6, 20.5.

1-(4-Methoxyphenyl)-3-phenylthiourea (3c). 1-(4-methoxyphenyl)-3-phenylthiourea was



prepared according to the general procedure (Method A) by reacting solutions of 4-methoxyaniline (2c, 0.62 g, 5.0 mmol) in toluene (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in toluene (10 mL) to afford **3c** in 91% yield. 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (s, broad, 2H), 7.39 (d, 4H, *J*=4.2 Hz), 7.29–7.27 (m, 3H), 6.94 (d, 2H, *J*=8.8 Hz), 3.82 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 180.7, 159.0, 129.6, 127.7, 127.0, 125.3, 115.0, 55.5.

1-(4-Iodophenyl)-3-phenylthiourea (3d). 1-(4-iodophenyl)-3-phenylthioureawas prepared according to the general procedure (*Method A*) by reacting solutions of *p*-iodoaniline (2d, 1.09 g, 5.0 mmol) in toluene (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in toluene (10 mL) to afford 3d in 60% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ 9.84 (d, 2H *J*=12.8 Hz), 7.66 (d, 2H, *J*=8.5 Hz), 7.47 (d, 2H, *J*=7.9 Hz), 7.33 (*t*, 4H, *J*= 8.3 Hz), 7.13 (*t*, 1H, *J*=7.3 Hz). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) 179.4, 139.3, 139.2, 137.0, 128.4, 125.6, 124.5, 123.6, 88.4.

**1-(4-Nitrophenyl)-3-phenylthiourea** (**3e**). 1-(4-nitrophenyl)-3-phenylthiourea was prepared according to the general procedure (*Method A*) by reacting solutions of *p*-nitroaniline (**2e**, 0.69 g, 5.0 mmol) in acetonitrile (10 mL) and phenylisothiocyanate (**1**, 0.07 g, 5 mmol) in

acetonitrile (10 mL). The reaction is refluxed for 24 h at 80 °C to give **3e** in 41% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, 2H, J = 9.0 Hz), 7.39–7.23 (m, 5H), 6.64 (d, 2H, J= 9.0 Hz), 4.42 (s, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 182.9, 147.6, 130.1, 120.8, 113.4, 109.2, 100.3.

1-(4-Bromophenyl)-3-phenylthiourea (3f). 1-(4-bromophenyl)-3-phenylthiourea was H H prepared according to the general procedure (*Method A*) by reacting solutions of *p*-bromoaniline (2f, 0.86 g, 5.0 mmol) in toluene (10 mL) and phenyl isothiocyanate (1, 0.07 g, 5 mmol)

in toluene (10 mL) to give **3f** in 65% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.79 (d, 2H, *J*=8.3 Hz), 7.47–7.40 (m, 4H), 7.33–7.26 (m, 4H), 7.08 (*t*, 1H, *J*=7.3 Hz), <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) 182.5, 142.1, 141.3, 131.3, 131.1, 128.1, 127.4, 126.5.

**1-(3-nitrophenyl)-3-phenylthiourea (3g).** 1-(3-nitrophenyl)-3-phenylthiourea was prepared according to the general procedure (*Method A*) by reacting solutions of *m*-nitroaniline (**2g**, 0.67 g, 5.0 mmol) in toluene (10 mL) and phenyl isothiocyanate (**1**, 0.07 g, 5 mmol) in toluene (10 mL) to afford **3g** in 67% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.08 (s,

2H),  $\delta$  8.50 (s, 1H) 7.91–7.85 (m, 2H), 7.55 (t, 1H, J= 8.2 Hz), 7.42 (d, 2H, J=7.6Hz), 7.33–

7.29 (*m*, 2H), 7.11 (*t*, 1H, *J*=7.3Hz) <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) 180.4, 148.1, 141.6, 139.5, 130.1, 129.2, 125.5, 124.5, 119.1, 118.2.

179.8, 154.8, 139.6, 130.4, 128.2, 126.2, 124.1, 123.6, 114.9.

1-(4'-amino-[1,1'-biphenyl]-4-yl)-3-phenylthiourea (3i). 1-(4'-amino-[1,1'-biphenyl]-4-yl)-



3-phenylthiourea was prepared according to the general procedure (*Method A*) from mixing solutions of benzidine (0.92 g, 5.0 mmol) in toluene (10 mL) and phenyl isothiocyanate (0.07 g, 5 mmol) in toluene (10 mL), producing a white solid

80% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) 9.76–9.73 (d, 2H *J*=12 Hz), 7.58–7.44 (*m*, 6H), 7.29 (*m*, 4H), 7.07 (*m*, 1H), 6.59–6.58 (*d*, 2H, *J*=4 Hz), 5.15 (*s*, 2H); <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, DMSO-d<sub>6</sub>) 180.1, 148.8, 140.1, 129.1, 127.6, 125.9, 124.6, 124.2, 114.9.

O-Phenylphenylcarbamothioate (5a). O-Phenylphenylcarbamothioate was prepared according to the general procedure (*Method B*) by reacting solutions of phenol (4a, 0.47 g, 5.0 mmol) in acetonitrile (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in acetonitrile (10 mL) to afford 5a in 60% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.17 (s, broad, 1H), 7.66–7.64 (m, 3H), 7.48–7.46 (m, 3H), 7.38 (t, 2H, *J*=7.16 Hz), 7.28 (t,

1H, *J*=7.92 Hz). <sup>13</sup>C {1H} NMR (100 MHz, CDCl<sub>3</sub>) *δ* 179.6, 138.4, 137.0, 129.9, 128.9, 126.8, 125.4, 123.5, 120.5.

**O-(4-Methoxyphenyl)phenylcarbamothioate** 

(5b). *O*-(4-Methoxyphenyl)



phenylcarbamodithioate was prepared according to the general procedure (*Method B*) by reacting solutions of 4-methoxyphenol (**4b**, 0.70 g, 5.0 mmol) in acetonitrile (10

mL) and phenyl isothiocyanate (1, 0.07 g, 5 mmol) in acetonitrile (10 mL) to afford **5b** in 55% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (bs, 1H), 7.58 (d, 2H, *J*=8.2 Hz), 7.46 (d, 2H, *J*=7.9 Hz), 7.34 (t, 2H, *J*=7.4 Hz), 7.26–7.21 (m, 1H), 7.04 (d, 2H, *J* = 8.7 Hz), 3.87 (s, 3H). 13C {1H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  180.7, 159.0, 129.6, 127.7, 127.0, 125.3, 115.0, 55.7.

*O*-(4-Nitrophenyl) phenylcarbamothioate (5c). *O*-(4-Nitrophenyl) phenylcarbamothioate H was prepared according to the general procedure (*Method B*) by reacting solutions of p-nitrophenol (4c, 0.69 g, 5.0 mmol) in acetonitrile (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in acetonitrile (10 mL) to afford 5c in 65% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.22 (bs, 1H), 7.69 (d, 2H, *J*=7.4 Hz), 7.51–7.49 (m, 4H), 7.43 (d, 2H, *J*=6.8 Hz), 7.31(s, 1H). <sup>13</sup>C

{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ182.9, 147.6, 130.1, 120.8, 113.4, 109.2, 100.3.

4-Bromophenylphenylcarbamodithioate (7a). 4-bromophenylphenylcarbamodithioate was  $H_{a}$  prepared according to the general procedure (Method B) by reacting solutions of p-bromo benzenethiol (6a, 0.89 g, 5.0 mmol) in acetonitrile (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in

acetonitrile (10 mL) to afford **7a** 70% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (s, broad, 1H), 7.65 (d, 2H, *J*=7.3 Hz), 7.48–7.40 (m, 4H), 7.38–7.36 (m, 2H), 7.28 (s, 1H). <sup>13</sup>C {1H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  179.6, 138.4, 137.0, 129.9, 128.9, 126.8, 125.4, 123.5, 120.5.

4-Methoxyphenylphenylcarbamodithioate (7b). 4-methoxyphenylphenylcarbamodithioate was prepared according to the general procedure (*Method B*) by reacting solutions of p-



methoxy benzenethiol (**6b**, 0.70 g, 5.0 mmol) in acetonitrile (10 mL) and phenylisothiocyanate (1, 0.07 g, 5 mmol) in acetonitrile (10 mL) to afford **7b** in 50% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ8.20 (bs, 1H), 7.61 (d, 2H, *J* = 8.2 Hz), 7.49 (d, 2H, *J*= 8.0 Hz), 7.37 (t, 2H, *J*= 7.9 Hz), 7.28– 7.24 (m, 1H), 7.07 (d, 2H, *J* = 8.7 Hz), 3.90 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ180.5, 158.8, 129.4, 127.6, 126.9, 125.1, 115.4, 114.8, 55.5.

4-Nitrophenylphenylcarbamodithioate (7c). 4-nitrophenylphenylcarbamodithioatewas H response of p-nitrobenzenethiol (6c, 0.77 g, 5.0 mmol)in acetonitrile (10 mL) and phenylisothiocyanate (1, 0.07 g, 5.0 mmol)

mmol) in acetonitrile (10 mL) to afford 7c in 60% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19

(s, broad, 1H), 7.65 (d, 2H, *J*=7.3 Hz), 7.47–7.45 (m, 4H), 7.39–7.36 (m, 2H), 7.29–7.25 (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 179.8, 137.1, 129.5, 127.1, 125.3, 125.1, 99.9.

**1,3-Diphenylselenourea (9a)**. 1,3-Diphenylselenourea was prepared according to the general procedure (Method C) by reacting phenyl isoselenocyanate (**8**, 3 mmol) and aniline (**2a**, 3 mmol) to afford **9a** in 85% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.14 (s, broad, 2H), 7.39–7.31 (m, 4H), 7.29–7.22 (m, 4H), 7.15 (t, 2H, *J*= 6.8 Hz). <sup>13</sup>C {1H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  179.2, 140.3, 129.1, 125.8, 125.2.



**1-(4-Methoxyphenyl)-3-phenylselenourea** (9b). 1-(4-Methoxyphenyl)-3-phenylselenourea was prepared according to the general procedure (Method C) reacting phenyl isoselenocyanate (8, 3 mmol) and 4-methoxyaniline (2c, 3 mmol)

to afford **9b** in 85% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.96 (d, 2H, *J*=9.2 Hz), 7.37–7.28 (m, 4H), 7.24 (d, 2H, *J*=8.8 Hz), 7.16–7.14 (m, 1H), 6.88 (d, 2H, *J*= 8.8 Hz), 3.72 (s, 3H). <sup>13</sup>C {1H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  179.2, 157.6, 140.3, 129.1, 127.4, 125.7, 125.4, 114.4, 55.8.

### tri-tert-Butyl2,2',2''-(10-(1-(tert-butoxy)-5-((4-mercaptophenyl)amino)-1,5-dioxopentan-



2-yl)-1,4,7,10-tetraazacyclododecane-1,4,7-triyl)triacetate

(10): The general procedure for its synthesis is described above in (*Method D*). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 6.91 (d, 2H, *J*=6.8 Hz), 6.61 (d, 2H, *J*=8.5 Hz), 5.18 (s, 1H), 4.37 (s, 1H), 3.32–3.31 (m, 3H), 2.91–2.60 (m, 12H), 2.38–1.96 (m, 12H), 1.39–1.35 (m, 8H), 1.31–1.28 (m, 28 H). <sup>13</sup>C {1H} NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  200.0, 174.5, 172.7, 149.1, 135.7, 115.6, 113.9, 113.3, 82.7, 82.1, 59.6, 55.8, 53.6, 52.6, 52.4, 48.4, 48.0, 47.1, 44.2, 41.1, 37.8, 20.1. ESI-MS calculated for C<sub>41</sub>H<sub>69</sub>N<sub>5</sub>NaO<sub>9</sub>S (M+Na)<sup>+</sup> 830.47, found 831.00.

#### 2,2',2''-(10-(1-Carboxy-4-((4-mercaptophenyl)amino)-4-oxobutyl)-1,4,7,10-



tetraazacyclododecane-1,4,7-triyl)triacetic acid (11): The general procedure for its synthesis is described above in (*Method E*). <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$  7.55 (s, 1H), 7.46 (d, 2H, *J*=8.3 Hz), 7.34

(d, 2H, J=8.6 Hz), 4.81 (s, 1H), 3.90–3.84 (m, 4H), 3.36–3.30 (m, 5H), 3.02–2.82 (m, 12H), 1.95–1.88 (m, 3H), 1.31–1.11 (m, 3H). ESI-MS calculated for C<sub>25</sub>H<sub>38</sub>N<sub>5</sub>O<sub>9</sub>S (M+H)<sup>+</sup> 584.23, found 584.00.

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### 8. Copies of NMR spectra:



Figure S18: <sup>13</sup>C NMR of 3a (100 MHz, DMSO-d<sub>6</sub>)



**Figure S19**: <sup>1</sup>H NMR of **3b** (400 MHz, DMSO-d<sub>6</sub>)



Figure S20: <sup>13</sup>C NMR of 3b (100 MHz, DMSO-d6)



Figure S22: <sup>13</sup>C NMR of 3c (100 MHz, CDCl<sub>3</sub>)



Figure S24: <sup>13</sup>C NMR of 3d (100 MHz, DMSO-d<sub>6</sub>)





Figure S26: <sup>13</sup>C NMR of 3e (100 MHz, CDCl<sub>3</sub>)



**Figure S28:** <sup>13</sup>C NMR of **3f** (100 MHz, DMSO-d<sub>6</sub>)

# 

-10.0805









Figure S31: <sup>1</sup>H NMR of 3h (400 MHz DMSO-d6)



Figure S32: <sup>13</sup>C NMR of 3h (100 MHz, DMSO-d<sub>6</sub>)

< 9.76< 9.737.587.547.747.747.027.027.027.026.59< 6.58



**Figure S33:** <sup>1</sup>H NMR of **3i** (400 MHz, DMSO-d<sub>6</sub>)



Figure S34: <sup>13</sup>C NMR of 3i (100 MHz, DMSO-d<sub>6</sub>)



Figure S36: <sup>13</sup>C NMR of 5a (100 MHz, CDCl<sub>3</sub>)



Figure S38: <sup>13</sup>C NMR of 5b (100 MHz, CDCl<sub>3</sub>)

#### - 8.2241 7.7073 7.7073 7.5195 7.5195 7.4996 7.4409 7.4409 7.4047 7.4047







Figure S42: <sup>13</sup>C NMR of 7a (100 MHz, CDCl<sub>3</sub>)



Figure S44: <sup>13</sup>C NMR of 7b (100 MHz, CDCl<sub>3</sub>)

#### - 8.1979 7.6660 7.6676 7.4783 7.4783 7.4783 7.3997 7.3397 7.3318 7.3318 7.3335 7.7.3933 7.7.3933 7.7.3933 7.7.2933 7.7.2533







**Figure S46**: <sup>13</sup>C NMR of **7c** (100 MHz, CDCl<sub>3</sub>)







Figure **S50:** <sup>13</sup>C NMR of **9b** (400 MHz, DMSO-d<sub>6</sub>)

C 600388 C 60038 C 60038 C 60037 C 70387 C 70377 C



Figure S52: <sup>13</sup>C NMR of 10 (100 MHz, CDCl<sub>3</sub>)



Figure S53: <sup>1</sup>H NMR of 11 (400 MHz, D<sub>2</sub>O)

## 9. Copies of Mass Spectra:



aminothiophenol

