Supporting Information for

Barium and Titanium Dithiocarbamates as Precursors for Colloidal Nanocrystals of Emerging Optoelectronic Materials

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Experimental Methods.

General. All synthetic manipulations were carried out under an atmosphere of ultrapure argon or dinitrogen gas in a glove box or using a Schlenk line unless otherwise stated. Oleylamine (70%) was purchased from Sigma-Aldrich and refluxed in vacuo at 120 °C over CaH₂ for two hours before distilling in vacuo, passed through activated alumina, and then stored over 4 Å molecular sieves in an N₂ glovebox prior to use. All other chemicals were purchased from standard chemical vendors and used without further purification unless otherwise stated. Toluene, hexane, diethyl ether, and tetrahydrofuran were degassed by bubbling with argon and dried by passage through a commercial solvent purification system from LC Tech, inc. Ethanol was dried by refluxing over magnesium ethoxide overnight and then distilling under an argon atmosphere. Dried solvents were stored over 4 Å molecular sieves in an N₂ glovebox prior to use.

Powder X-Ray Diffraction. Samples for powder X-ray diffraction were dropcast from solution onto a zerobackground silicon plate. In general, PXRD samples were prepared in the glovebox but data collection was carried out under air. PXRD data was collected using Cu Kα radiation with an AXRD Benchtop diffractometer from Proto Manufacturing equipped with a Dectris MYTHEN2 R 1D hybrid photon-counting detector in Bragg-Brentano geometry.

UV-Vis-NIR Absorbance. Portions of the nanocrystal samples were dried to remove the original toluene solvent, resuspended in tetrachloroethylene with sonication, transferred to a quartz cuvette, and then measured using a Perkin Elmer Lambda 900 spectrometer. In some cases a small amount of additional oleylamine (~5 μ L) was added to the sample before drying in order to improve the homogeneity of the resulting tetrachloroethylene suspension. Sample preparation and measurement were carried out in air with non-dried solvents.

Transmission electron microscopy (TEM): TEM samples were prepared in air. Samples for TEM were dispersed at low concentration in toluene by sonicating for several minutes, then a drop of the resulting colloidal dispersion was allowed to air-dry on a carbon-coated copper TEM grid. In some cases, a small amount of additional oleylamine (~5 μ L) was added to the dispersion before sonication in an effort to prevent excessive aggregation of the nanoparticles on the TEM grid. Samples were dried in a vacuum desiccator for several hours prior to analysis. Imaging was performed using a JEOL 2100 TEM operating at 200 kV.

Synthesis of titanium tetrakis(N,N-diisopropyldithiocarbamate). This synthesis was reproduced with minor modifications from a reported procedure.¹ *Synthesis of lithium diisopropyldithiocarbamate*. This preparation was carried out identically to the literature report, except that the gooey orange-red crude material was further purified by triturating with diethyl ether, resulting in the formation of an off-white solid, which was then isolated atop a ground glass frit and washed with several additional portions of diethyl ether. This procedure washed away an orange-red colored impurity, leaving 2.6 g (75%) of white microcrystalline solid as the final product after drying *in vacuo. Synthesis of titanium tetrakis(N,N-diisopropyldithiocarbamate)*. Lithium diisopropyldithiocarbamate (3.58 g, 19.6 mmol) was dissolved in toluene (50 mL) and cooled to -40 °C using a dry ice/acetonitrile bath. TiBr₄ (1.75 g, 4.75 mmol) was added as a solid to the reaction mixture, resulting in an immediate color change to dark red. The reaction mixture was allowed to stir overnight (16 hours) while warming slowly to room temperature, then filtered through Celite. The volume of the filtrate was reduced to approximately 20 mL and then layered with pentane and stored at -35 °C in a freezer overnight, resulting in the precipitation of a redorange microcrystalline powder, which isolated atop a ground glass frit and washed with pentane followed by drying *in vacuo* (1.97 g, 55%).

Syntheses of barium dithiocarbamates. Syntheses of barium dithiocarbamate complexes described below were adapted from the reported procedure for the synthesis of $Sr(S_2CN^iPr)_2(THF)_2$.^{2,3}

Synthesis of barium bis(N,N-diisopropyldithiocarbamate) (1). Deionized water (200 mL) was added to a 500 mL round-bottomed flask. It was degassed by bubbling the water with nitrogen gas for one hour. Diisopropylamine (40 mL, 283.4 mmol) was added to the degassed water. Carbon disulfide (4.73 mL, 78.28 mmol) was added to the solution via syringe while the solution stirred vigorously. After the addition of carbon disulfide, the solution became bright yellow. The solution was stirred vigorously for 1 hour at room temperature, and then cooled in an ice/water bath. Barium pieces (5.5 g, 40.0 mmol) were then added to the solution in several portions. After the addition of the barium, the solution began to bubble/fizz. The round-bottomed flask was allowed to stir overnight and gradually rise to room temperature. After 24 hours, a fine white solid had begun to form in the flask. After 2 more days of stirring, the solution was again cooled to 0 °C using an ice bath. The precipitated solid was collected over a ground glass frit and washed with cold deionized water and diethyl ether, giving a bright, microcrystalline white powder. The powder was dried *in vacuo* at room temperature for 24 hours, giving analytically pure material which was transferred into the nitrogen glovebox (13.6 g, 71%). If desired, the product can be further recrystallized from THF/Et₂O and dried at 80° C in vacuo, however this additional purification did not have a noticeable impact on the nanocrystal syntheses using this precursor. X-ray quality crystals were grown by vapor diffusion of diethyl ether into a concentrated THF solution of the complex. ¹H NMR (300 MHz, DMSO- d_{6} , 298 K, see NMR discussion below): δ (ppm): 6.30 (br, -CH(CH₃)₂), 3.71 (br, -CH(CH₃)₂), 1.62 (br, -CH(CH₃)₂), 1.05 (br, -CH(CH₃)₂). ¹³C{¹H} NMR (75 MHz, CD₃OD, 298 K): δ (ppm): 209.3 (s, -S₂CNⁱPr₂), 55.5 (s, N-CH(CH₃)₂), 49.7 (s, N-CH(CH₃)₂), 19.8 (s, N-CH(CH₃)₂), 18.1 (s, N-CH(CH₃)₂). Anal. Calc. (found) for C₁₄H₂₈BaN₂S₄: C: 34.32 (34.23), H: 5.76 (5.74), N: 5.72 (5.66) %.

Synthesis of barium bis(N,N-diisobutyldithiocarbamate) (2). Ethanol (200 mL) and deionized water (300 mL) were combined in a 1000 mL round-bottomed flask and degassed by bubbling with nitrogen gas for one hour. Diisobutylamine (58.7 mL, 336.0 mmol) was added to the solution, followed by carbon disulfide (5.8 mL, 96 mmol) while stirring vigorously. The solution turned a vibrant yellow after the addition of carbon disulfide. After stirring for 2 hours at room temperature, a piece of barium (6.6 g, 48.3 mmol) was added to the solution. The solution stirred for 2 more days at room temperature, resulting in the formation of a white microcrystalline solid. The reaction mixture was concentrated by rotary evaporation until nearly all of the ethanol and water had evaporated. Diethyl ether was added to the solid, resulting in the precipitation of copious white needle-like crystals that were isolated atop a ground glass frit. The product was dried in vacuo overnight at 60 °C. The dried solid, which was analytically pure, was then transferred into a nitrogen glovebox (17.7 g, 68%). If desired, the material can be further recrystallized from THF/Et₂O. X-ray quality crystals were grown by vapor diffusion of diethyl ether into a concentrated THF solution of the complex. ¹H NMR (300 MHz, CD₃OD, 298 K): δ 3.94 $(d, J = 7.5 Hz, 8H, -CH_2CH(CH_3)_2), 2.50 (m, 4H, -CH_2CH(CH_3)_2), 0.94 (d, J = 6.7 Hz, 24H, -CH_2CH(CH_3)_2).$ ¹³C{¹H} NMR (125.7 MHz, CD₃OD, 298 K): δ (ppm): 211.9 (s, -S₂CN/Bu₂), 61.1 (s, N-CH₂CH(CH₃)₂), 26.7 (s, N-CH₂CH(CH₃)₂), 19.2 (s, N-CH₂CH(CH₃)₂). Anal. Calc. (found) for C₁₈H₃₆BaN₂S₄: C: 39.59 (39.33), H: 6.65 (6.63), N: 5.13 (5.04) %.

Synthesis of barium bis(N,N-dibenzyldithiocarbamate) (3). Ethanol (100 mL) and deionized water (50 mL) were combined in a 500 mL round-bottomed flask and degassed by bubbling with nitrogen gas for one hour. Dibenzylamine (15 mL, 78 mmol) was then added to the solution, followed by carbon disulfide (1.23 mL, 20.4 mmol) while stirring vigorously. The colorless reaction mixture became cloudy, and was stirred for 2 hours at room temperature. Barium shot (1.44 g, 10.5 mmol) was then added in several portions, and stirring was continued overnight at room temperature. In the morning, the biphasic reaction mixture separated upon standing, giving a layer of yellowish oil on the bottom of the flask. The reaction mixture was concentrated by rotary evaporation to a volume of approximately 50 mL (removing most of the ethanol), and the remaining water was decanted from the gooey yellow residue. Diethyl ether was added to the residue, resulting in the formation of copious amounts of a white needle-like, microcrystalline precipitate. This precipitate was isolated atop a ground glass frit and washed copiously with deionized water and diethyl ether, followed by drying in vacuo at 70 °C overnight, giving a white microcrystalline powder. The powder was transferred to a nitrogen glovebox for the final purification step, where it was redissolved in THF and filtered through Celite. The filtrate was concentrated to a minimal volume (~20 mL) and diethyl ether was added to produce a white precipitate, which was isolated atop a ground glass frit and dried in vacuo at room temperature (4.86 g, 64%). ¹H NMR (300 MHz, CD₃OD, 298 K): δ (ppm): 7.36 – 7.18 (m, 20H, Ph), 5.37 (s, 8H, -CH₂Ph). ¹³C{¹H} NMR (75 MHz, CD₃OD, 298 K): δ (ppm): 214.5 (s, -S₂CNBz₂), 137.4 (s, *i*-C_{Ph}), 128.0 (s, CH_{Ph}), 127.4 (s, CH_{Ph}), 126.7 (s, CH_{Ph}), 53.9 (s, -N(CH₂Ph)₂). Anal. Calc. (found) for C₃₀H₂₈BaN₂S₄: C: 52.82 (52.48), H: 4.14 (4.17), N: 4.11 (4.05) %.

Synthesis of barium bis(N,N-dicyclohexyldithiocarbamate) (4). Ethanol (200 ml) and deionized water (100 ml) were combined in a 1 L round bottom flask and degassed by bubbling with nitrogen gas for one hour. Dicyclohexylamine (79.5 ml, 400 mmol) was then added to the solution, followed by carbon disulfide (6.3 ml, 127 mmol) while stirring. The reaction mixture became cloudy and was stirred for 2 hours at room temperature, giving rise to copious light yellow precipitate. Additional ethanol (100 ml) and THF (100 ml) were added to the solution. A piece of barium (7.39 g, 53.8 mmol) was then added, and stirring was continued overnight at room temperature. In the morning, the resulting white precipitate was isolated atop a ground glass frit and washed copiously with deionized water, ethanol, and diethyl ether, followed by drying *in vacuo* at 80°C overnight, giving a white microcrystalline

powder. The powder was transferred to a nitrogen glovebox for the final purification step, where it was redissolved in THF (~500 mL; compound is not highly soluble in THF) and filtered through Celite. The filtrate was concentrated to a minimal volume (~100 mL) and diethyl ether was added; the resulting white precipitate was isolated atop a ground glass frit and dried *in vacuo* at 80 °C overnight (22 g, 33.8 mmol, 63%). ¹H NMR (300 MHz, CD₃OD, 298 K; *see NMR discussion below*): δ (ppm) 5.93 (br, C_{1-cy}H), 3.7-3.3 (br m, C_{1-cy}H), 2.1-1.0 (br m, C_{(2-4)-cy}H₂). ¹³C{¹H} NMR (75 MHz, CD₃OD, 253 K; *see NMR discussion below*): δ (ppm) 210.1 (s, -S₂CNCy₂), 64.2 (s), 60.9 (s), 32.0 (s), 29.5 (s), 29.3 (s), 26.6 (s), 26.5 (s), 25.2 (s), 25.0 (s). Anal. Calc. (found) for C₂₆H₄₄BaN₂S₄: C: 48.03 (47.83), H: 6.82 (6.84), N: 4.31 (4.23) %.

Nanoparticle synthesis. *Standard conditions*: In a nitrogen glovebox, the barium dithiocarbamate precursor (0.1 mmol) is combined with titanium(IV) tetrakis(N,N-diisopropyldithiocarbamate) (0.05 mmol, 37 mg) in 3 g of dried and degassed oleylamine in a 20 mL scintillation vial and stirred vigorously for 30 minutes to give an orange suspension (the barium complexes dissolve readily in oleylamine, but the titanium precursor is poorly soluble at room temperature). The reaction mixture (including Teflon stir bar) is transferred to a 25 mL Schlenk reaction tube equipped with a Teflon adapter and glass sheath (NMR tube) for a thermocouple probe (see Figure S1). The Teflon adapter is sealed with a small amount of vacuum grease and affixed with springs (see figure). The reaction flask is removed from the glovebox and heated to 350 °C in a heating mantle using a PID temperature controller and a thermocouple probe protected by the glass sheath which was immersed in the reaction mixture, with vigorous stirring. At approximately 120 °C, the reaction mixture was observed to turn deep brown-black and homogeneous; the temperature at which this color change occurred was independent of the Ba²⁺ precursor used. The reaction mixture was maintained at 350 °C for 30 minutes, then removed from the heating mantle and allowed to cool to room temperature.

Workup: The reaction mixture was then transferred back into a nitrogen glovebox. Ethanol was added to the reaction mixture to precipitate a dark brown-black solid; the mixture was centrifuged at 3500 rpm and the supernatant was discarded. The precipitate was washed two additional times by redissolving in minimal toluene and precipitating with ethanol. The final precipitate was redissolved in a small amount of toluene for analysis and storage.

←B			
		Description	Chemglass Part #
L L	Α	Airfree reaction tube	AF-0537-20
A	В	 (1) 1/8" uncoated Type K thermocouple (2) 5 mm, 8" long NMR tube 	(1) CG-3498-303 (2) CG-502-8
	С	PTFE universal inlet adapter	CG-1047-03
	D	Springs	CG-110-02
Ϋ́́μ			

Figure S1. Setup used for the nanocrystal synthesis reactions. Reactants and solvent are sealed inside the tube in a glovebox.

NMR Spectra

1

Note: The solubility properties of the barium dithiocarbamate complexes limited the choice of NMR solvents to CD_3OD and $DMSO-d_6$. However, some of the compounds (notably **1** and **4**) exhibited gradual decomposition in methanol/ CD_3OD solution, giving rise to an unidentified white precipitate as well as free amine (diisopropyl amine for **1** and dicyclohexylamine for **4**). While this issue seems to be avoided in DMSO, DMSO could not be used for variable temperature studies due to its high freezing point. Therefore, spectra taken in CD_3OD , including variable temperature NMR spectra, show a small but notable impurity of the free amine.



Figure S2. ¹H NMR (500 MHz, 298 K) of compound **1** in d_6 -DMSO. Solvent resonances are observed at 2.50 ppm ((CHD₂)CH₃SO) and 3.33 ppm (H₂O). *Note*: The NMR properties of this compound, including variable temperature spectra, are discussed further below.



Figure S3. ¹H NMR (300 MHz, 298 K) of compound **1** in CD₃OD. The free diisopropylamine impurity (*vide supra*) shows sharp peaks at 2.94 ppm and 1.06 ppm.



Figure S4. Illustration of the decomposition of compound **1** in CD₃OD at room temperature. Spectra are ¹H NMR (300 MHz) spectra acquired at room temperature (298 K).



Figure S5. Overlay of the ¹H NMR spectrum of compound **1** (blue) in CD₃OD with pure diisopropylamine (maroon), confirming the identity of the impurity/decomposition product.



Figure S6. ¹³C NMR (75 MHz, 243 K) of compound 1 in CD₃OD.



Figure S7. ¹H NMR (300 MHz, 298 K) of compound 2 in CD₃OD.



Figure S8. ¹³C NMR (125.7 MHz, 298 K) of compound **2** in CD₃OD.



Figure S9. ¹H NMR (300 MHz, 298 K) of compound **3** in CD₃OD.



Figure S10. ¹³C NMR (300 MHz, 298 K) of compound 3 in CD₃OD.



Figure S11. ¹H NMR (300 MHz, 298 K) of compound **3** in CD₃OD.



Figure S12. ¹³C NMR (75 MHz, 253 K) of compound **4** in CD₃OD. The quality of the spectrum is limited by the low solubility of the compound in CD₃OD and the need to carry out the measurement at low temperature; not all peaks may be resolved, especially those that may correspond to minor conformers.



Variable Temperature ¹H NMR of Compounds 1 and 4

Figure S13. Range of variable temperature ¹H NMR (300 MHz) spectra for compound **1** in CD₃OD.



Figure S14. Low-temperature ¹H NMR (300 MHz, 243 K) of compound 1 in CD₃OD.

Discussion: At room temperature, compound **1** shows two sets of broad isopropyl resonances, suggestive of slow interconversion of two different species or conformers in solution. As expected, these resonances sharpen as the temperature is lowered, reaching a low-temperature limit around 243 K. At higher temperatures, the resonances begin to coalesce into a single set of resonances, although the high-temperature limit is not reached at temperatures readily accessible in this solvent. Notably, the two species/conformers exhibit a large difference in the chemical shifts of the isopropyl protons, especially the methine CH proton (3.9 ppm vs. 6.3 ppm). This behavior, which likely originates from hindered rotation about the C_{iPr}-N bonds, has previously been observed in other diisopropyldithiocarbamate compounds, including in simple alkali metal salts of diisopropyldithiocarbamate, and the kinetics and mechanism of this process have been investigated in some detail.^{1,4-7}

The different chemical shifts originate from the gearing of the isopropyls and depend on whether each isopropyl methine proton is pointed "out" (towards one of the sulfur atoms of the dithiocarbamate group) or "in" (towards the other isopropyl substituent) (Figure S15), where the "out" methine septet is the further downfield shifted of the two.

In the 243 K NMR spectrum (Figure S14), in addition to the two dominant sets of isopropyl resonances that are assigned to the lowest-energy "in, out" conformer (Figure S15), two other sets of isopropyl resonances are observable. One, at 2.95 ppm and 1.06 ppm, is attributed to free diisopropylamine (*vide supra*). The second, with resonances at 6.35 ppm (septet) and 1.39 ppm (doublet), is consistent with an isopropyl group in the "out" conformation. This is tentatively attributed to the presence of some

population of the "out, out" conformer of the ligand. In order to confirm that this is plausible, we optimized the three possible conformers of the diisopropyldithiocarbamate anion by DFT and determined their relative energies. Although not expected to be quantitively accurate for the relative conformer energies in compound **1** itself, the results (Figure S15) show that it is plausible for a nontrivial amount of the "out, out" conformer to be present. Conversely, the "in, in" conformer lies considerably higher in energy and would not be expected to be observed. The presence of some population of this "out, out" conformer also explains why the two septet peaks of the ¹H NMR spectrum of compound **1** at room temperature (Figures S2 and S3) do not integrate 1:1, as would be expected if only the "in, out" conformer were present.



Figure S15. (Left) Orientation of isopropyl methine protons designated "in" and "out". (Right) Three possible conformers of the diisopropyldithiocarbamate anion with respect to the in/out orientation of isopropyl groups, showing geometry as optimized by DFT. The energy of the "out, out" and "in, in" conformers relative to the lowest-energy "in, out" conformer is shown. DFT methodology: Carried out using Gaussian 16 at the B3LYP/def2tzvp level of theory; frequency calculations were carried out to confirm that the optimized geometry is a local minimum on the potential energy surface. The crystallographically determined structure of the diisopropyldithiocarbamate ligand from compound **1** was used as the starting point for the "in, out" conformer; starting points for the other compounds were generated by rotating by 180° about the C-N-C-H dihedrals.



Figure S16. Range of variable temperature ¹H NMR (300 MHz) spectra for compound **4** in CD₃OD.



Figure S17. Low-temperature ¹H NMR (300 MHz, 253 K) of compound 4 in CD₃OD.

The variable temperature NMR spectra of compound **4** show qualitatively similar slow-interconversion effects as in compound **1**, likely of a similar origin, and are again suggestive that several different conformers of the ligand are present in solution.





Nanocrystal synthesis under different conditions and characterization:

Nanocrystal synthesis was carried out with each barium dithiocarbamate complex as the Ba²⁺ source in order to probe the potential effect of the dithiocarbamate substituents on the reactivity and resultant nanocrystal properties and morphology. Several examples of results for each precursor are shown below (some of these results were already shown in the main text but are duplicated here for reference and clarity). It can be observed that there is some sample-to-sample variability even for syntheses carried out with the same precursors and under the standard conditions. This variability may result from small differences in factors such as heating rate, stirring rate, etc., which can affect nanocrystal nucleation and growth and are difficult to control perfectly. For example, although most samples synthesized under our standard conditions had a rod-like morphology, occasionally samples with more irregular shapes (e.g. Figure S19, Sample 2) were produced; for such samples, powder XRD and UV-Vis data are still consistent with the formation of BaTiS₃ as the major (i.e., the only detected) product.

Example Nanocrystal Characterization Data



Figure S19. Example characterization data for nanocrystals synthesized under the standard conditions using barium precursor **1**. TEM (left), UV-Vis, and PXRD (right) data are shown for each sample. Black bars in the PXRD data correspond to the standard reference pattern for stoichiometric BaTiS₃.

R = ⁱBu Sample 3



Figure S20. Example characterization data for nanocrystals synthesized under the standard conditions using barium precursor **2**. TEM (left), UV-Vis, and PXRD (right) data are shown for each sample. Black bars in the PXRD data correspond to the standard reference pattern for stoichiometric BaTiS₃.



Figure S21. Example characterization data for nanocrystals synthesized under the standard conditions using barium precursor **3**. TEM (left), UV-Vis, and PXRD (right) data are shown for each sample. Black bars in the PXRD data correspond to the standard reference pattern for stoichiometric BaTiS₃.





Figure S22. Example characterization data for nanocrystals synthesized under the standard conditions using barium precursor **4**. TEM (left), UV-Vis, and PXRD (right) data are shown for each sample. Black bars in the PXRD data correspond to the standard reference pattern for stoichiometric BaTiS₃.



Figure S23. Histograms of lengths and widths for the nanoparticles shown in Figure 4 of the main text, measured based on TEM imaging.



Effect of Stoichiometry

Figure S24. Comparison between the results of nanocrystal synthesis reactions carried out using either a 2:1 Ba:Ti molar ratio (as in the standard conditions, blue) or a 1:1 Ba:Ti molar ratio (red). PXRD data is shown on the left (black bars = standard reference pattern for stoichiometric BaTiS₃); only in the case of

the 2:1 ratio was crystalline $BaTiS_3$ detected. UV-Vis-NIR absorbance spectra are shown on the right; the sharp peak at 600 nm in the spectrum from the 1:1 ratio is characteristic of TiS_2 (see ref. S8 for example), suggesting that possibly amorphous or very thin nanosheets of TiS_2 may be formed in this reaction.

Ť,

41 mM [Ba]

Effect of Concentration



Figure S25. Reaction concentration comparison. TEM images, UV-Vis spectra, PXRD data, and width/length histograms are shown for reactions carried out with concentrations of 41 mM or 20 mM in

the barium precursor (the titanium precursor concentration is half that of the barium precursor in all cases). Concentration was varied by holding the number of moles of precursors constant while decreasing or increasing the amount of oleylamine solvent relative to the standard conditions.

Crystallographic Details for Compound 1:

A colorless needle single crystal of $C_{50}H_{100}Ba_3N_6O_2S_{12}$, approximate dimensions (0.074 x 0.091 x 0.504) mm³, was selected for the X-ray crystallographic analysis and mounted on a cryoloop using an oil cryoprotectant. The X-ray intensity data was measured at low temperature (T = 100K), using a three circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized Mo X-ray radiation (λ = 0.71073 Å) was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software⁹ using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 123164 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 18293 were independent (average redundancy 6.733, completeness = 100.0%, R_{int} = 13.98%, R_{sig} = 7.77%) and 11459 (62.64%) were greater than 2 σ (F²).

The final cell constants of <u>a</u> = 14.5911(7) Å, <u>b</u> = 23.6067(12) Å, <u>c</u> = 22.2683(12) Å, β = 105.991(2) °, volume = 7373.5(7) Å³, are based upon the refinement of the XYZ-centroids of 1569 reflections above 20 σ (I) with 5.138° < 20 <60.94°. Data were corrected for absorption effects using the Multi-Scan method implemented in the program (SADABS).¹⁰ The ratio of minimum to maximum apparent transmission was 0.769. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4380 and 0.8680. Structure was solved in a monoclinic unit cell; Space group: P 1 2(1)/n 1, with Z = 4 for the formula unit, $C_{50}H_{100}Ba_3N_6O_2S_{12}$. Using the Bruker SHELXT Software Package³, refinement of the structure was carried out by least squares procedures on weighted F² values using the SHELXTL-2018/3 ¹¹ included in the APEX3 v2019, 11.0, AXS Bruker program.¹² Hydrogen atoms were localized on difference Fourier maps but then introduced in the refinement as fixed contributors in idealized geometry with an isotropic thermal parameters fixed at 20 % higher than those carbons atoms they were connected. The final anisotropic full-matrix least-squares refinement on F^2 with 858 variables converged at R1 = 4.83%, for the observed data and wR2 = 8.87% for all data. The goodness-of-fit: GOF was 1.005. The largest peak in the final difference electron density synthesis was 1.261 e/Å³ and the largest hole was -1.368 e⁻ /Å³ with an RMS deviation of 0.138 e⁻/Å³. Based on the final model, the calculated density was 1.454 g/cm³ and F (000), 3272 e⁻.

Identification code	C_SC_002			
Chemical formula	$C_{50}H_{100}Ba_3N_6O_2S_{12}$	$C_{50}H_{100}Ba_3N_6O_2S_{12}$		
Formula weight	1614.09 g/mol	1614.09 g/mol		
Temperature	100(2) K			
Wavelength	0.71073 Å	0.71073 Å		
Crystal size	(0.074 x 0.091 x 0.504	4) mm³		
Crystal system	monoclinic			
Space group	P 1 2(1)/n 1			
Unit cell dimensions	a = 14.5911(7) Å	α = 90°		
	b = 23.6067(12) Å	β = 105.991(2)°		

Table S1. Sam	ple and ci	ystal data	for C	SC	002
		/			

	c = 22.2683(12) Å	γ = 90°
Volume	7373.5(7) ų	
Z	4	
Density (calculated)	1.454 g/cm ³	
Absorption coefficient	1.961 mm ⁻¹	
F(000)	3272	

Table S2. Data collection and structure refinement for C_SC_002.

Theta range for data collection	1.94 to 28.28°		
Index ranges	-19<=h<=19, -31<=k<=31, -29<=l<=29		
Reflections collected	123164		
Independent reflections	18293 [R(int) = 0.1	398]	
Coverage of independent reflections	100.0%		
Absorption correction	Multi-Scan		
Max. and min. transmission	0.8680 and 0.4380	1	
Structure solution technique	direct methods		
Structure solution program	XT, VERSION 2014/5		
Refinement method	Full-matrix least-squares on F ²		
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)		
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$		
Data / restraints / parameters	18293 / 635 / 858		
Goodness-of-fit on F ²	1.005		
Δ/σ_{max}	0.002		
Final R indices	11459 data; I>2σ(I)	R1 = 0.0483, wR2 = 0.0759	
	all data	R1 = 0.0994, wR2 = 0.0887	
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0195P) ² +16.4116P] where P=(F_o^2 +2 F_c^2)/3		
Extinction coefficient	0.0001(0)		
Largest diff. peak and hole	1.261 and -1.368 eÅ ⁻³		
R.M.S. deviation from mean	0.138 eÅ ⁻³		

Crystallographic Details for Compound 2

A colorless rod like single crystal of $C_{36}H_{72}Ba_2N_4S_8$, approximate dimensions (0.125 x 0.143 x 0.511) mm³, was selected for the X-ray crystallographic analysis and mounted on a cryoloop using an oil cryoprotectant. The X-ray intensity data was measured at low temperature (T = 100K), using a three

circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized Mo X-ray radiation $(\lambda = 0.71073 \text{ Å})$ was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software⁹ using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 86389 reflections to a maximum θ angle of 30.64° (0.70 Å resolution), of which 16021 were independent (average redundancy 5.392, completeness = 99.8%, R_{int} = 4.84%, R_{sig} = 3.48%) and 13489 (84.20%) were greater than 2σ (F²). The final cell constants of a = 11.5655(9) Å, b = 15.3903(12) Å, c = 16.1262(12) Å, α = 104.395(3) °, β = 104.143(3) °, γ = $100.801(3)^\circ$, volume = 2600.2(4) Å³, are based upon the refinement of the 1890 XYZ-centroids of reflections above 20 σ (I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4510 and 0.8010. The structure was solved in a triclinic unit cell; Space group: P -1, with Z = 2 for the formula unit, $C_{36}H_{72}Ba_2N_4S_8$. Using the Bruker SHELXT Software Package,¹¹ refinement of the structure was carried out by least squares procedures on weighted F² values using the SHELXTL-2018/3 included in the APEX3 v2019, 11.0, AXS Bruker program.¹² Hydrogen atoms were localized on difference Fourier maps but then introduced in the refinement as fixed contributors in idealized geometry with an isotropic thermal parameters fixed at 20 % higher than those carbons atoms they were connected. The final anisotropic full-matrix least-squares refinement on F^2 with 467 variables converged at R1 = 2.45%, for the observed data and wR2 = 5.08% for all data. The goodness-of-fit: GOF was 1.044. The largest peak in the final difference electron density synthesis was 0.855 e⁻/Å³ and the largest hole was -0.865 e⁻/Å³ with an RMS deviation of 0.097 e⁻/Å³. On the basis of the final model, the calculated density was 1.395 g/cm³ and F (000), 1112 e^{-1} .

C_SC_012	
$C_{36}H_{72}Ba_2N_4S_8$	
1092.13 g/mol	
100(2) K	
0.71073 Å	
(0.125 x 0.143 x 0.511)	mm ³
triclinic	
P -1	
a = 11.5655(9) Å	$\alpha = 104.395(3)^{\circ}$
b = 15.3903(12) Å	β = 104.143(3)°
c = 16.1262(12) Å	γ = 100.801(3)°
2600.2(4) Å ³	
2	
1.395 g/cm ³	
1.853 mm ⁻¹	
1112	
	C_SC_012 $C_{36}H_{72}Ba_2N_4S_8$ 1092.13 g/mol 100(2) K 0.71073 Å (0.125 x 0.143 x 0.511) f triclinic P -1 a = 11.5655(9) Å b = 15.3903(12) Å c = 16.1262(12) Å 2600.2(4) Å ³ 2 1.395 g/cm ³ 1.853 mm ⁻¹ 1112

Table S3. Sam	ple and cr	ystal data	for C_S	5C_012.
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Table S4. Data collection and structure refinement for C_SC_012.

Theta range for data collection	1.88 to 30.64°
Index ranges	-16<=h<=16, -22<=k<=22, -23<=l<=23

Reflections collected	86389		
Independent reflections	16021 [R(int) = 0.0484]		
Max. and min. transmission	0.8010 and 0.45	510	
Refinement method	Full-matrix least	t-squares on F ²	
Refinement program	SHELXL-2018/3	(Sheldrick, 2018)	
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$		
Data / restraints / parameters	16021 / 0 / 467		
Goodness-of-fit on F ²	1.044		
Δ/σ_{max}	0.004		
Final R indices	13489 data; I>2σ(I)	R1 = 0.0245, wR2 = 0.0474	
	all data	R1 = 0.0355, wR2 = 0.0508	
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0109P) ² +1.1752P] where P=(F _o ² +2F _c ²)/3		
Largest diff. peak and hole	0.855 and -0.865 eÅ ⁻³		
R.M.S. deviation from mean	0.097 eÅ ⁻³		

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