Photodegradation of crystal violet dye in water using octadecylamine-capped CdS nanoparticles synthesized from Cd(II) \(N,N'\)-diarylformamidine dithiocarbamates and their 2,2-bipyridine adducts

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ABSTRACT
Cadmium(II) complexes of \(N,N'\)-diarylformamidine dithiocarbamate of the general formula \([\text{Cd-}(L)_{2}] (L = N,N'-\text{bis}(2,6\text{-dimethylphenyl})\text{-formamidine dithiocarbamate} L1 (1), N,N'-\text{bis}(2,6\text{-disopropylphenyl})\text{-formamidine dithiocarbamate} L2 (2), N'-(2,6\text{-dichlorophenyl})-N(2,6\text{-dimethylphenyl})\text{-formamidine dithiocarbamate} L3 (3), N'-\text{bis}(2,6\text{-dichlorophenyl})-N(2,6\text{-disopropylphenyl})\text{-formamidine dithiocarbamate} L4 (4) and their 2,2-bipyridine (bipy) adducts, [Cd-\(L1\)_2bipy] (5), [Cd-\(L2\)_2bipy] (6), [Cd-\(L3\)_2bipy] (7), [Cd-\(L4\)_2bipy] (8)) have been synthesized and characterized using various spectroscopic and analytical techniques. For one of the 2,2-bipyridine adducts, the molecular structure was determined using single crystal X-ray structure as a six-coordinate Cd(II) complex in which two pairs of sulfur atoms from two dithiocarbamate ligands and a pair of nitrogen atoms from bipy completed the distorted octahedral geometry. Complexes 1, 3 and 5 were used as single source precursors for formation of octadecylamine capped cadmium nanoparticles, CdS1, CdS3 and CdS5. HR-TEM images of as-synthesized CdS1, CdS3 and CdS5 particles are nano-spherical in shape with size distributions ranging between 4 and 9 nm. The as-synthesized CdS nanoparticles were used as photocatalysts for degradation of crystal violet, with degradation efficiency of 75-84% and rate constants of 0.0050, 0.0043 and 0.0039 \(\text{min}^{-1}\) for CdS1, CdS3 and CdS5, respectively.

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Supplementary material can be accessed at http://doi:10.1080/00958972.2022.2123274

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1. Introduction

The discharge of wastewater from laboratories, industries and factories has caused havoc to the environment. These wastewaters contain azo dyes, herbicides, and pesticides which can be toxic to aquatic life, microorganisms, and even human beings [1]. Industrial dyes, most especially textile dyes, constitute a major organic water pollutant that pose great environmental danger [2]. They are known to be endocrine-disrupting chemicals [3] in addition to a host of other severe environmental impacts. Therefore, water polluted with organic dyes needs to be treated before discharging into the environment.

Photocatalytic degradation, using semiconductors, often affords complete elimination of organic pollutants from water [4]. Semiconductors absorb photons with energy equal or higher than their bandgap energy, which facilitates promotion of electrons from the valence band to the conduction band, creating electron holes in the valence band. Provided charge separations are valid, the photo-generated electrons and holes could migrate to the surface of the semiconductors (photocatalyst) and be used for degradation of pollutants via redox reactions [5]. Superoxide anion radicals (O$_2^-$) are produced from reduction of dissolved oxygen molecules by photo-generated electrons and simultaneously, photo-generated holes reacting with surface OH$^-$ ions of water molecules, to generate hydroxyl radicals (OH$^-$). Both *OH and O$_2^-$ participate in degradation of organic dyes [6]. However, it has been observed that the recombination rates of photo-generated electron-hole pair before superoxide activation step is very fast. Also, there is normally low light absorption yield. These two factors have been a major set-back to semiconductor-based photo-catalysts for dye degradation, hence the urge for development of new ones with less limitation [5].

Among semiconductors used in most technologies, CdS is extensively used due to their bandgap of ~2.42 eV which leads to a range of colors in the visible region when there is reduction in size [7]. In the photo-degradation of organic pollutants in water under visible light, CdS nanoparticles have been extensively exploited [8, 9]. They have also found use in photocatalytic water splitting and hydrogen production processes [10]. Their ability to absorb visible light effectively can be attributed to their conduction band edge which is sufficiently more negative than the reduction potential of protons, resulting in a relatively narrow band gap [11].

A limitation of the use of CdS in photocatalytic reactions is poor quantum efficiency. The main issue is the fast recombination of photo-generated charge carriers...
and photo-corrosion by self-oxidation during photocatalytic reaction [12]. Different methods have been adopted to improve the photocatalytic activity of CdS nanoparticles. Such methods include changing the surface structure of CdS nanoparticles (size and morphology) [13], deposition of CdS on polymers [14], or Nafion membranes [15] to afford well-distributed quantum sized CdS nanoparticles and doping with either metal or non-metal into the structure of CdS [16]. It has been established that the optical properties together with photocatalytic activities of photocatalysts highly depend on the morphology, particle shape and size, crystalline phase and active surface area [17].

In the preparation of CdS nanoparticles, various techniques such as microwave irradiation [18], biosynthesis [19], microemulsion [20], solvothermal [21], and thermal decomposition of single-source precursors [22] have been exploited. Among these techniques, thermal decomposition of single-source precursors has been reported to afford CdS nanoparticles of good size and shape with less impurities, which resulted in excellent photocatalytic properties [22]. We have previously reported the use of formamidine-based dithiocarbamate metal complexes to prepare well-dispersed metal sulfide nanoparticles with desirable photocatalytic properties [23]. Herein, we present the synthesis of cadmium(II) $N,N'$-diarylformamidine dithiocarbamate complexes and their 2,2-bipyridine adducts and their use as single source precursor to prepare CdS nanoparticles. The photocatalytic degradation of crystal violet dyes using the CdS nanoparticles, kinetics of photocatalysis and pH effects are discussed.

2. Experimental

2.1. Materials

All solvents (ACS reagent grades ≥ 99.5%) were obtained from Sigma-Aldrich and used as obtained without purification. Reagents: 2,2-bipyridine (99%), 2,6-diisopropylaniline (97%), 2,6-dimethylaniline (99%), 2,6-dichloroaniline (98%), triethyl orthoformate (99%) and carbon disulfide were also obtained from Sigma-Aldrich. CdCl$_2$H$_2$O (97%) and KOH (85%) were both obtained from Promark Chemicals South Africa.

2.2. Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded at 25 °C on a Bruker Avance III 400 MHz spectrometer. Both $^1$H and $^{13}$C NMR data were measured in parts per million relative to the residual solvent signals (chloroform-$d$ for $^1$H with $\delta = 7.26$ ppm and $^{13}$C NMR $\delta = 77.00$ ppm) or (DMSO-$d_6$ for $^1$H with $\delta = 2.50$ ppm and $^{13}$C NMR $\delta = 39.52$ ppm). Elemental analyses were recorded on a Vario elemental EL cube CHNS analyzer. IR spectra were obtained on a Perkin Elmer Universal ATR spectrum 100 FT-IR spectrometer. Photoluminescence emission spectra were recorded on Perkin Elmer LS 55 fluorescence spectrometer while UV–visible absorption spectra were recorded on Shimadzu UV–vis-NIR spectrophotometer. Structural and morphological characterization of the CdS nanoparticles were done using a field emission scanning microscope (SEM: JEOL JSM 6100) and a high-resolution transmission electron microscope (HR-TEM JEOL JEM 2100). Energy dispersive spectra were processed using EDS attached to (SEM: JEOL...
The powder XRD spectra was obtained using a Bruker D8 Advance with a high intensity Cu Kα radiation (λ = 0.15406 nm).

3. General synthesis method

3.1. Synthesis of Cd(II) dithiocarbamate complexes

The respective N,N'-diarylformamidine dithiocarbamate salts (2 mmol) L1–L4 (where L1 = N,N'-bis(2,6-dimethylphenyl)formamidine dithiocarbamate, L2 = N,N'-bis(2,6-diisopropylphenyl)formamidine dithiocarbamate, L3 = N'- (2,6-dichlorophenyl)-N-(2,6-dimethylphenyl)formamidine dithiocarbamate and L4 = N'-(2,6-dichlorophenyl)-N-(2,6-diisopropylphenyl)formamidine dithiocarbamate) were dissolved in 20 mL of acetonitrile. To the resulting mixtures, 1 mmol of hydrated cadmium chloride (CdCl2.C12H2O) dissolved in 5 mL of water was added dropwise and stirred for 30 min at room temperature. The pale cream solids were collected by filtration and washed thoroughly with diethyl ether four times. The complexes were then dried in an oven at 50°C and stored in a desiccator.

3.1.1. Synthesis of Cd-(L1)2 (1)

The reaction of L1 (0.3 g, 0.8 mmol) and CdCl2.C12H2O (0.08 g, 0.4 mmol) in acetonitrile furnished 1 as a pale cream powder. Yield 75%. Melting point 241-243°C. 1H NMR (DMSO, 400 MHz) δ (ppm): 1.99 (s, 12H, CH3–Ar), 2.15 (s, 12H, CH3–Ar), 6.86 (t, 2H, JH,H =7.52, Ar–H), 6.99 (d, 4H, JH,H = 7.52, Ar–H), 7.15 (s, 6H, Ar–H), 9.35 (s, 2H, –C(H)-N). 13C NMR (DMSO, 100 MHz) δ (ppm): 16.26, 17.06, 122.28, 125.99, 126.51, 126.89, 133.59, 138.91, 146.69, 214.62. IR v (cm⁻¹): 2945, 1643, 1468, 1246, 1126, 994, 429. UV–vis (CHCl3, λmax, nm), 292 and 314 (shoulder). Anal. Calcd for C36CdH26N4S4: C, 56.35; H, 4.99; N, 7.30; S, 16.71. Found: C, 56.29; H, 4.97; N, 7.25; S, 16.65.

3.1.2. Synthesis of Cd-(L2)2 (2)

The reaction of L2 (0.3 g, 0.6 mmol) and CdCl2.C12H2O (0.08 g, 0.3 mmol) in acetonitrile furnished 2 as a pale cream powder. Yield 80%. Melting point 250–252°C. 1H (CDCl3, 600 MHz): δ (ppm) 1.10 (m, 45H, –CH3–CH), 1.12 (m, 3H, –CH3–CH), 2.66 (m, 3H, CH–CH3), 2.77 (m, 3H, CH-CH3), 2.79 (m, 2H, CH-CH3), 7.06 (d, 4H, Ar–H), 7.09 (d, 6H, Ar–H), 7.13 (t, 2H, Ar–H), 9.30 (s, 2H, –C(H)-N). 13C NMR (CDCl3, 400 MHz) δ (ppm): 23.997, 24.04, 24.11, 24.92, 27.40, 28.14, 28.17, 29.06, 30.93, 123.42, 123.89, 124.13, 124.19, 129.40, 136.49, 145.32, 145.38, 145.79, 151.82, 207.04. IR v (cm⁻¹): 2960(w), 1637(s), 1467(s), 1129(s), 1001(s), 429. UV–vis (CHCl3, λmax, nm), 292 and 314 (shoulder). Anal. Calcd. for C52CdH70N4S4: C, 62.97; H, 7.11; N, 5.65; S, 12.93. Found: C, 62.77; H, 7.00; N, 5.60; S, 12.86.

3.1.3. Synthesis of Cd-(L3)2 (3)

The reaction of L3 (0.3 g, 0.74 mmol) and CdCl2.2H2O (0.07 g, 0.37 mmol) in acetonitrile furnished 3 as a pale cream powder. Yield 69%. Melting point 248–250°C. 1H-NMR (CDCl3, 400 MHz) δ (ppm) 2.33 (s, 12H, CH3–Ar), 6.92 (t, 2H, JH,H =8.00 Ar–H), 7.10 (s, 6H, Ar–H), 7.35 (d, 3H, JH,H =7.96 Ar–H), 7.66 (s, 1H, Ar–H), 8.70 (s, 2H, –C(H)-N). 13C NMR
3.1.4. Synthesis of Cd-(L4)2 (4)

The reaction of L4 (0.30 g, 0.64 mmol) and CuCl2•H2O (0.07 g, 0.32 mmol) in acetonitrile furnished 4 as a pale cream powder. Yield 72%. Melting point 254–255°C.

3.2. Synthesis of 2,2'-bipyridine adduct of Cd(II) dithiocarbamate complexes [Cd-(L)2(2,2'-bipy)]

The 2,2'-bipyridine adduct of the cadmium complexes were synthesized following literature procedures [24, 25] with slight modifications. 50 mL hot chloroform solution of 2,2'-bipyridine (1 mmol) was added to 50 mL hot acetonitrile solution of the parent complexes [Cd-(L)2] (1 mmol). The resultant mixture was refluxed for 1 h, filtered to a beaker and left undisturbed for 48 h. On evaporation, yellow solids were separated out and washed with diethyl ether three times and dried in an oven at 50°C.

3.2.1. Synthesis of [Cd-(L1)2bipy] (5)

The reaction of Cd(L1)2 (0.30 g, 0.4 mmol) and 2,2'-bipy (0.061 g, 0.4 mmol) in chloroform furnished 5 as a yellow powder. Yield 61%. Melting point 236-238°C. 1H NMR (CDCl3, 400 MHz) δ (ppm): 2.07 (s, 12H, CH3–Ar), 2.20 (s, 12H, CH3–Ar), 6.83 (t, 2H, JH,H=7.50 Ar–H), 6.94 (d, 4H, JH,H=7.50 Ar–H), 7.11 (d, 4H, JH,H=7.50 Ar–H), 7.17 (t, 2H, JH,H=7.92 Ar–H), 7.51 (t, 2H, JH,H=7.92 Ar–H), 7.98 (t, 2H, JH,H=7.50 Ar–H), 8.18 (d, 2H, JH,H=7.80 Ar–H), 9.46 (s, 2H, -C(H)=N). 13C NMR (CDCl3, 100 MHz) δ (ppm): 17.89, 18.70, 18.78, 121.40, 123.39, 125.56, 127.94, 127.99, 128.22, 128.90, 135.26, 139.12, 140.29, 147.88, 149.57, 151.40 and 216.98. IR ν (cm⁻¹): 2941(w), 1643(s), 1592(w), 1436(s), 1008(m), 871(s), 487(w). UV-Vis (CHCl3, λmax nm), 233, 292 and 319 (shoulder). Anal. Calcd. for C46CdH46N6S4: C, 59.82; H, 5.02; N, 9.10; S, 13.80. Found: C, 59.65; H, 4.97; N, 9.00; S, 13.74.

3.2.2. Synthesis of [Cd-(L2)2bipy] (6)

The reaction of Cd(L2)2 (0.40 g, 0.4 mmol) and 2,2'-bipy (0.063 g, 0.4 mmol) in chloroform furnished 6 as a yellow powder. Yield 55%. Melting point 247–249°C. 1H NMR (CDCl3, 400 MHz) δ (ppm): 1.16 (d, 17H, JH,H=6.84, CH–CH), 1.24 (m, 3H, CH3–CH), 2.84 (m, 3H, JH,H=6.72, CH–CH3), 2.98 (m, 3H, JH,H=6.76, CH–CH3), 3.24 (m, 1H, JH,H=6.88,
Table 1. The summary of X-ray crystal data collection and structure refinement parameters for 6.

| Empirical formula | C$_{31}$H$_{39}$Cd$_{0.5}$N$_{3}$S$_{2}$ |
|-------------------|---------------------------------|
| Formula weight    | 573.97                          |
| Crystal system    | Triclinic                       |
| Space group       | $P - 1$                         |
| $a$/Å             | 11.9075(2)                     |
| $b$/Å             | 12.1896(2)                     |
| $c$/Å             | 21.6229(3)                     |
| $\alpha$/$^\circ$| 88.9750(10)                    |
| $\beta$/$^\circ$ | 86.5570(10)                    |
| $\gamma$/$^\circ$| 79.5690(10)                    |
| Volume/Å$^3$      | 3081.00(8)                     |
| $Z$               | 4                               |
| $\rho$/g/cm$^3$   | 1.237                           |
| $\mu$/mm$^{-1}$   | 0.531                           |
| $F(000)$          | 1208.0                          |
| Crystal size/mm$^3$| $0.40 \times 0.25 \times 0.21$ |
| $\theta$ Range for data collection/$^\circ$ | 3.484 to 56.732 |
| Index ranges      | $-15 \leq h \leq 15$           |
|                   | $-16 \leq k \leq 15$           |
|                   | $-28 \leq l \leq 28$           |
| Reflections collected | 36713                      |
| Independent reflections | 15101 [Rint=0.0209]           |
| Data / restraints / parameters | 15101/0/674               |
| Goodness-of-fit on $F^2$ | 1.050                      |
| Final R indexes [I$>$ $=2\sigma$ (I)] | $R_1=0.0344$, $wR_2=0.08806$ |
| Final R indexes [all data] | $R_1=0.0453$, $wR_2=0.0865$  |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.44 and $-0.41$ |

CH-CH$_3$, 3.31 (m, 1H, $J_{H,H}=6.72$, CH–CH$_3$), 7.10 (m, 4H, Ar–H), 7.17 (d, 2H, Ar–H), 7.25 (t, 4H, $J_{H,H}=7.64$, Ar–H), 7.42 (t, 2H, $J_{H,H}=7.76$, Ar–H), 7.50 (t, 2H, $J_{H,H}=7.70$, Ar–H), 7.98 (t, 2H, $J_{H,H}=7.60$, Ar–H), 8.17 (d, 2H, $J_{H,H}=7.52$, Ar–H), 9.59(s, 2H, –CH-N), IR ν (cm$^{-1}$): 2959(w), 1639(s), 1592(w), 1407(w), 1017(m), 875(s), 500(w). UV–vis (CHCl$_3$, $\lambda_{max}$ nm), 232, 292, 322 (shoulder). UV–vis (CHCl$_3$, $\lambda_{max}$ nm), 232, 292 and 322 (shoulder). Anal. Calcd. for C$_{62}$CdCl$_4$H$_{78}$N$_6$S$_4$: C, 64.71; H, 3.29; N, 8.29; S, 12.61.

3.2.3. Synthesis of [Cd-(L3)$_2$bipy] (7)

The reaction of Cd(L3)$_2$ (0.36 g, 0.4 mmol) and 2,2’-bipy (0.058 g, 0.4 mmol) in chloroform furnished 7 as a yellow powder. Yield 65%. Melting point 239–241 °C. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 2.24 (s, 12H, CH$_3$–Ar), 6.87 (t, 2H, $J_{H,H}=8.08$ Ar–H), 7.11 (d, 5H, $J_{H,H}=7.40$ Ar–H), 7.17 (d, 2H, $J_{H,H}=7.96$ Ar–H), 7.23 (t, 5H, $J_{H,H}=7.67$, Ar–H), 7.54 (t, 2H, $J_{H,H}=7.54$, Ar–H), 8.00 (t, 2H, $J_{H,H}=7.60$, Ar–H), 8.16 (d, 2H, $J_{H,H}=8.04$, Ar–H), 9.60 (s, 2H, –CH-N). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 17.90, 18.83, 121.53, 124.50, 125.88, 127.02, 128.10, 128.23, 128.73, 135.60, 139.49, 139.57, 144.94, 149.55, 154.06 and 218.12. IR ν (cm$^{-1}$): 2920(w), 1642(s), 1595(w) 1434(s), 1017(m), 875(s), 494(w). UV–vis (CHCl$_3$, $\lambda_{max}$ nm), 232, 292 and 321 (shoulder). Anal. Calcd. for C$_{42}$CdCl$_4$H$_{34}$N$_6$S$_4$: C, 64.71; H, 6.77; N, 7.21; S, 11.14.

3.2.4. Synthesis of [Cd-(L4)$_2$bipy] (8)

The reaction of Cd(L4)$_2$ (0.40 g, 0.4 mmol) and 2,2’-bipy (0.074 g, 0.4 mmol) in chloroform furnished 8 as a yellow powder. Yield 68%. Melting point 243–245 °C. 1H NMR (CDCl$_3$, 400 MHz) δ (ppm): 1.18 (d, 12H, $J_{H,H}=6.76$, CH$_3$–CH), 1.22 (d, 12H, $J_{H,H}=6.76$, 2H, $J_{H,H}=6.76$, CH$_3$–CH), 2.24 (s, 12H, CH$_3$–Ar), 6.87 (t, 2H, $J_{H,H}=6.76$, CH–CH), 7.11 (d, 5H, $J_{H,H}=7.40$ Ar–H), 7.17 (d, 2H, $J_{H,H}=7.96$ Ar–H), 7.23 (t, 5H, $J_{H,H}=7.67$, Ar–H), 7.54 (t, 2H, $J_{H,H}=7.54$, Ar–H), 8.00 (t, 2H, $J_{H,H}=7.60$, Ar–H), 8.16 (d, 2H, $J_{H,H}=8.04$, Ar–H), 9.60 (s, 2H, –CH-N). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 17.90, 18.83, 121.53, 124.50, 125.88, 127.02, 128.10, 128.23, 128.73, 135.60, 139.49, 139.57, 144.94, 149.55, 154.06 and 218.12. IR ν (cm$^{-1}$): 2920(w), 1642(s), 1595(w) 1434(s), 1017(m), 875(s), 494(w). UV–vis (CHCl$_3$, $\lambda_{max}$ nm), 232, 292 and 321 (shoulder). Anal. Calcd. for C$_{42}$CdCl$_4$H$_{34}$N$_6$S$_4$: C, 64.71; H, 6.77; N, 7.21; S, 11.14.
3.3. Single crystal X-ray diffraction

Structure refinement parameters as well as crystallographic data for 6 are given in table 1. Evaluation of crystals and collection of data were done on a Bruker Smart APEXII diffractometer with Mo Kα radiation (0.71073 Å) equipped with an Oxford Cryostream low temperature apparatus operating at 101 K for all samples. Reflections were collected at different starting angles and the APEXII program suite was used to index the reflections [26]. Reduction of data was carried out using the SAINT software [27] and the absorption corrections and scaling were applied using SADABS multi-scan technique [28]. The structure was solved by direct methods using the SHELXS program and refined using SHELXL program [29]. Graphics of the crystal structure was drawn using Mercury software [30]. Non-hydrogen atoms were first refined isotropically and then by anisotropic refinement with the full-matrix least squares method based on $F^2$ using SHELXL.

3.4. Preparation of ODA capped CdS nanoparticles

The cadmium sulfide nanoparticles were prepared following a literature procedure [31]. 5 g of octadecylamine (ODA) was placed in a three-neck flask, degassed under pressure at 50°C and then heated to 180°C under nitrogen. Thereafter, 0.5 g of each of the respective precursors (complexes 1, 3 and 5) was dissolved in 5 mL of Trioctylphosphine (TOP) and immediately injected into the hot ODA at 180°C. A decrease in temperature of about 20°C was observed and the solution was allowed to stabilize at 180°C and further heated for 1 h. The reaction solution was cooled to 60-70°C and 80 mL of methanol was added to the solution to precipitate the ODA-capped CdS nanoparticles. The resulting CdS nanoparticles were separated by centrifugation and washed five times with methanol to ensure removal of excess ODA. The ODA-capped CdS nanoparticles were then dispersed in toluene for further analyses. In this report, the ODA-capped CdS nanoparticles synthesized from 1, 3, and 5 are named CdS1, CdS3, and CdS5.

3.5. Photocatalytic degradation of crystal violet dye under visible light using ODA-capped CdS nanoparticles nanoparticles

Photodegradation of crystal violet dye was carried out by dispersing 50 mg of the photocatalyst (CdS1, CdS3, or CdS5) into 50 mL crystal violet (10 mg/L) and stirring in the dark for 60 min to achieve the adsorption–desorption equilibrium. The resulting suspension was illuminated with 70W incandescent mercury lamp to initiate
photoreaction. During the irradiation, the degraded samples were monitored at regular intervals (60 min) for 6 h. The concentration of crystal violet was determined at maximum wavelength of 590 nm. The degradation efficiency was calculated using Equation (1) [32],

\[
\text{Degradation} \, (\%) = \frac{C_0 - C_t}{C_0} \times 100
\]

where \( C_0 \) and \( C_t \) are concentration of the dye initially and at a specific time “t”, respectively. To study the effect of pH on the photodegradation process, the initial solution was adjusted to pH 3, pH 6 and pH 10 using 0.1 M NaOH or 0.1 M HCl.

4. Results and discussion

4.1. Synthesis of Cd(II) dithiocarbamate complexes and their 2,2-bipyridine adducts

The synthesis of the potassium salts of \( N,N' \)-diarylformamidine dithiocarbamate \( \text{L1–L4} \) have been reported in the previous work [33, 34] while the synthesis route of the complexes and their bipy adducts are presented in Scheme 1. Complexes \( \text{1–4} \) were prepared by reaction of appropriate dithiocarbamate ligands (\( \text{L1–L4} \)) with hydrated cadmium chloride in a 2:1 ratio to afford air stable pale cream solids. The resulting Cd(II) complexes, \( \text{1–4} \), were reacted with bipy in a ratio of 1:1 to give their respective adducts \( \text{5–8} \) which are also air stable and yellow. The adducts generally had lower
melting points (236–249°C) relatively to the parent complexes 1–4 (241–255°C). All the complexes were soluble in chloroform, dichloromethane and dimethyl sulfoxide but partially soluble in other polar solvents.

4.2. Spectroscopic studies

4.2.1. Nuclear magnetic resonance

NMR spectra (1H and 13C) of 1–4 were obtained in DMSO-d while the ones for adduct complexes were obtained in chloroform-d. 2D NMR was utilized to assign the peaks of each complex. The azomethine proton (NC(H)/C1N) was used to follow the transformation of the potassium dithiocarbamate salts (L1–L4) to Cd(II) dithiocarbamate complexes (1–4) and to their respective bipy adducts (5–8). The azomethine proton shifted from 9.86 to 10.39 ppm in L1–L4 to 8.70–9.79 ppm in 1–4 and then shifted downfield to 9.43–9.80 ppm in adducts 5–8 (Table 2). A slight upfield shift was observed in the signals of the aliphatic protons from 1–4 to 5–8. For example, the methyl protons in 1 (parent complex) were observed at 1.99 and 2.15 ppm but downfield to 2.07 and 2.20 ppm in 5 (adduct). The aromatic protons due to dithiocarbamate ligands were observed in 1–4 at 6.86–7.46 ppm while the ones for 5–8 appeared at 7.51–8.17 ppm. Comparing the quaternary thiouride carbon peaks (–NCS2) of 1–4 to 5–8 in the 13C-NMR spectra; it was observed that peak values of 5–8 seem to be higher when compared to 1–4. The deshielding of carbon signals (–NCS2) in 5–8 could be attributed to the ability of bipy to withdraw electron donating from these compounds and is consistent with the effect of reduced electronic cloud over the MS2CN region of dithiocarbamate metal complexes [25, 35].

4.2.2. Fourier-transform infrared and UV-visible spectroscopy

FT-IR spectra of 1–8 exhibited two vibrational bands; v(N–CS2) and v(C–S) characteristic of dithiocarbamate complexes [36, 37] and v(C–Nstr) of the azomethine [38, 39]. The v(C–N) has been used as a measure of contribution of the thiouride form to the complexes [40, 41]. The vibrational frequencies at 1408–1479 cm⁻¹ in all the complexes is attributed to the v(N–CS2) thiouride band. The position of these bands in 1–8 indicate partial double bond character of C–N [42, 43]. The values of v(C–N) in 5–8 is lower than 1–4, ascribed to the change in coordination geometry around the metal center from tetrahedral in the parent complexes to octahedral in the adducts. The v(C–S) band appears at 989–1017 cm⁻¹ as a single peak in all the complexes and
this confirms the bidentate coordination of dithiocarbamate as reported earlier [44–46]. The vibrational frequencies at 1635–1643 cm⁻¹ in 1–8 can be assigned to ν(C-Nstr) of the azomethine in the dithiocarbamate ligands [37, 47]. Vibrational bands associated to bipy are observed at 1000–1600 cm⁻¹ [48, 49]. In this study, these bands are masked by the dithiocarbamate ligands except the ones at 1592–1600 cm⁻¹.

In the electronic absorption spectra of 1–8 (Figure 1a and b), one major band and one shoulder were observed. All these bands are below 380 nm, confirming the presence of intraligand π-π* transition, mainly ascribed to N–C–S and S–C–S of the dithiocarbamate ligands [23].
4.3. X-Ray structural analysis

Single crystals of 6 were grown out from a mixture of dichloromethane and methanol at 3:1 by evaporating the solvent slowly. The molecular structure is presented in Figure 2 while selected bond distances and angles are given in Table 3. The asymmetric unit contains one whole molecule. Complex 6 is mononuclear with Cd(II) six-coordinate with two pairs of sulfurs from two dithiocarbamate ligands and a pair of nitrogens from bipy to adopt a distorted octahedral geometry. The deviation from perfect octahedral geometry is mainly due to the small bite angle of the planar bipyridine; [N1–Cd1–N2 = 69.39(6)], and this is not exceptional to other complexes with N,N donor adducts [50, 51]. The C–N bond distances of the –NCS$_2$ fragment of the ligands in the complexes [C–N = 1.375(2)] fall between a typical single C–N bond (1.47 Å) and ideal C–N bond (1.28 Å), table 3, and this implies the delocalization of π-electron over the –NCS$_2$ fragment in the complexes [52, 53]. Also, the C–S bond lengths of the –NCS$_2$ fragment in the complex are intermediate between typical C–S (1.82 Å) and C–S (1.67 Å) [54, 55].

4.4. Preparation and characterization of ODA-capped CdS nanoparticles

Compounds 1, 3, and 5 were used as a source to prepare the CdS nanoparticles. These complexes were chosen to study the possible effect of varying the ligand backbone of the complexes on the morphology of the as-synthesized CdS nanoparticles. For example, 1 has a symmetrical formamidine backbone with electron-donating group, i.e. CH$_3$, 3 has unsymmetrical formamidine backbone with electron-withdrawing, i.e. Cl and 5 is a bipy adduct of 1. The as-synthesized CdS nanoparticles were prepared by dissolving the precursor, Cd(II) metal complexes in 5 mL of trioctylphosphine (TOP) and immediately injected into hot octadecylamine (ODA) at 180 °C under suitable apparatus set-up and experimental conditions. Methanol (80 mL) was added to the solution in the flask to precipitate the ODA-capped CdS nanoparticles and were

| Parameters | 1 |
|------------|---|
| Bond distances | |
| Cd1–S1       | 2.7140(5) |
| Cd1–S2       | 2.6124(5) |
| Cd1–N1       | 2.6965(5) |
| Cd1–S4       | 2.6379(5) |
| Cd1–N1       | 2.3636(17) |
| Cd1–N2       | 2.3508(16) |
| CSBA–N3      | 1.375(2) |
| CSBA–N5      | 1.375(2) |
| CSBA–S1      | 1.6972(2) |
| CSBA–S2      | 1.708(2) |
| C4BA–S3      | 1.708(2) |
| C4BA–S4      | 1.700(2) |
| Bond angles  | |
| S1–Cd1–S2    | 67.748(16) |
| S3–Cd1–S4    | 67.367(16) |
| N1–Cd1–N2    | 69.39(6) |
| S1–CSBA–S2   | 121.08(12) |
| S3–C4BA–S4   | 120.46(11) |
separated by centrifugation. The as-synthesized CdS nanoparticles were thoroughly washed with methanol five times to remove excess ODA.

4.4.1. Powder X-ray diffraction studies of ODA capped CdS nanoparticles

Powder XRD patterns for CdS1, CdS3 and CdS5 are shown in Figure 3a–c. The diffraction peaks in all the spectra were indexed to be a hexagonal phase (Greenockite, syn CdS) which perfectly match standard data from the JCPDS card No 00-041-1049 with space group $P_{6_3}mc$. The X-ray diffraction patterns of all the CdS nanoparticles exhibit five peaks at 24.80°, 26.51°, 36.62°, 43.68° and 51.83° that can be indexed to (100), (002), (102), (110) and (112). An extra peak which can be indexed to (103) was observed in the spectra of CdS5. We can note that

Figure 3. Powder XRD diffraction pattern of (a) CdS1 (b) CdS3 (c) CdS5.

Figure 4. Energy dispersive X-ray spectra of (a) CdS1 (b) CdS3 (c) CdS5.
the patterns were very similar pointing to the possibility of little influence of ligand backbone with regard to structure.

4.4.2. Energy-dispersive X-ray spectral (EDAX) studies

Energy-dispersive X-ray spectra of CdS₁, CdS₃ and CdS₅ are given in Figure 4a–4c. EDAX spectra of CdS₁, CdS₃ and CdS₅ showed the presence of strong signals for Cd and S. The elemental analytical data of the as-synthesized cadmium sulfide nanoparticles showed that the atomic ratio of Cd to S is 4:1 in all the spectra. This indicates that, the introduction of 2,2-bipyridine to the cadmium complexes had no effect on the elemental analysis of the as-synthesized CdS materials. Traces of carbon were also seen on the spectra, and this can be attributed to carbon of the ODA.

4.4.3. Field emission scanning electron microscopy (FESEM) studies of ODA capped CdS nanoparticles

The cadmium complex precursors gave different morphologies for the as-synthesized cadmium sulfide nanoparticles as seen from the FESEM images, Figure 5a–c. The CdS nanoparticles have rough surfaces and it was evident that different precursors gave images with different porosity. The FESEM images of CdS₃ and CdS₅ showed that the particles are porous and have uniform particles shapes when compared to CdS₁. CdS₅ has the highest porosity. The difficulty to estimate the crystallite size of the CdS nanoparticles from their powder XRD diffraction pattern might be due to their rough surfaces as seen in FESEM images [56]. The mapping diagram for CdS₁, CdS₃, and CdS₅, Figure 5d–f, showed that both Cd and S are well distributed on the surface of the cadmium sulfide nanoparticles.

Figure 5. FESEM images (a) CdS₁ (b) CdS₃ (c) CdS₅ mapping of (d) CdS₁ (e) CdS₃ and (f) CdS₅.
4.4.4. High-resolution transmission electron microscope (HR-TEM) studies of ODA-capped CdS nanoparticles

The HR-TEM images of CdS1, CdS3, and CdS5 are presented in Figure 6a–c. The HR-TEM images of the CdS nanoparticles synthesized from different precursors showed remarkable changes in the dispersity of the nanoparticles and they are all spherical in shape. CdS5 synthesized using 5 (2,2-bipyridine of 1) are well dispersed when compared to their counterparts, CdS1 synthesized from 1. The average size ranges between 6-9 nm for CdS5 and 4–7 nm for CdS1 and CdS3. This showed that, the 2,2-bipyridine in precursor does not affect sizes of nanoparticles remarkably as previously reported by Srinivasa and Thirumaran [25]. Aggregation of particles is observed, especially in the images of CdS1 and CdS3. This could be attributed to the effect of small dimensions and high surface energy associated with nanoparticles [56].

4.4.5. FT-IR of ODA-capped CdS nanoparticles

FT-IR spectroscopy was used to confirm the presence of ODA on the surface of the as-synthesized CdS nanoparticles. The peaks at 2913–2911 and 2847–2848 cm\(^{-1}\) are
ascribed to the asymmetric and symmetric stretching vibration of C–H of the capping agent (ODA). The N–H stretching and bending vibrational frequencies appear at 3313–3311 cm\(^{-1}\) and 1661–1662 cm\(^{-1}\), at lower frequency when compared to free octadecylamine and this indicates the binding of the amine group of ODA to the CdS nanoparticles via nitrogen lone pairs [57].

**4.4.6. Optical properties of ODA-capped CdS nanoparticles**

The UV–visible spectra of CdS1, CdS3, and CdS5 were recorded in toluene and are given in figure 7a. The electronic spectra of CdS1 showed absorption maximum at 250 nm while the ones for CdS3 and CdS5 were at 251 nm and are attributed to the exciton peak of CdS. The broad shoulder peaks around 290 nm in all the spectra might result from surface states of the aggregated particles [58].

In the photoluminescence (PL) spectra of the as-synthesized cadmium sulfide nanoparticles, figure 7b, two emission peaks were observed at 520 and 530 nm when excited at 370 nm. The peak at 520 nm corresponds to the near band edge (NBE) emission, while the peak at 530 nm corresponds to the deep levels or the trap-stated emission due to the presence of many defects such as interstitial vacancies [59].

**5. Photocatalytic degradation of crystal violet using ODA-capped CdS photocatalyst**

The photocatalytic activity of the synthesized CdS nanoparticles was evaluated using crystal violet dye under visible light irradiation. Figure 8a–c shows the absorption spectrum of the dye at different time intervals. The decolorization of crystal violet is indicated by the decrease in absorption intensity as indicated in the spectrum, which confirms the destruction of the chromophore responsible for absorption. An almost complete degradation was observed after 360 min of irradiation time at 84.4%, 81.1% and 75.23% for CdS1, CdS3, and CdS5 (Figure 8d). CdS5 has a lower degradation efficiency; this could be due to short transportation length during immigration of electron-hole recombination because of large particle size and hence they cannot participate in the reaction process [32]. The degradation efficiencies of the as-synthesized ODA-capped CdS nanoparticles were compared to the ones previously reported. The use of uncapped CdS nanoparticles as a photocatalyst (0.25 g) in the degradation of crystal violet gave 43.27% efficiency for 180 min as reported by Upadhyay et al. [60] while thioglycolic acid-capped CdS, potassium pyrosulphate-capped CdS and disodium salt of EDTA-capped CdS (0.1 g for each) gave 96%, 95% and 76% degradation efficiency for 105 min as reported by Prasad et al. [61].

Pseudo-first order kinetics equation was used to determine the rate of reaction. The rate constant “k” was calculated using equation (2) [62] and their graphical plot shown in Figure 8e–f.

\[
k = \frac{\ln(C_0/C_t)}{t_{(time)}}
\]  

(2)
The rate constant values for crystal violet degradation are 0.0050, 0.0043 and 0.0039 min$^{-1}$ for CdS1, CdS3, and CdS5, respectively. Relating to this result, it is evident that CdS5 has low efficiency due to its fast electron-hole recombination [63].
Effect of pH

The surface-charge of photocatalyst is always affected by pH which makes it an important parameter of consideration for photodegradation. As a result of surface-charge alteration, there is a shift in adsorption of dye on the photocatalyst surface, hence affecting the rate of reactivity [64]. Figure 9a–b shows the degradation rates of activity in acidic (pH 3) and alkaline (pH 10) media. The degradation rate in acidic media is low due to cationic properties of crystal violet, which results in absence of electrostatic attraction between the photocatalyst and the dye while in the alkaline media the electrostatic attraction increases thus increasing the degradation rate [65].

6. Conclusion

We report the synthesis and characterization of cadmium(II) complexes of \( N,N' \)-diarylformamidine dithiocarbamate and their 2,2-bipyridine adducts. The complexes were characterized by spectroscopic techniques and elemental analysis. X-ray structural analysis of 6 showed that, the Cd(II) metal center was six-coordinate with two pairs of sulfur atoms from two dithiocarbamate ligands and a pair of nitrogen atoms from 2,2-bipyridine rings to adopt a distorted octahedral geometry. Complexes 1, 3 and 5 were used to prepare octadecylamine-capped cadmium sulfide \( \text{CdS}1 \), \( \text{CdS}3 \), and \( \text{CdS}5 \) with sizes ranging from 4 to 9 nm. The powder XRD pattern confirms hexagonal phase (Greenockite, syn CdS) of cadmium sulfide in all the as-synthesized CdS nanoparticles. The as-synthesixed CdS nanoparticles were used as photocatalysts for degradation of crystal violet with degradation efficiencies of 75–84% at 360 min.

Disclosure statement

The authors declare no competing financial interest.
**Funding**

The authors acknowledge the college of Agriculture, Science and Engineering, University of Kwazulu-Natal (UKZN), and the National Research Foundation (NRF) South Africa for financial support (Grant number: 119342).

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