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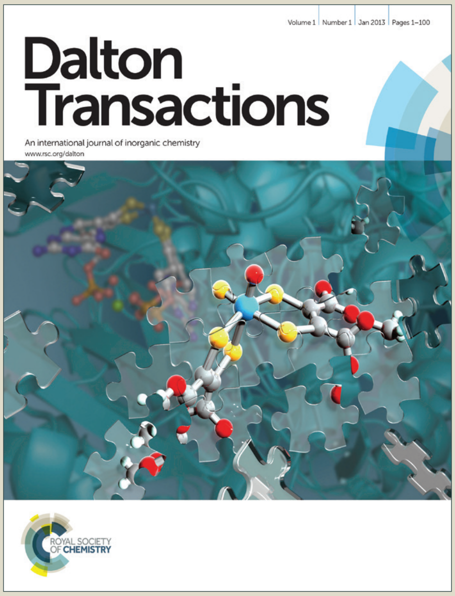

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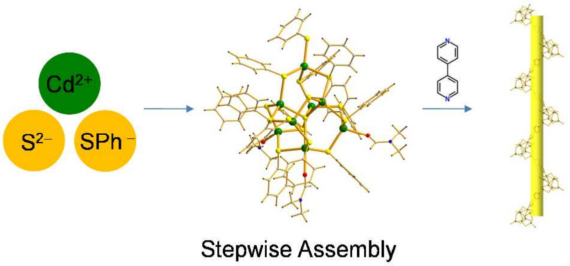

A semiconducting coordination polymer with 1D helical structure was constructed by stepwise assembly of chalcogenolate clusters and organic linkers.

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ARTICLE

Stepwise assembly of a semiconducting coordination polymer $[Cd_8S(SPh)_{14}(DMF)(bpy)]_n$ and its photodegradation of organic dyes

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Chalcogenolate clusters can be interlinked with organic linkers into semiconducting coordination polymers with photocatalytic properties. Here, discrete clusters of $Cd_8S(SPh)_{14}(DMF)_3$ were interlinked with 4,4'-bipyridine into a one dimensional coordination polymer of $[Cd_8S(SPh)_{14}(DMF)(bpy)]_n$ with helical chains. A stepwise mechanism for the assembly of the coordination polymer in DMF was revealed by an *ex situ* dynamic light scattering study. The cluster was electrostatically neutral and showed a penta-supertetrahedral structure. During the assembly each cluster was interlinked with two 4,4'-bipyridine molecules, which replaced the two terminal DMF molecules of the clusters. In their solid-state forms, the cluster and the coordination polymer were semiconductors with wide band gaps of 3.08 and 2.80 ev. They photocatalytically degraded rhodamine B and methylene blue in aqueous solutions. The moderate conditions used for the synthesis could allow for further *in-situ* studies of the reaction-assembly of related clusters and coordination polymers.

Introduction

Coordination polymers (CPs) or metal-organic frameworks (MOFs) continue to attract attention due to their intriguing structures and potential applications in gas storage, separation, and catalysis.[1-6] CPs with different topologies have been well developed during the last few decades;[7-8] however, large inorganic clusters with multiple coordination sites are largely unexplored building blocks for functional CPs.[9-11]

Supertetrahedral chalcogenide and chalcogenolate (SCC) clusters are such large inorganic clusters with diamond-like structures and size-dependent properties.[12-13] The ability of the sulphur atom to coordinate and form chemical bonds with three (μ_3) or four (μ_4) metal atoms is crucial to the construction of the large SCC clusters. Since Dance *et al.* developed such clusters in the 1980s, many efforts have been made to synthesize large clusters and superlattices with well-defined structures and semiconducting properties.[14-18] The semiconducting SCC clusters with a Cd–S–SPh composition is the largest group of SCC clusters.[19] The phenyl groups are at the interface of the clusters where they exert a stabilising power, and contribute positively to the solubility of the clusters in organic solvents. As expected, the relative fraction of phenyl groups in the clusters decreases with size.[20] Discrete SCC clusters can contain from one up to hundreds of chemically bonded cadmium atoms with diameters up to 2.3 nm.[20-21] By linking SCC clusters with multi-functional organic linkers, CPs with properties different from the constituting units can be synthesised.[22] Several examples of such CPs with well-defined crystal structures and optical properties have been reported. Examples of CPs are those based on SCC clusters with Zn_8, Cd_8, Cd_{10}, Cd_{17}, and Cd_{32} cores.[22-27] In addition, Vaqueiro *et al.* prepared CPs by linking SCC clusters of $[Ga_{10}S_{16}(NC_7H_9)]^{2-}$ with bipyridines.[28] Feng *et al.* prepared the first three-dimensional (3D) CPs by linking In–(Cd)–S based SCC clusters with imidazoles. These CPs were microporous with a relatively high uptake of CO_2.[29] Recently, we reported on a 3D CP based on heterometallic $Cd_6Ag_4(SPh)_{16}$ clusters interlinked by rigid and conjugated bipyridines. This CP was semiconducting and microporous.[30] In that study, both the clusters and the CP were effective photocatalysts for the degradation of rhodamine B in aqueous solution. Here, we expand on that study and present a cadmium chalcogenolate cluster of $Cd_8S(SPh)_{14}(DMF)_3$ (**1**) and its one dimensional CP of $[Cd_8S(SPh)_{14}(DMF)(\mathbf{bpy})]_n$ (**2**) (DMF: *N,N'*-dimethylformamide, **bpy**: 4,4'-bipyridine). The formation mechanism of CP **2** and the photocatalytic effect of cluster **1** and CP **2** were investigated.

Experimental section

General method

All the chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. $Cd(SPh)_2$ was prepared according to a literature method.[31] Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyser. Fourier transform infrared (FT-IR) spectra were recorded using a Varian 670-IR FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a PANalytical powder X-ray diffractometer with an X'Celerator detector (CuKα1 radiation; λ = 1.5418 Å). Thermal gravimetric analysis (TGA) was performed on data recorded on a TGA-Perkin Elmer TGA 7 analyser. UV/vis absorption and solid-state reflectance spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. $BaSO_4$ was used as a 100% reflectance substance for the detected solid state reflectance spectra. Dynamic light scattering (DLS) experiments were conducted using a Malvern Instruments Zetasizer Nano ZS.

Preparation of $Cd_8S(SPh)_{14}(DMF)_3$ (1)

$Cd(SPh)_2$ (198 mg, 0.6 mmol) was dissolved in a mixture of 4 mL of DMF and 2 mL of CS_2. After being stirred overnight, the clear yellow solution was carefully covered by 10 mL of CH_3OH. Large colourless crystals of **1** were obtained in one week. Yield: 131 mg (73% based on $Cd(SPh)_2$). Anal. Calcd. for $C_{93}H_{91}N_3O_3S_{15}Cd_8$: C, 41.69; H, 3.42; N, 1.57. Found: C, 41.59; H, 3.45; N, 1.55. IR (cm^{-1}): ν (C–H) 3068 (w), ν (C=O) 1643 (s), ν (C–S) 684(s).

Preparation of $[Cd_8S(SPh)_{14}(DMF)(bpy)]_n$ (2)

Cluster **1** (80 mg, 0.03 mmol) and **bpy** (16 mg, 0.1 mmol) was mixed and dissolved in 3 mL of DMF. The mixture was then stirred and heated to 100°C for 24 h. By a slow evaporation of the pale yellow filtration, yellow crystals of **2** were obtained within two weeks. Yield: 55 mg (65% based on **1**). Anal. Calcd. for $C_{100}H_{90}N_4O_2S_{15}Cd_8$: C, 43.52; H, 3.29; N, 2.03. Found: C, 43.63; H, 3.27; N, 2.05. IR (cm^{-1}): ν (C–H) 3069 (w), ν (C=O) 1644 (s), ν (C=N) 1596 (w), 1528 (w), ν (C–S) 683 (s).

Photocatalysis measurement

The photocatalytic activities of cluster **1** and CP **2** were evaluated regarding the degradation of Rhodamine B (RhB) and methylene blue (MB) aqueous solution under visible light irradiation. A 250W incandescent lamp was used as a visible light source. Typically, 20 mg of **1** or **2** were dispersed in 10 mL of aqueous dye solution (4.18×10^{-5} M). These suspensions were irradiated by light during stirring. Aliquots of 1 mL were withdrawn at an interval of 30 min during the irradiation. Dispersed **1** or **2** were removed by centrifugation, and the concentration of the dye in the sample solution was analysed by UV/vis spectroscopy.

X-ray crystallography

Crystallographic data and experimental details of **1** and **2** are summarised in Table 1. The data were collected on a Bruker SMART Apex 2000 CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 296(2) K. Data reductions were performed with SAINT.[32] Absorption corrections were applied using SADABS.[33] Structures were solved by direct methods and refined by least squares on F^2 using the SHELXL software package.[34-35] All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically for **1** and **2**.

Results and discussions

The SCC cluster **1** was synthesised in DMF, at room temperature, by reacting $Cd(SPh)_2$ and CS_2. An excess of CS_2 was used during the synthesis, and it served as both a co-solvent and source of sulphur. Cluster **1** was soluble in DMF and dimethyl sulfoxide but insoluble in other common solvents. Thermal gravimetric analysis (TGA) showed that it was quite thermally stable with a decomposition onset temperature of 450 °C under a N_2 atmosphere (Fig. S3). The residue after TGA was hexagonal CdS, as shown by the analysis of PXRD data (Fig. S4). (With controlled and optimised conditions, cluster **1** could be a precursor for the preparation of semiconducting CdS nanocrystals).

Table 1 Crystal data and structure refinement details of cluster **1** and coordination polymer **2**.

Compound	1	2·DMF
Empirical formula	$C_{93}H_{91}N_3O_3S_{15}Cd_8$	$C_{100}H_{90}N_4O_2S_{15}Cd_8$
Formula weight	2678.79	2759.86
Crystal system	triclinic	monoclinic
Space group	P–1	$P_2(1)/n$
a (Å)	13.9033(3)	13.5519(14)
b (Å)	18.5803(3)	26.283(3)
c (Å)	21.1933(4)	32.050(4)
α (°)	94.8390(10)	90.00
β (°)	96.9180(10)	98.004(7)
γ (°)	105.8390(10)	90
V (Å^3)	5189.06(17)	11305(2)
Z	2	4
ρ (g cm^{-1})	1.714	1.622
μ (mm^{-1})	1.954	1.796
F(000)	2636	5432
T/K	296(2)	296(2)
Observed reflections	96974	94590
Unique reflections	23752 (R_{int} = 0.0321)	19880 (R_{int} = 0.1563)
GOF	1.032	1.017
$R1$, w$R2$ [I>2σ(I)]	0.0399, 0.0947	0.0706, 0.1654
$R1$, w$R2$ (all data)	0.0651, 0.1071	0.1694, 0.2138

The CP **2** formed from clusters **1** and **bpy** linkers by crystallisation from a DMF solution upon slow evaporation. It seemed the good solubility and the formal neutrality of cluster **1** were important for the formation of CP **2**. The weak basic nitrogen atoms of the heterocycle based linker (**bpy**) ligated with the terminal Cd atoms and formed relatively strong single-coordination M–N bonds.[36] Related pyridyl and imidazolyl groups have been shown to be effective for organising SCC clusters into CPs.[22-30] Multi-carboxylic acid ligands, commonly used to construct CPs or metal-organic frameworks (MOFs) are, however, not suitable for organising SCC clusters, as the chelate bond O–M–O may destroy the tetrahedral coordination structure.

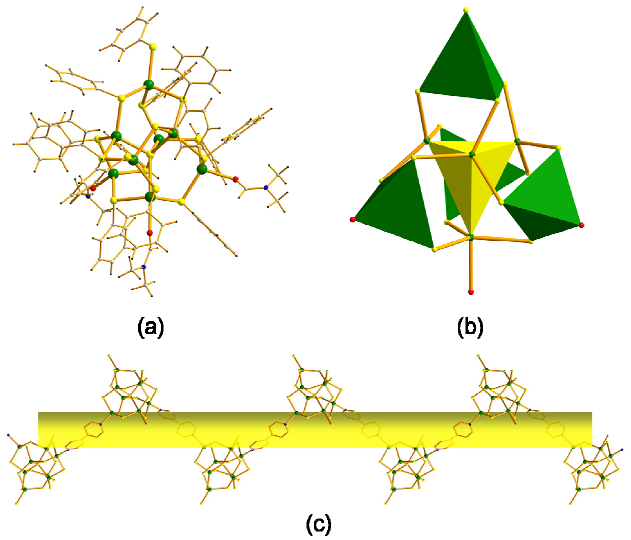


Fig. 1 (a) Molecular structure and (b) core structure of cluster **1** $Cd_8S(SPh)_{14}(DMF)_3$. Green, cadmium; yellow, sulphur; red, oxygen; blue, nitrogen; grey, carbon; black, hydrogen. (c) One dimensional helical chain of the coordination polymer **2** $[Cd_8S(SPh)_{14}(DMF)(bpy)]_n$ based on the clusters and the **bpy** linkers.

In cluster **1**, seven of the Cd atoms are tetrahedrally coordinated and chemically bonded with four S atoms (or three S and one O atom). One Cd atom is bonded with four S atoms and coordinated/bonded to one O atom in a DMF molecule forming a distorted trigonal bipyramid coordination environment for the Cd. The bond distances of Cd–S (2.7887(11) Å) and Cd–O (2.360(4) Å) are much longer than those of Cd–S (2.4586(16) Å ~ 2.5939(12) Å) and Cd–O (2.221(5) Å ~ 2.267(4) Å) in other CdS_4 or $CdOS_3$ tetrahedrons. Such long Cd–S and Cd–O distances were also observed in $[Cd_{10}(SCH_2CH_2OH)_{16}(ClO_4)_4{\cdot}8H_2O]$ with similar CdS_4O species (Cd–S: 2.767(4) ~ 2.824(4) Å; Cd–O: 2.41 (1) Å).[37] Cluster **1** showed a penta-supertetrahedral (*P*1) structure, with a centre Cd_4S anti-tetrahedron linked to four terminal CdS_4 or $CdOS_3$ tetrahedrons by corner sharing of –SPh groups (Fig. 1a). Compared to the reported discrete P1 cluster with a formula of $[Cd_8S(SPh)_{16}]^{2-}$,[38] two of the terminal –SPh groups were substituted by DMF molecules and led to a neutrality of cluster **1**, which also contained a third DMF molecule. The coordination bond of Cd–O(DMF) could be replaced more easily than the former Cd–SPh bond with a strong covalent (partly ionic) nature. The two terminal DMF molecules in cluster **1** were replaced by **bpy** linkers, which coordinated with terminal Cd atoms *via* N donors. Each cluster was twice ligated by the **bpy** linkers, building a 1D helical chain structure of the CP **2** (Fig. 1c).

Note that most CPs based on SCC clusters have been synthesised under quite delicate and solvothermal conditions.[22-29] For these reactions, the formation mechanisms are still somewhat unclear due to the difficulties of probing the transformations during the solvothermal chemistry. In this study, we conducted an *ex situ* DLS study to reveal aspects of the formation mechanism of CP **2**. DLS is a good method to determine the particle size of soluble clusters.[39-41] The DLS data showed a solvodynamic diameter for the discrete cluster **1** in a DMF solution, which was consistent with the crystal structure. The particle size of the precursor solution of the CP **2** (cluster **1** mixed with the **bpy** ligand in DMF) was 1.74 nm, slightly larger than the size of cluster **1**. When the mixture was heated to 100 °C, the particle size increased approximately linearly with the reaction time. This time dependency indicated a stepwise assembly and linear growth of CP **2** (Fig. 2). A stepwise assembly might also be used to explain the formation of other CPs based on SCC clusters that have been synthesised under solvothermal conditions. In such a descriptor, the precursors (metal salts and thiolate/S sources) form the initial clusters, while the organic linkers further ligated the clusters into CPs. The strategy of a “bottom up” synthesis and the mechanism of stepwise assembly offer additional predictability and expand the synthetic opportunities of CPs based on SCC clusters under mild conditions.

In the solid state, cadmium chalcogenolate clusters are semiconductors, and exhibit quantum dot properties.[42-43] Their rich chemistry and well-defined atomic structures have allowed studies of size-dependent quantum confinement effects.[44-45] In addition, when semiconducting clusters are interlinked or counterparted with conjugated organic ligands, one would expect the band gap to widen due to synergetic electronic coupling.[25,30,46] It provides a new way to control the optical and electronic properties of such clusters for applications like photocatalysis and photovoltaic cells. For example, ion-pair charge transfer between cluster ions of $[Cd_8S(SPh)_{16}]^{2-}$ and methyl viologen cations resulted the cluster salts with dramatically red-shift UV-visible absorptions.[47] Here, the semiconducting properties of cluster **1** and CP **2** were indirectly studied by analysing their solid state diffuse reflectance UV/vis spectra (Fig. 3). Cluster **1** had an absorption onset at a wavelength of 402 nm (3.08ev). This absorption onset was assigned to a charge transfer from the SPh^- moiety to Cd-atoms and the rest of the SCC cluster atoms. Compared to the starting material of $Cd(SPh)_2$ with a polymeric structure of $[Cd_4(SPh)_8]_n$ (with an absorption onset at a wavelength of 352 nm, 3.52 ev),[30] the absorption of cluster **1** was red-shifted due to its eight d^{10} centres instead of four. The absorption of the coordination polymer was further red-shifted with an absorption onset at 443 nm (2.80 ev). This red shift could be interpreted as a charge transfer between the clusters and the **bpy** linkers[48] and, speculatively, an electronic coupling across the SCC clusters. Kundu *et al.* showed that core level X-ray photoelectron spectroscopy (Cd_{3d} and S_{2p}) were quite sensitive to the size of thiophenol capped CdS clusters, which could be relevant to future studies of related clusters and CPs. [49]

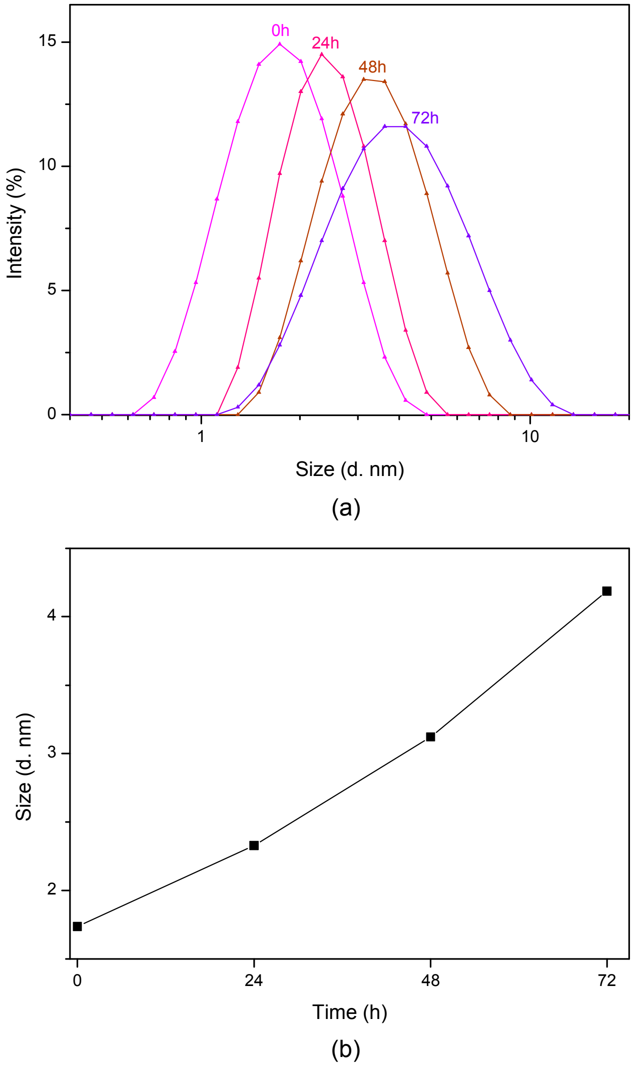
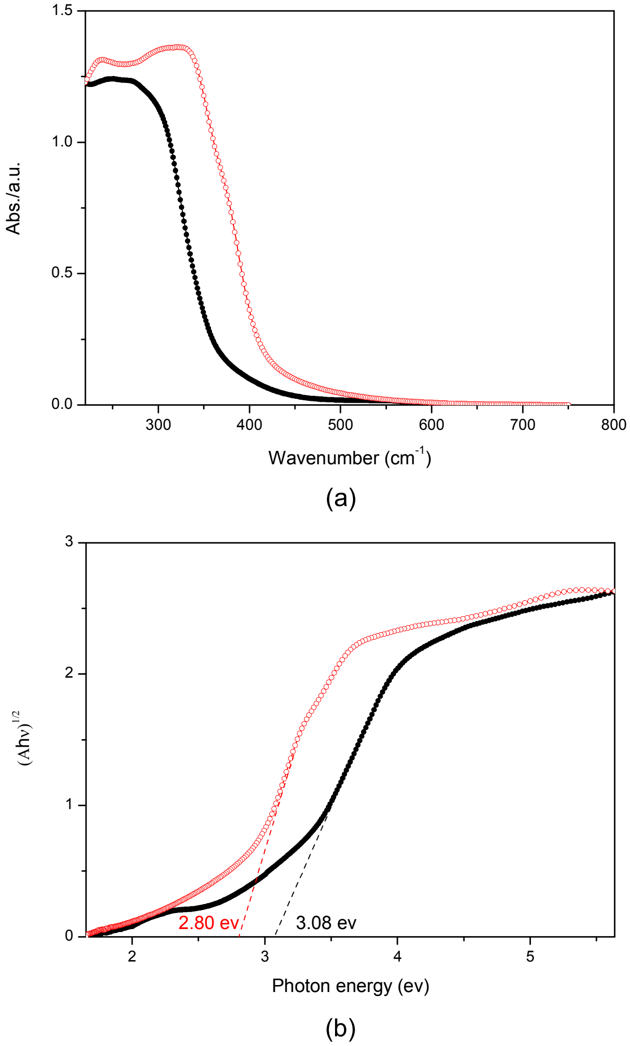


Fig. 2 (a) Particle size distributions from dynamic light scattering of the precursor solution of coordination polymer **2** at different reaction time; (b) The most probable particle size *vs*. the reaction time for the evolving coordination polymer **2**.

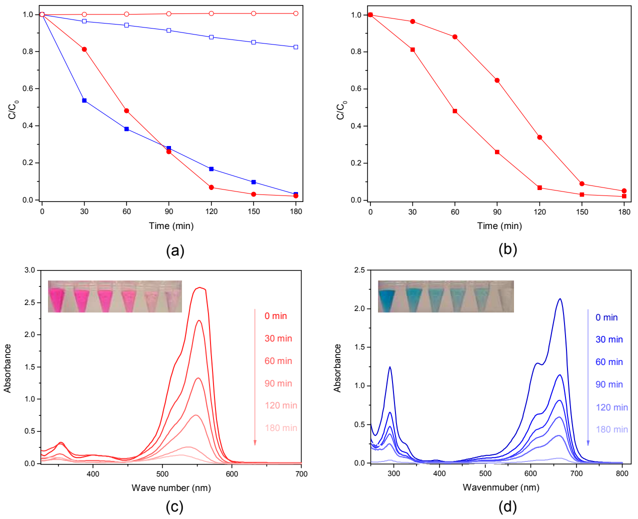


(a)

(b)

Fig. 3 (a) UV/vis absorption spectra of cluster **1** Cd$_8$S(SPh)$_{14}$(DMF)$_3$ (●) and the coordination polymer **2** [Cd$_8$S(SPh)$_{14}$(DMF)(bpy)]$_n$ (○) measured by solid-state diffuse reflectance spectroscopy. (b) Plots of $(Ahv)^{1/2}$ versus the photon energy of cluster 1 (●) and the coordination polymer **2**(○).

Given the hybrid nature and wide band gap of CP **2**, we expected that it could be an effective photocatalyst for the degradation of organic dyes, such as rhodamine B (RhB) and methylene blue (MB). RhB and MB are widely used in the textiles industry due to their good chemical stability[50] and, consequently, occur as common pollutants in wastewater.[51] Traditional inorganic photocatalysts, such as TiO$_2$, CdS and ZnO effectively degrade various organic dyes in aqueous media.[52] Recent studies have shown that many MOFs and CPs are quite efficient photocatalysts,[53-54] with a potential to remove organic pollutants from wastewater.[5,55-56] Their tailor-made structures and diverse set of properties could offer some advantages over traditional inorganic photocatalysts.[57] CP **2** was effective in supporting the photodegradation of RhB and MB in aqueous solutions. With CP **2**, the concentrations of RhB and MB were reduced by ~70% at 90 min and by 95% after 180 min, under white light illumination. Compared with cluster **1**, the CP **2** showed a faster degradation rate of RhB, which was ascribed to the broader visible absorption of **2**. It is worthy to note that the photocatalysts are moderately stable in water. The crystallinity was partly lost after soaking the crystals in water for 2 days. (Fig. S2) The UV-vis spectra in Fig. 4c-d display a successively fading absorbance of RhB and MB. The photodegradation could be mainly attributed to the cleavage of the conjugated chromophore groups. Interestingly, the characteristic absorption band of RhB at 555 nm shifted slightly to 526 nm during the photodegradation process. This could be explained by stepwise deethylation in the RhB structure.[58-59] Note that no degradation of RhB and only slight photolysis of MB occurred in the blank experiments.



(a) (b)

(c) (d)

Fig. 4(a) Concentration changes of RhB (●) and MB (■) photocatalysed by the coordination polymer (CP) **2** in water, and RhB (○) and MB (□) photolysed without photocatalyst. The concentration was calculated from UV/vis absorbance at 555 nm (RhB) and 664 nm (MB). (b) Comparison of degradation of RhB photocatalysed by the cluster **1** and the CP **2**. (c) UV/vis spectra and fading images of aqueous RhB and (d) MB photocatalysed by the CP **2**.

Conclusions

A cadmium chalcogenolate cluster with a penta-supertetrahedral structure was isolated and further organised into a 1D CP by **bpy** linkers. In contrast to most studies of CPs based on SCC clusters, solvothermal synthesis was not used. Both the cluster and the CP are semiconductors in their solid forms, and photocatalytically degraded various organic dyes when suspended in water. The **bpy** linkers in the CP red-shifted the UV/vis absorption spectrum, which appeared to enhance its photocatalytic performance in comparison to the clusters. We expect that other related clusters and linkers could be used to assemble related CPs. Due to the good solubility of the cluster and the good dispensability of CP, it could be possible to prepare them as semiconducting films or fibres through casting or evaporation processes. Dynamic light scattering showed that the CP was formed from the soluble and neutral clusters and the polydentate ligand by a stepwise assembly process. The moderate conditions used for the synthesis in this study, would allow further *in situ* studies of the reaction/assembly mechanisms for related clusters and CPs.

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