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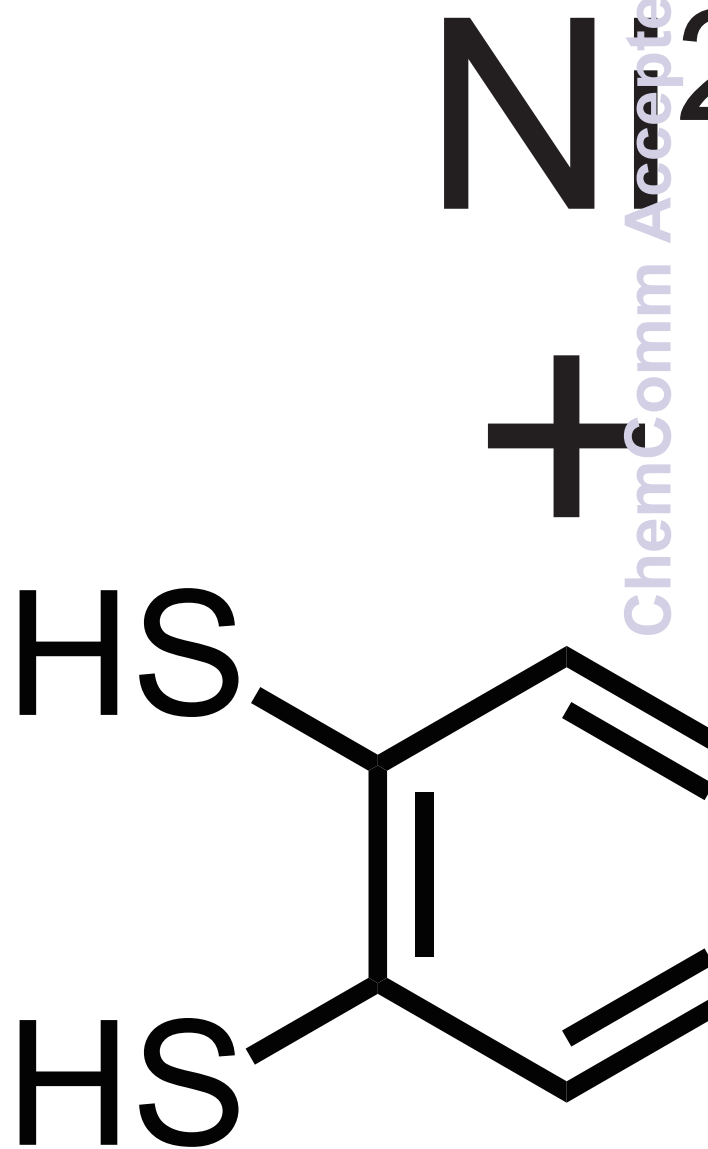
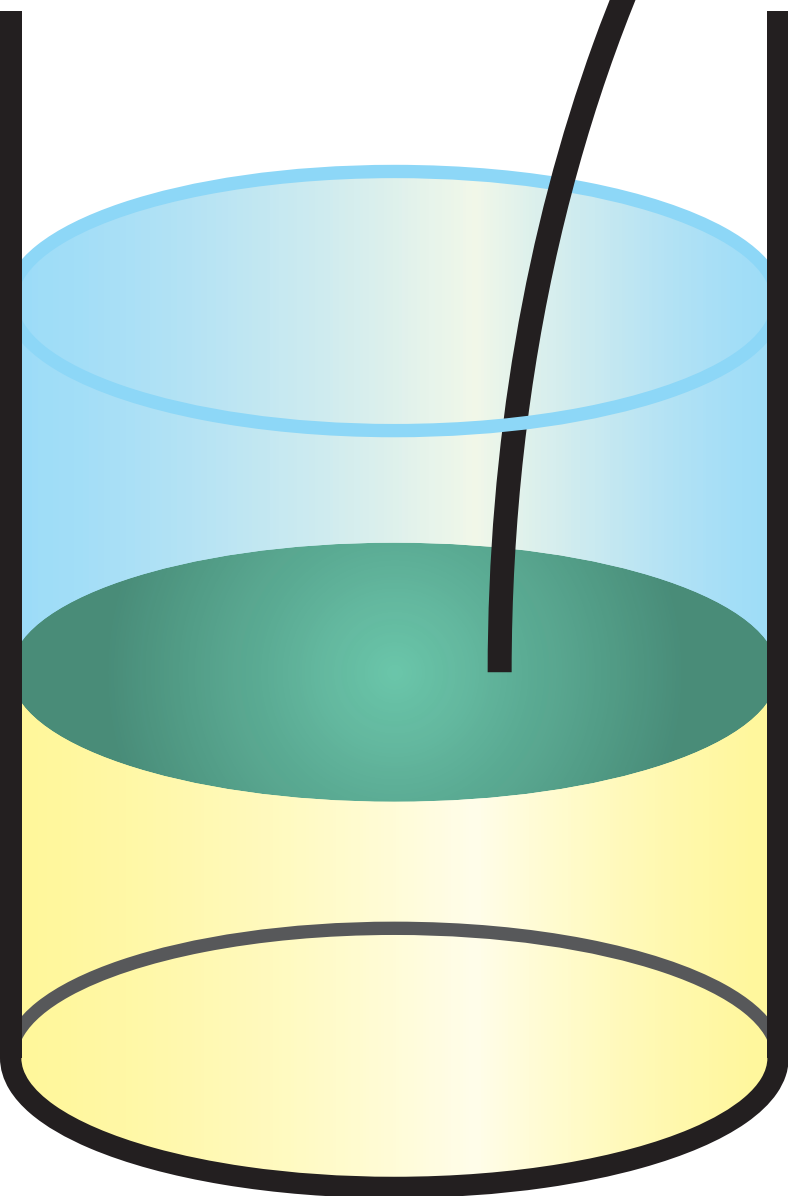
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A liquid-liquid interfacial reaction between 1,2,4,5-benzenetetrathiol and nickel(II) ion produced a  $\pi$ -conjugated coordination polymer that aligns regularly.



## COMMUNICATION

# Ordered Alignment of a One-Dimensional $\pi$ -Conjugated Nickel Bis(dithiolene) Complex Polymer Produced via Interfacial Reaction†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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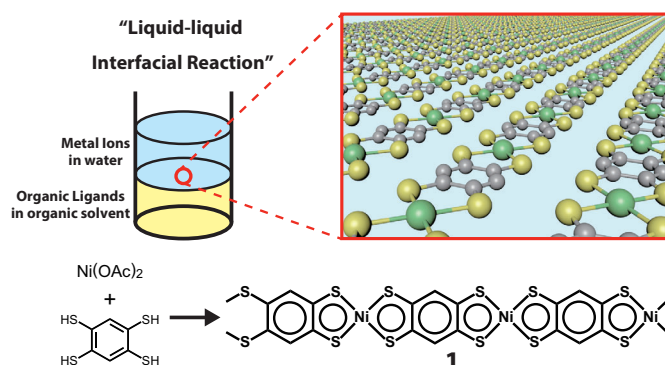
**A liquid-liquid interfacial synthesis using 1,2,4,5-benzenetetrathiol and nickel(II) ions produced a thin black film of a  $\pi$ -conjugated polymer featuring the nickel bis(dithiolene) motif. Its ordered structure was not originally identified due to its amorphicity; however, it was observed to align regularly on a highly oriented pyrolytic graphite substrate by scanning tunnelling microscopy.**

One-dimensional (1D) coordination polymers (CPs) have attracted significant attention because of their broad potential applicability in electronics, optics, and magnetic devices.<sup>1</sup> Their bottom-up fabrication from constitutive ligand molecules and metal atoms or ions allows diversity in both composition and physical properties.<sup>1b-d</sup> Synthesis is also often by self-assembly.<sup>1a-c, e</sup> However, controlling the secondary structures of 1D CPs (*e.g.* sheets, wires, rods, fibres, and tubes) is difficult: most 1D CPs are insoluble in any solvent, and are likely to aggregate randomly.<sup>1b-e</sup> As part of several efforts to compensate for this weakness, Hou and coworkers demonstrated the formation of tubular assemblies of 1D CPs using a layer-by-layer template method,<sup>2</sup> and Petra and coworkers efficiently generated CP nanofibres using a microfluidic method.<sup>3</sup>

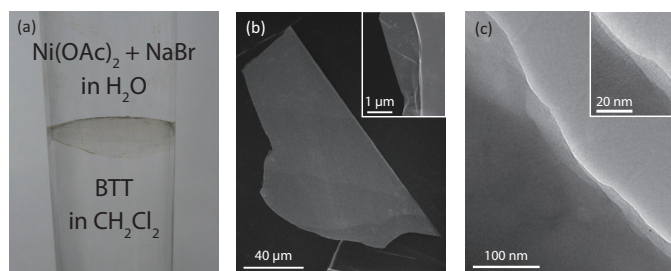
$\pi$ -conjugation shown by 1D CPs based on metal bis(dithiolene) complexes sets them apart from other CPs.<sup>4,5</sup> They can assume a number of stable oxidation states containing open-shell electronic structures, which makes them promising conductive and magnetic materials. These benefits are especially apparent when the metal bis(dithiolene) motif is incorporated into the main chain in a  $\pi$ -conjugated fashion, as demonstrated by systems comprising metal ions and aromatic tetrathiols [*e.g.*, tetrathiooxalic acid,<sup>4a-c</sup> ethylenetetrathiol,<sup>4d</sup> tetrathiosquaric acid,<sup>4e</sup> tetrathiafulvalenetetrathiol,<sup>4f</sup> tetrathianaphthalene,<sup>4g</sup> and benzenetetrathiol (BTT)<sup>4h</sup>]. However, these polymers are essentially insoluble amorphous solids with no ordered secondary structures, except for faint ordering, which has been deduced from large angle X-ray scattering (LAXS) and extended X-ray absorption fine structure (EXAFS) analyses.<sup>4i</sup>

We recently fabricated a two-dimensional CP nanosheet comprising benzenhexathiol and Ni(II) ions.<sup>5</sup> Its fabrication was distinct in that dichloromethane (holding benzenhexathiol) and water (containing Ni(II) ions) were layered, and the coordination reaction was conducted at the flat and calm liquid-liquid interface. This synthesis allowed controlled coordination, which resulted in a crystalline product of stacked nanosheets. This contrasts with the amorphous solid that results from a conventional one-phase synthesis.<sup>5</sup> The current work reports the liquid-liquid interfacial synthesis and characterisation of 1D CPs composed of BTT and Ni(II) ions (abbreviated **1**, Scheme 1).

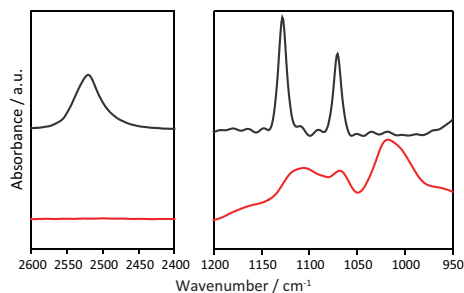
Our new synthetic procedure for 1D CP **1** is as follows. Ni(OAc)<sub>2</sub> (50 mM) and the charge-compensating counter cation Na<sup>+</sup> (as NaBr) (10 mM) were mixed in water to form the aqueous phase. BTT (0.48 mM) in dichloromethane constituted the organic phase. The organic layer was initially overlaid with pure water; the aqueous solution was then added carefully to the pure water layer, thus allowing a calm liquid-liquid interface to be maintained. Storing the biphasic system under an Ar atmosphere without disturbance (*e.g.* vibration) for 1 day resulted in **1** forming as a thin black film at the interface (Fig. 1a).



**Scheme 1** Fabrication of nickel bis(dithiolene) 1D CP **1** using a liquid-liquid interfacial reaction. Grey, C; yellow, S; green, Ni.



**Fig. 1** (a) Photograph of the liquid–liquid synthesis with a thin black film of **1** at the interface. (b) FE-SEM image of **1**. (c) HR-TEM image of **1**. Insets show high-magnification images.

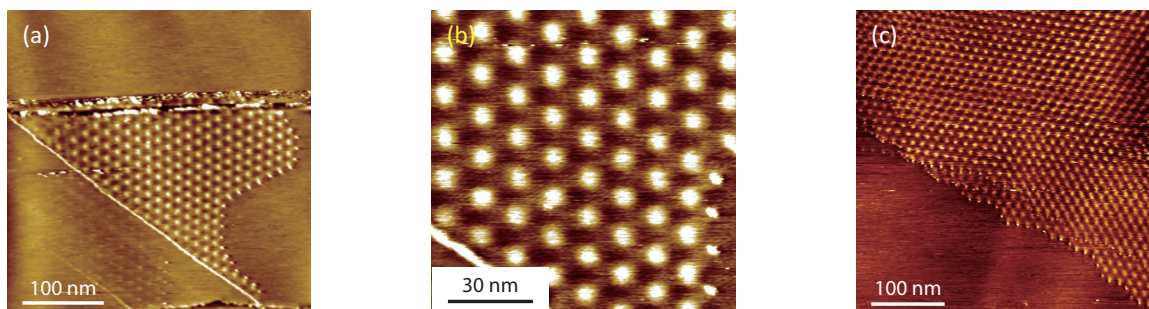


**Fig. 2** ATR-IR spectra of BTT (black) and **1** (red).

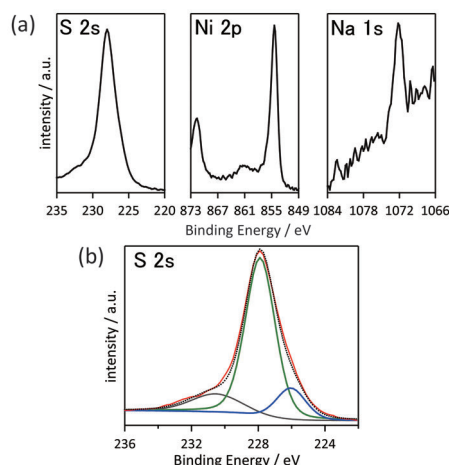
Fig. 1b and 1c show field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) images of **1**. SEM showed thin films with lateral sizes of  $\sim 100 \mu\text{m}$ ; TEM also showed film-like nanostructures. High-magnification reveals a stair-like morphology at the edge of **1**, indicative of a layered structure.

Attenuated total reflection IR (ATR-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to identify **1**. Fig. 2 shows ATR-IR spectra of **1** and BTT. BTT showed a distinctive signal at  $2520 \text{ cm}^{-1}$ , ascribed to the S–H stretching vibration.<sup>6</sup> The corresponding peak was not shown by **1**, indicating that all the thiol groups of BTT coordinated with Ni(II) ions. BTT also showed sharp absorption peaks at  $1128$  and  $1070 \text{ cm}^{-1}$ , assignable to the C–S stretching,<sup>6</sup> whereas **1** exhibited three broad signals at  $1017$ ,  $1068$ , and  $1106 \text{ cm}^{-1}$ , which are ascribable to the C–S\* stretching of the nickel bis(dithiolene) complex. A mononuclear nickel bis(dithiolene) complex in the  $-1$  oxidation state features the C–S\* stretching mode at  $1114 \text{ cm}^{-1}$ , which splits into two bands at  $1029$  and  $1099 \text{ cm}^{-1}$  in the  $0$  oxidation state.<sup>7</sup>

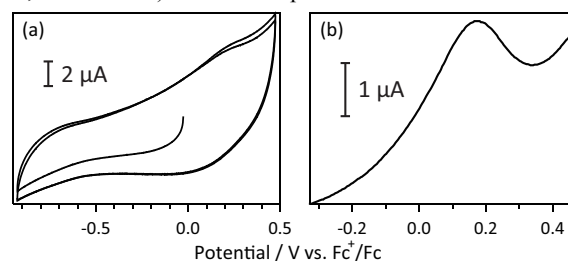
Fig. 3 shows the S, Ni, and Na XPS of **1** deposited on highly oriented pyrolytic graphite (HOPG). The oxidation state of the nickel bis(dithiolene) unit is reflected in the binding energy of the S atom,<sup>5</sup>



**Fig. 5** (a) STM topological image of **1** on HOPG. Tip bias ( $V_{\text{tip}}$ ) =  $-700 \text{ mV}$ ; average tunnelling current ( $I_t$ ) =  $30.0 \text{ pA}$ . (b) Magnification of the hexagonal pattern observed in (a). (c) Hexagonal pattern covering a large area.



**Fig. 3** (a) XPS of **1** focusing on the S 2s, Ni 2p, and Na 1s regions. (b) Deconvolution of the S 2s peak. Two Gaussian curves are derived from nickel bis(dithiolene) moieties in the  $0$  (green) and  $-1$  (blue) oxidation states. A “shake-up” peak (gray) is also present. Experimental (red) and simulated (the sum of the three Gaussian curves, dotted black) overall S 2s peaks are also shown.



**Fig. 4** (a) Cyclic voltammogram and (b) differential pulse voltammogram of **1** on HOPG in  $1 \text{ M Bu}_4\text{NClO}_4$ -dichloromethane.

and can be found by deconvoluting the S 2s envelope. Three deconvoluted bands emerge at  $226.1$ ,  $227.9$ , and  $230.5 \text{ eV}$ . The first two are respectively due to the  $-1$  and  $0$  oxidation states of the nickel bis(dithiolene) motif. The broad band at  $230.5 \text{ eV}$  is assignable to a “shake-up” peak, which is often observed in metal bis(dithiolene) complexes.<sup>8</sup> The area ratio between the signals at  $226.1$  and  $227.9 \text{ eV}$  suggests a  $5:1$  ratio of the  $0$  and  $-1$  oxidation states of the nickel bis(dithiolene) moiety (Fig. S1, ESI†). This result is consistent with the fact that Na is included in **1** as a counter cation. The oxidation state of **1** can be modulated by a treatment with a reductant, 7,7,8,8-tetracyanoquinodimethane radical anion sodium salt (NaTCNQ): Partial reduction was confirmed by means of XPS (Figure S2, ESI†).

Cyclic voltammetry and differential pulse voltammetry were conducted using a working electrode of HOPG modified with **1** (Fig.



4). One reversible redox wave was observed at 0.20 V vs. ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) and was assigned to the 0/−1 couple of the nickel bis(dithiolene) moiety.<sup>7</sup> The wave derived from the −1/−2 couple was not observed in the available potential window.

The electrical conductivity of a film of as-prepared **1** transferred on a mica substrate was measured using a preliminary two-electrode configuration. It gave a conductivity in the order of  $10^{-5}$  S  $\text{cm}^{-1}$  at 298 K.

To observe the ordered structure of **1**, scanning tunnelling microscopy (STM) was conducted using **1** on an HOPG substrate (Fig. 5). The height images show a hexagonal pattern with a periodicity of  $a = b = 14.3$  nm. The periodicity is too great to suggest that the hexagonal pattern is assignable directly to **1** (the Ni–Ni distance is estimated to be 0.85 nm from DFT calculation; Fig. S3, ESI†). Instead, we suggest that it is a moiré interference superlattice arising from two ordered structures: a monolayer of **1** aligned in an A–B–A–B... fashion to form a quasi-hexagonal lattice, and the hexagonal lattice of the HOPG substrate (see ESI†, Fig. S4–S6 and Tables S1–S2 for details).<sup>9</sup> A moiré pattern was also found in a two-dimensional nickel bis(dithiolene) nanosheet comprising benzenehexathiol and Ni(II) ions on an HOPG substrate.<sup>5</sup> The hexagonal pattern covers an area of  $500 \times 300$  nm (Fig. 5c), indicating that 1D chains of at least 350 mers of **1** are aligned orderly to form the two-dimensional sheet-like structure.

The authors note that a gas-liquid interfacial synthesis<sup>5</sup> also produced a parallel alignment of **1** similar to that of the present liquid-liquid interfacial procedure (Fig. S7, ESI†).

In conclusion, we synthesised  $\pi$ -conjugated 1D CP comprising BTT and Ni(II) ions via a liquid-liquid interfacial synthesis. The resulting thin film of **1** was characterised using SEM, HR-TEM, XPS, ATR-IR, and cyclic voltammetry. STM also revealed that a nanofilm of **1** deposited on an HOPG substrate featured a hexagonal pattern that covered an area of  $500 \times 300$  nm, which suggests that chains of at least 350 mers of **1** aligned orderly in an A–B–A–B... fashion. We demonstrated that the oil–water interfacial synthesis allowed the creation of ordered secondary structures of 1D CPs.

This work was supported by Grants-in-Aid from MEXT of Japan (Nos. 21108002, 24750054, 25107510, 25620037, 26708005, 26107510, 26110505, 26248017, 26620039, areas 2107 [Coordination Programming], 2406 [All Nippon Artificial Photosynthesis Project for Living Earth], 2506 [Science of Atomic Layers], 2509 [Molecular Architectonics]). R.S. is grateful to Japan Association for Chemical Innovation, The Asahi Glass Foundation, and The Noguchi Institute, Ogasawara Foundation for the Promotion of Science & Engineering, The Kao Foundation for Arts and Sciences, The Iketani Science and Technology Foundation, and The Tokuyama Science Foundation for financial supports. R.M., T.K., and K.T. appreciate JSPS fellowship for young scientists. The authors acknowledge the Research Hub Advanced Nano Characterization (Graduate School of Engineering, The University of Tokyo) for the XPS study.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental methods, XPS data, computational study, analysis of the moiré pattern of **1** on HOPG, and results of gas-liquid interfacial synthesis]. See DOI: 10.1039/b000000x/

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