

Importance of alkyl chain-length on the self-assembly of new Ni(qdt)₂ complexes and charge transport properties†

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A series of ionic complexes composed with [Ni(qdt)₂]²⁻ and alkyl substituted asymmetric viologen derivatives (AV⁺) as cations have been synthesized and characterized. A slight change in the length of the alkyl chain of AV⁺ alters the cation–anion packing and leads to different charge transport properties of these complexes. Here, we establish a structure–property relationship of Ni(qdt)₂ complexes by structurally modifying the cations.

Introduction

In recent years, the synthesis of functional molecular based materials has attracted huge interest not only for fundamental reasons but also for various applications. Among them, metal compounds are the most interesting components due to their unique properties.^{1–5} Tremendous efforts have been made towards the metal–dithiolene complexes due to their ability to provide redox active ligands to form highly electron-delocalized complexes.^{2,6–8} Particularly, the design and synthesis of metal bis(dithiolene) complexes are under vigorous investigation due to their interesting properties such as conductivity,^{9–13} magnetism,^{6,14–17} near-infrared^{18,19} and non-linear optical properties.²⁰ The counter cations used in these complexes not only play a crucial role in the stacking mode of the anion complexes, but also make contributions to their properties.^{21–24} Organic materials or metal complexes generally transfer carries through π – π interactions^{2,25–29} between the molecules which are almost square planar.

There are reports on the charge transfer properties of ionic metal complexes on the π – π interactions between anions,^{11,30,31} but less reports on the π – π interactions between anion and cation. Nickel bis(quinoxaline-2,3-dithiolate) ([Ni(qdt)₂]²⁻) exhibits mostly a square planar structure.^{7,32,33} However, there are barely any reports on the influence of different cationic groups on the charge transport properties of this family of materials. On this aspect, nickel based ionic complexes with cation and anion pair have been selected in which the structure of the nickel bis(quinoxaline-2,3-dithiolate) ([Ni(qdt)₂]²⁻) anion is kept unchanged while the length of the alkyl substituted asymmetric viologen derivatives AV⁺ (AV⁺ = mono-*n*-alkylated 4,4'-bipyridine) cation has been varied (*n* = 5,6,7) (see Scheme 1). Here, we select the number of carbon chain length as 5, 6, and 7 so that the length of the cation could match length of the anion to form layer by layer packing of cation and anion. By this, an understanding of the influence of alkyl chain length³⁴ on the self-assembly³⁵ formation and their respective electronic properties is analysed.

Experimental

C-5, C-6, and C-7 were prepared by a simple substitution reaction of [NBU₄]₂[Ni(qdt)₂] (NBU₄ = tetrabutyl ammonium) and the

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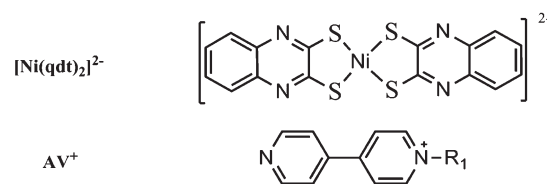
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Complexes (AV⁺)₂[Ni(qdt)₂]²⁻ names are: C-5: when R₁=(CH₂)₄CH₃,

C-6: when R₁=(CH₂)₅CH₃,

C-7: when R₁=(CH₂)₆CH₃

Scheme 1 Chemical structures of the complexes studied herein.

corresponding alkyl substituted asymmetric cation viologen derivatives AV^+ (AV^+ = mono-*n*-alkylated 4,4'-bipyridine, $n = 5,6,7$).^{36,37} The detailed synthesis and characterization of these complexes are described as follows;

[NBu₄]₂[Ni(qdt)₂]: 2,3-Quinoxalinedithiol (0.25 g, 1.29 mmol) and sodium metal (0.1 g, 4.35 mmol) were added to 5 ml methanol. The mixture was stirred at room temperature under nitrogen for 1 h. During the course of reaction, the reaction mixture changed from a yellowish to brownish clear solution. Nickel(II) chloride hexahydrate (0.1025 g, 0.43 mmol) in 30 ml methanol was added dropwise to the reaction mixture over a period of 30 min. The mixture was stirred at room temperature under nitrogen for 3 h. Dark red clear solution was obtained. The solution was filtered. The filtrate was reduced by adding 10 ml tetrabutyl ammonium bromide (0.323 g, 1 mmol) to the solution and 100 ml water was added to precipitate the product. The solids were filtered, collected, washed with methanol and then vacuum-dried, Yield: (0.29 g, 75%). ¹HNMR (400 MHz, CDCl₃): δ 7.66 (m, 4H), 7.24 (m, 4H), 3.40 (t, 16H, $J = 7.6$ Hz), 1.52 (m, 16H), (m, 16H), 0.73 (t, 16H, $J = 7.6$ Hz). ESI-MS (-ve mode): m/z 684.6. Anal. Calcd for C₄₈H₈₀N₆NiS₄: C, 62.11; H, 8.69; N, 9.05. Found: C, 62.01; H, 8.72; N, 9.11.

C-5: Mono-pentyl-4,4'-bipyridine bromide (0.24 g, 0.8 mmol) was dissolved in chloroform (5 ml). [NBu₄]₂[Ni(qdt)₂] (0.93 g, 0.1 mmol) in chloroform (5 ml) was added to the solution. The mixture was refluxed under nitrogen for three hours. Solids precipitated were filtered, collected, and washed extensively with acetonitrile and then vacuum-dried. Yield: (0.076 g, 76%). ¹HNMR (400 MHz, [D₆]DMSO): δ 9.22(d,4H) 8.86(d, 4H) 8.62(d, 4H) 8.00(d, 4H) 7.45(m, 4H) 7.20(m, 4H) 4.61(m, 4H) 1.93(t, 4H) 1.29(m, 8H) 0.86(t, 6H). ESI-MS (+ve mode): 226.5 (AV⁺), (-ve mode): 443.0 [[Ni(qdt)₂]²⁻ + H⁺]⁻. Anal. Calcd for C₄₆H₄₆N₈NiS₄: C, 61.53; H, 5.16; N, 12.48. Found: C, 61.94; H, 5.08; N, 12.93.

C-6: C-6 was prepared by a similar procedure except with an addition of mono-hexyl-4,4'-bipyridine bromide. Yield: 76%. ¹HNMR (400 MHz, [D₆]DMSO): δ 9.22(d,4H) 8.86(d, 4H) 8.61(d, 4H) 8.00(d, 4H) 7.45(m, 4H) 7.20(m, 4H) 4.61(m, 4H) 1.93(t, 4H) 1.27(m, 12H) 0.84(t, 6H). ESI-MS (+ve mode): 241.2 (AV⁺), (-ve mode): 443.0 [[Ni(qdt)₂]²⁻ + H⁺]⁻. Anal. Calcd for C₄₈H₅₀N₈NiS₄: C, 62.26; H, 5.44; N, 12.10. Found: C, 62.30; H, 5.38; N, 12.16.

C-7: C-7 was prepared by a similar procedure except with an addition of mono-heptyl-4,4'-bipyridine bromide. Yield: 75%. ¹HNMR (400 MHz, [D₆]DMSO): δ 9.23(d,4H) 8.83(d, 4H) 8.61(d, 4H) 8.00(d, 4H) 7.45(m, 4H) 7.20(m, 4H) 4.61(m, 4H) 1.92(t, 4H) 1.25(m, 16H) 0.83(t, 6H). ESI-MS (+ve mode): 255.2 (AV⁺), (-ve mode): 443.0 [[Ni(qdt)₂]²⁻ + H⁺]⁻. Anal. Calcd for C₅₀H₅₄N₈NiS₄: C, 62.95; H, 5.71; N, 11.75. Found: C, 63.03; H, 5.68; N, 11.80.

Results and discussion

To investigate the self-assembly of C-5, C-6 and C-7, solutions of these complexes (C-5, C-6 and C-7) have been prepared in DMSO and evaporated to remove the solvents under vacuum at 80 °C. As obtained microcrystalline materials were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 1a-f). All the complexes formed micro-

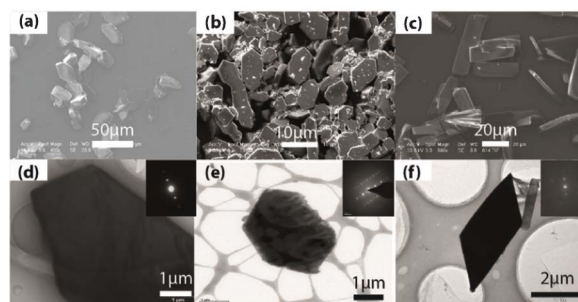


Fig. 1 SEM images of C-5 (a), C-6 (b), C-7 (c); TEM images and patterns (inset) of C-5 (d), C-6 (e), C-7 (f).

structures with lengths of tens of micrometers and widths of several micrometers.

The single crystals of C-5, C-6, and C-7 were obtained from the slow evaporation of MeOH solution of C-5, C-6, and C-7, respectively. The single crystal X-ray crystallographic structures C-5, C-6 and C-7 are shown in Fig. 2a-c and the crystal data was described in Table S1(ESI[†]). Crystallographic analysis reveals that complex C-5 crystallizes in triclinic form with a space group of $P\bar{1}$, while complexes C-6 and C-7 crystallize in monoclinic form with a space group of $P2_1/c$. The relevant asymmetric unit contains one $[\text{Ni}(\text{qdt})_2]^{2-}$ and two AV^+ . These two cations distributed on either sides of the anion with inverse directions for all the complexes. In anion $[\text{Ni}(\text{qdt})_2]^{2-}$, four sulfur atoms from two -qdt (qdt = quinoxaline-2,3-dithiolate) ligands geometrically surrounded the Ni^{2+} ion and are almost in square planar due to S-Ni-S coordination angles that are in the range of $87.89(4)^\circ$ and $92.11(4)^\circ$ and with small dihedral angle between two -qdt planes, which is 2.76° , 5.76° , and 14.82° for C-5, C-6, and C-7 respectively. The average bond distance of Ni-S in the present study is 2.174 \AA , which is comparable to other reports.^{32,33}

Fig. 2d-k show the crystal packing diagrams of C-5, C-6, and C-7, respectively. For complex C-5, the five carbon aliphatic substituent is not extended on the same aromatic plane. The aromatic rings of cations are distributed at one side of $[\text{Ni}(\text{qdt})_2]^{2-}$ plane and almost perpendicular with anion molecules. A number of C-H \cdots N and C-H \cdots S weak interactions can be found in different directions (Fig. S1a in ESI[†]). For complex C-6, *n*-hexyl substituent is not found to be tortuous and blended with each other. The cations are distributed at the top and bottom of $[\text{Ni}(\text{qdt})_2]^{2-}$ anion plane and almost parallel to the anion molecule. The bond distances of the cations and anion are depicted in Fig. S1b (ESI[†]). The shortest bond distance between the opposite rings is 3.220 \AA which indicates that π - π interactions between the cation and anion with some C-H \cdots N and C-H \cdots S weak interactions. For complex C-7, the seven carbon aliphatic substituent found to be tortuous with the aromatic plane. Similar to C-5, the aromatic rings of cations are distributed at the edge of $[\text{Ni}(\text{qdt})_2]^{2-}$ plane and almost perpendicular with anion molecules. In addition, the alkyl chains are far away with $[\text{Ni}(\text{qdt})_2]^{2-}$ plane. Therefore, there are some C-H \cdots N and C-H \cdots S weak interactions but and no π - π interactions between the cations and anion. (Fig. S1c in ESI[†]).

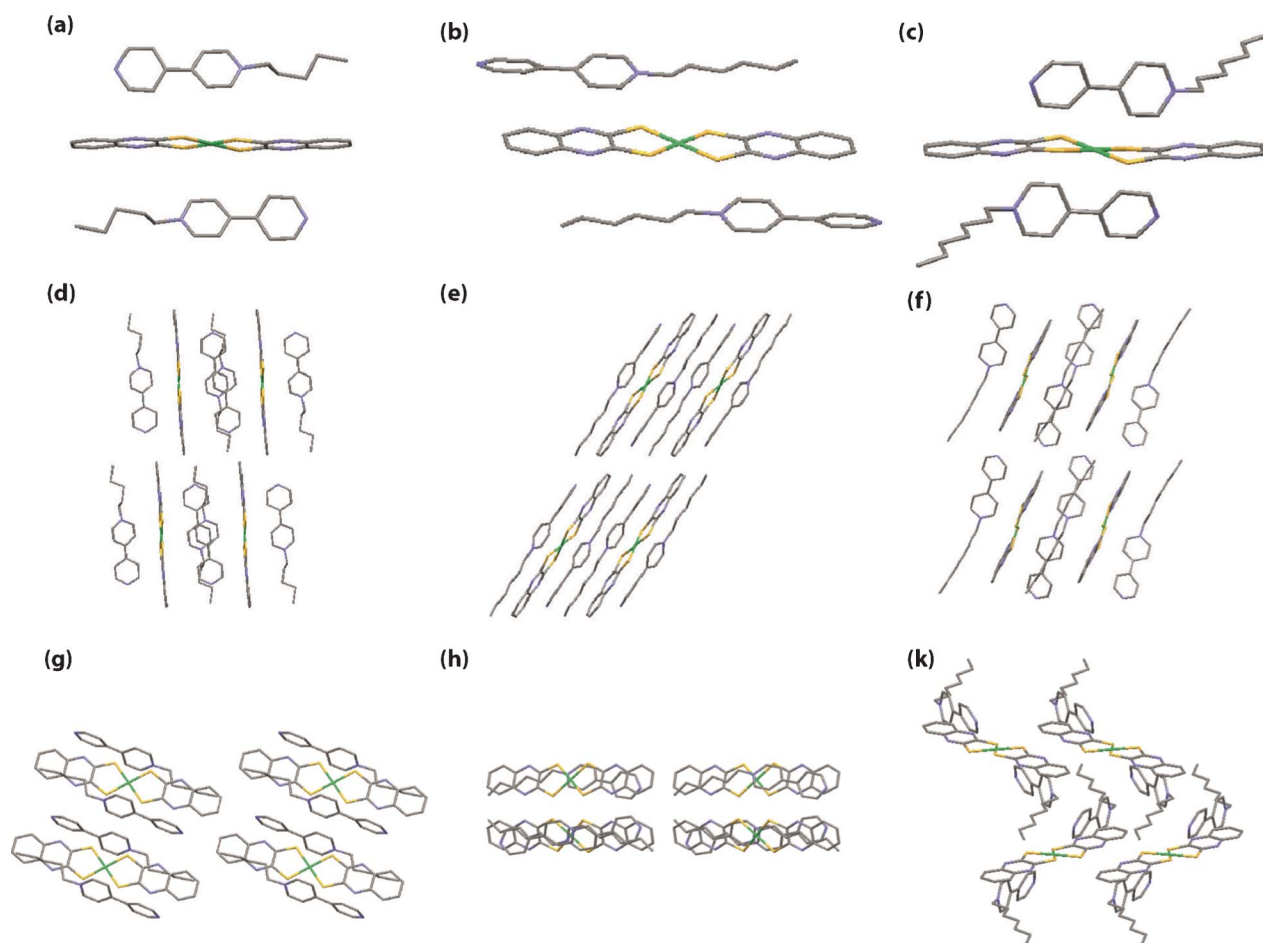


Fig. 2 Crystal structures (a, b, and c), crystal packing diagrams (d–k) in the cation and anion pairs of C-5, C-6, and C-7, respectively.

Transmission electron microscopy (TEM) images and the corresponding selected-area electron diffraction (SAED) patterns (inset) of complexes are shown in Fig. 1d–f. The SAED patterns of all complexes exhibit typical crystal diffraction pattern indicating the ability of molecular self-assembly to form single crystal structures.³⁸

The UV-vis absorption spectra of the solution and crystal samples of complexes are shown in Fig. 3 (C-6) and Fig. S2† (C-5, C-7) respectively. The solution samples were prepared in DMSO with a concentration of 1×10^{-5} mol dm⁻³ and crystal samples were prepared by spreading the crystals obtained from the evaporation of DMSO solution in a vacuum oven at 80 °C. The absorption bands of solution samples observed in the visible region are due to the charge transfer transitions involving electronic excitation from HOMO (mixture of dithiolate (π) and metal (d) orbital) to LUMO (π^* orbital of the dithiolate).³² A drastic spectral change was observed for all the microcrystals in comparison with their solution counterpart. The absorption spectra of C-5, C-6 and C-7 are significantly broadened for microcrystals due to interactions between the cation and anion molecules at the solid state.

To further investigate the influence of substituted alkyl chain length on the charge transport properties of the self-assembly

crystalline microstructure, bottom-contact field-effect transistor (FET) devices were fabricated by drop-casting the complexes in DMSO onto the Si substrate with 100 nm thick SiO₂ as the dielectric layer. The source and drain contacts were prefabricated using a standard photolithography lift-off process followed by e-beam evaporation of 100 nm Au contacts. A schematic

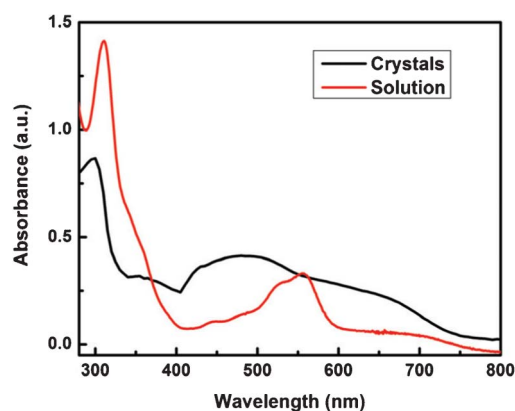


Fig. 3 UV-vis absorption spectra of solution and crystal of C-6.

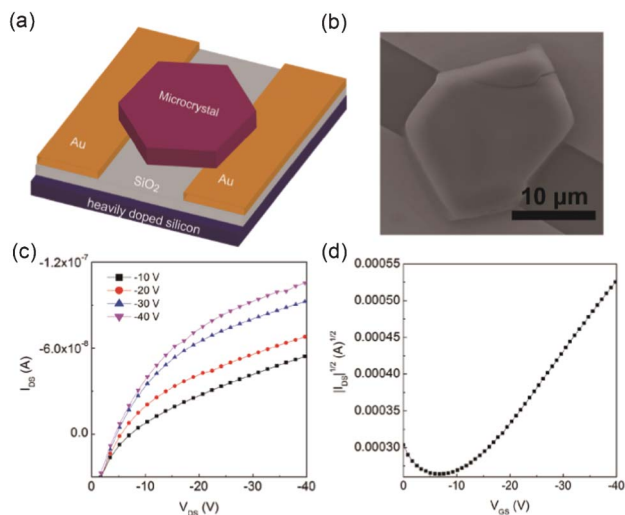


Fig. 4 (a) schematic illustration of FET structure; (b) SEM image of FET device of complex C-6; (c) output characteristics and (d) transfer characteristics ($V_{DS} = -40$ V) of the FET device of C-6.

illustration of FET structure employed in this study and SEM image of the FET device consists of complex C-6 are shown in Fig. 4(a) and 4(b), respectively. The microcrystal bridge the source and drain electrodes to form a conducting channel with a length (L) and width (W) of $10\ \mu\text{m}$ and $20\ \mu\text{m}$, respectively. The output characteristics and transfer characteristics of the FET device are shown in Fig. 4(c) and 4(d). The FET device shows typical p -channel transistor behaviour where the drain current increases with increasing negative gate voltages. The transistor exhibited a mobility of $4.6 \times 10^{-3}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$.

The output characteristics and transfer characteristics of the single-crystals based FET devices of C-5 and C-7 are shown in Fig. S3.† They also exhibited typical p -channel transistor behaviour. However, the mobility of C-5 and C-7 are lower than that of C-6. As is known, stronger π - π interactions lead to larger charge carrier mobility of the materials. As explained above, the cations and anions arranged face to face in the complex C-6. The stronger π - π interactions between the cations and anions resulted in better planar charge transport properties. On the other hand, as suggested from the molecular packing arrangement in complex C-5 and C-7, the cation plane is perpendicular to the anion plane separated by a long distance in comparison with C-6. Therefore, the π - π interactions between the cations and anions are found to be minimal.

Conclusions

In summary, a series of new nickel bis(1,2-dithilene) complexes with cations containing aliphatic substituents of variable length have been synthesized and characterized. The complexes self-assemble to form crystalline microstructures through solvent evaporation. The microstructures display different but uniform morphology which are confirmed by single-crystal X-ray diffraction and selected areal electron diffraction. The X-ray single-crystal data of complexes reveal that the molecular packing has a direct

relationship with the length of different aliphatic substituents at the cation. In addition, we establish a structure-charge transport property relationship by analysing their planar charge transport behaviour using FET structure. An increase or decrease in the carbon chain at the cation completely alters the cation-anion packing and leads to different charge transport properties of these complexes. With n -hexyl chain, the cation are packed face to face with the $\text{Ni}(\text{qdt})_2$ plane and C-6 exhibited the highest electronic properties. This study is not to report a high performing device nevertheless to understand the influence of alkyl chains on the molecular packing and charge transport properties of the $\text{Ni}(\text{qdt})_2$ complexes. To the best of our knowledge, it is the first report to study the π - π interactions between the cations and anions and its effect on charge transport properties. It potentially provides a new way to design new $\text{Ni}(\text{qdt})_2$ complexes as electronic materials.

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