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Variation of *cis*/*trans* configuration of 3,8-dithiophen and 3,8-di-3-methylthiophen-substituted 1,10-phenanthroline in their cadmium(II) nitrate complexes originating from substituent and anionic effects

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A pair of 3,8-dithiophen (dtphen) and 3,8-di-3-methylthiophen (dmtphen) substituted 1,10-phenanthroline cadmium(II) nitrates, formulated as [Cd(dmtphen)$_2$(NO$_3$)$_2$] (**1**) and [Cd(dtphen)$_2$(NO$_3$)$_2$] (**2**), exhibit *cis* and *trans* configuration in the whole complexes because of the substituent effects of methyl group in the dmtphen ligand. In **1** and **2**, both ligands possess similar *cis*/*trans* configuration but different dihedral angles from 19.0(1)° to 45.5(1)° in **1** and 2.6(1)° to 5.9(1)° in **2** due to the spatial crowding effects of methyl group. Additionally, anionic effects of NO_3^-, Cl^-, and Br^- have been studied where two *cis* Cd(II) complexes formulated as [CdBr$_2$(dmtphen)$_2$] (**3**) and [CdCl$_2$(dtphen)] (**4**) are obtained and the side thiophene and methyl-thiophene rings in each ligand adopt the *cis*/*trans* and *trans*/*trans* configuration relative to the central phen unit.

1. Introduction

Studies on the design and control of the molecular configuration such as *cis*/*trans* position isomerism have attracted increasing attention in recent years because of their potential applications in various subjects ranging from inorganic [1] to organic and biological chemistry [2,3]. In particular, the molecular configuration of metal coordination complexes can be rationally designed by careful regulation on temperature and solvents [4,5], photo and proton-induced effects [6], steric interactions [7], counterions, electronic features and configuration of ligands [8,9]. The most famous example is the anti-cancer drug *cis*-[(NH$_3$)$_2$PtCl$_2$] (also known as *cis*-platin) which still attracts considerable attention for its outstanding cytostatic properties up till now [1].

By means of rational design and slight modification of ligands, one could finely tune their conformation and energy levels, resultantly impact the photophysical properties and functions of the transition-metal complexes. However, it should be mentioned that investigations on the configurational alterations for a series of metal complexes originated from the substituent and anionic effects are rarely reported. Earlier work from our laboratory shows that the *cis* and *trans* isomers of bis(4,4′-dimethyl-2,2′-bipyridine)cadmium(II) nitrates can be yielded simultaneously and obtained individually by the mechanical separation *via* a one-pot reaction [10].

In the previous work, we have focused on the preparation and optoelectronic properties for a series of linear 1,10-phenanthroline based heterocyclic aromatic semiconducting compounds by introducing thiophene, imidazole, pyridyl, phenyl and oligothiophene groups into the 3 and 8 positions of 1,10-phenanthroline *via* the carbon–carbon and carbon–nitrogen crossing coupling reactions [11–16]. Recently we have reported four nickel(II), zinc(II), and copper(II) perchlorate complexes of 3,8-di(thiophen-2′,2″-yl)-1,10-phenanthroline (dtphen) with different metal-to-ligand ratios [17]. In order to investigate how the substituent and anionic effects affect the configuration of ligands as well as final metal complexes, we firstly use 3,8-di-3-methylthiophen-1,10-phenanthroline (dmtphen) to prepare its metal complexes and make comparisons with similar dtphen-based metal complexes. In this contribution, we report four Cd(II) complexes of dtphen or dmtphen with NO_3^-, Cl^-, and Br^- ions and discuss the *cis*/*trans* variations of configuration both in the ligands and metal complexes (Scheme 1).

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were of analytical grade and used without any further purification. The anhydrous solvents were

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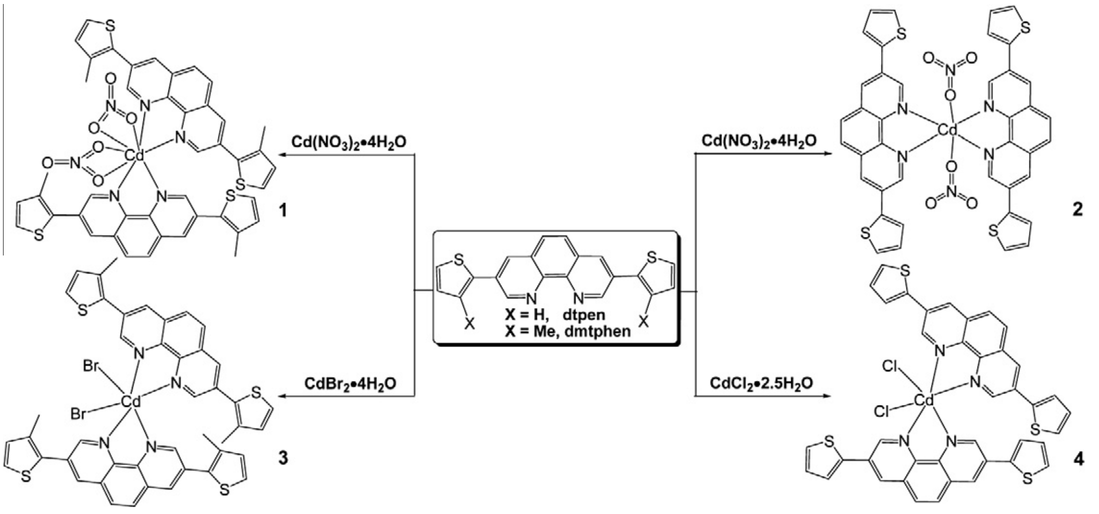

Scheme 1. Schematic illustration for the preparation of Cd(II) compounds **1–4**.

drawn into syringes under a flow of dry N_2 gas and directly transferred into the reaction flask to avoid contamination. 3,8-Dibromo-1,10-phenanthroline [18], 3,8-di(thiophen-2′,2″-yl)-1,10-phenanthroline (dtphen) [19] and 3,8-di(3-methylthiophen-2-yl)-1,10-phenanthroline (dmtphen) [11] were prepared *via* a previously reported approaches.

Elemental analyses (EA) for carbon, hydrogen, and nitrogen were performed on a Perkin–Elmer 1400C analyzer. Infrared (IR) spectra (4000–400 cm^{-1}) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. UV–Vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a Pyrex cell with a path length of 10 mm. Luminescence spectra were recorded on a Hitachi 850 fluorescent spectrophotometer at room temperature (25 °C). ^1H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature.

2.2. Syntheses of metal complexes

2.2.1. Preparation of complex [Cd(dmtphen)$_2$·(NO$_3$)$_2$] (**1**)

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (15.4 mg, 0.05 mmol) and dmtphen (37.2 mg, 0.1 mmol) were dissolved in ethanol (10 cm^3). After stirred and refluxed for 3 h, the mixture was cooled and filtered, and the filtrate was left for slow evaporation in air at room temperature. Yellow single crystals suitable for X-ray diffraction determination were obtained after 7 days. Yield: 21.0 mg (42.8% based on ligand). Main FT-IR absorptions (KBr pellets, v, cm^{-1}): 3441 (b), 1605 (m), 1539 (w), 1502 (m), 1441 (vs), 1385 (s), 1352 (m), 1304 (m), 1121 (w), 1034 (w), 914 (w), 837 (w), 816 (w), 727 (m), 716 (m), 628 (w), and 515 (w). Elemental *Anal.* Calc. for $C_{44}H_{32}CdN_6O_6S_4$: C, 53.85; N, 8.56; H, 3.29. Found: C, 53.52; N, 8.64; H, 3.52%. ^1H NMR (500 MHz, DMSO-d_6) δ: 9.13 (s, 2H, phen), 8.86 (s, 2H, phen), 8.28 (s, 2H, phen), 7.71 (d, 2H, J = 5.1 Hz, thiophenyl), 7.15 (d, 2H, J = 5.1 Hz, thiophenyl), 2.34 (s, 6H, Me). UV–Vis in ethanol: $\lambda_{max}/\varepsilon$ (L mol^{-1} cm^{-1}) = 360 (38068), 286 (43561), and 252 (42229) nm.

2.2.2. Preparation of complex [Cd(dtphen)$_2$·(NO$_3$)$_2$] (**2**)

Complex **2** was prepared in the same method as that of **1** except that dtphen (34.4 mg, 0.1 mmol) was used instead of dmtphen. Yield: 17.8 mg (56.0% based on ligand). Main FT-IR absorptions (KBr pellets, v, cm^{-1}): 3427 (b), 1606 (m), 1528 (w), 1481 (m), 1440 (m), 1385 (vs), 1283 (s), 1271 (s), 1228 (w), 1119 (w), 1022 (w), 914 (w), 852 (w), 814 (w), 721 (m), and 526 (w). Elemental *Anal.* Calc. for $C_{40}H_{24}CdN_6O_6S_4$: C, 51.92; N, 9.08; H, 2.61. Found: C, 51.75; N, 9.26; H, 2.87%. ^1H NMR (500 MHz, DMSO-d_6) δ: 9.30 (d, 2H, J = 1.9 Hz, phen), 9.11 (s, 2H, phen), 8.27 (s, 2H, phen), 7.91 (d, 2H, J = 3.2 Hz, thiophenyl), 7.86 (d, 2H, J = 5.0 Hz, thiophenyl), 7.36–7.31 (m, 2H, thiophenyl). $\lambda_{max}/\varepsilon$ (L mol^{-1} cm^{-1}) = 360 (34773) and 282 (41079) nm.

2.2.3. Preparation of complex [CdBr$_2$(dmtphen)$_2$] (**3**)

Complex **3** was prepared in the same method as that of **1** except that $CdBr_2{\cdot}4H_2O$ (17.2 mg, 0.05 mmol) was used instead of $Cd(NO_3)_2{\cdot}4H_2O$. Yield: 21.4 mg (42.1% based on ligand). Main FT-IR absorptions (KBr pellets, v, cm^{-1}): 3483 (b), 1603 (m), 1537 (w), 1504 (w), 1472 (w), 1443 (vs), 1416 (w), 1379 (w), 1350 (w), 1263 (w), 1225 (w), 1121 (m), 1020 (w), 914 (m), 837 (w), 779 (w), 726 (s), 629 (w), and 515 (w). Elemental *Anal.* Calc. for $C_{44}H_{32}Br_2CdN_4S_4$: C, 51.95; N, 5.51; H, 3.17. Found: C, 52.13; N, 5.74; H, 3.36%. ^1H NMR (500 MHz, DMSO-d_6) δ: 9.40 (s, 2H, phen), 8.90 (s, 2H, phen), 8.29 (s, 2H, phen), 7.73 (d, 2H, J = 4.8 Hz, thiophenyl), 7.16 (d, 2H, J = 4.7 Hz, thiophenyl), 2.42 (s, 6H, Me). UV–Vis in ethanol: $\lambda_{max}/\varepsilon$ (L mol^{-1} cm^{-1}) = 366 (37407), 287 (42973), and 253 (37464) nm.

2.2.4. Preparation of complex [CdCl$_2$(dmtphen)$_2$] (**4**)

Complex **4** was prepared in the same method as that of **2** except that. $CdCl_2{\cdot}4H_2O$ (12.8 mg, 0.05 mmol) was used instead of $Cd(NO_3)_2{\cdot}4H_2O$. Yield: 24.3 mg (55.7% based on ligand). Main FT-IR absorptions (KBr pellets, v, cm^{-1}): 3439 (b), 1605 (m), 1529 (w), 1387 (w), 1350 (w), 1439 (vs), 1387 (w), 1348 (w), 1271 (w), 1119 (w), 1067 (w), 908 (w), 849 (w), 779 (w), 725 (s), 694 (m), 598 (w), and 525 (w). Elemental *Anal.* Calc. for $C_{40}H_{24}CdCl_2N_4S_4$: C, 55.08; N, 6.42; H, 2.77. Found: C, 55.22; N, 6.54; H, 2.99%. ^1H NMR (500 MHz, DMSO-d_6) δ: 9.51 (s, 2H, phen), 9.00 (s, 2H, phen), 8.19 (s, 2H, phen), 7.86 (s, 2H, thiophenyl), 7.83 (s, 2H, thiophenyl), 7.32 (s, 2H, thiophenyl). UV–Vis in ethanol: $\lambda_{max}/\varepsilon$ (L mol^{-1} cm^{-1}) = 372 (44540) and 290 (43710) nm.

2.3. X-ray data collection and solution

Single-crystal samples of **1–4** were covered with glue and mounted on glass fibers and then used for data collection at 291(2) K. The diffraction data were collected on a Bruker SMART 1 K CCD diffractometer using graphite mono-chromated Mo Kα radiation (λ = 0.71073 Å). The crystal systems were determined