

APPENDICES

Appendix 1Pascal's Constant in $\times 10^{-5}$ /g atom or $\times 10^{-6}$ erg*G⁻² mol⁻¹

H	2.93
C	6.00
N (ring)	4.61
N (open chain)	5.57
F	6.30
Cl	20.10
Fe ²⁺	12.80
Co ²⁺	12.80
H ₂ O	13.00
ClO ₄ ⁻	34.00

Journal Name

RSCPublishing

ARTICLE

Spin-crossover, mesomorphic and thermoelectrical properties of cobalt(II) complexes with alkylated N_3 -Schiff bases

Cite this: DOI: 10.1039/C4TC02923B

Received 08th January 2014,
Accepted 08th January 2014

DOI: 10.1039/C4TC02923B

www.rsc.org

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Three new cobalt(II) complexes, $[\text{Co}(\text{L}^{12})_2](\text{BF}_4)_2$ (1), $[\text{Co}(\text{L}^{14})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (2) and $[\text{Co}(\text{L}^{16})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (3), where L^{12-16} are N_3 -Schiff bases appended with linear C_{12-16} carbon chains at the nitrogen atoms, were obtained in good yields by facile one-pot reactions. The single crystal X-ray structure of complex 1 shows a tetragonally compressed CoN_6 coordination geometry. The melting temperatures of 1–3 were lower than 373 K, while their decomposition temperatures were above 473 K. All complexes have high-spin Co(II) centres at 300 K and exhibit a columnar mesophase above 383 K. Complexes 1 and 3 showed a normal thermal spin-crossover behaviour with weak hysteresis loops at about 320 K. Hence, these complexes showed uncoupled phase transitions (class iii). The values for the Seebeck coefficient (S_s) of the cobalt redox couples formed from 1 and 2 were $1.89 \pm 0.02 \text{ mV K}^{-1}$ and $1.92 \pm 0.08 \text{ mV K}^{-1}$, respectively, identifying them as potential thermoelectrochemical materials.

1. Introduction

The spin-crossover (SCO) phenomenon, where spin states may be switched reversibly between low-spin (LS) and high-spin (HS) configurations by external stimuli such as temperature, pressure and light,^{1–6} may be exhibited by complexes of multidentate N - and N,O -donor ligands with first-row transition-metal ions (valence electronic configurations d^4).^{1,2,7–9} Among these, the most extensively studied SCO materials are complexes of iron(II) (d^6),^{10,11} and cobalt(II) (d^7),^{12,13} which have attracted the interest of many researchers as potential functional materials in fields such as molecular electronics, memory storage, thermochromic indicators and sensors.^{14,15} However such applications require that the spin transition occurs abruptly at ambient temperature (ideally room temperature) and with wide thermal hysteresis (for memory effect).

temperature that is the key to thermoelectrochemical device applications.¹⁶ For thermal energy harvesting based on the latter devices, research attention has long focused on the $[\text{Fe}(\text{CN})_6]^{3-4}$ couple in aqueous systems,¹⁷ most recently with respect to the benefits of using high-surface-area electrodes in these devices.^{18,19} The efficacy of a redox couple for thermal energy harvesting depends significantly on the dependence of the redox potential, E , on temperature, which is given by the Seebeck coefficient, $S_s = dE/dT$. This Seebeck coefficient is related thermodynamically to the entropy change associated with the redox reaction.

The Seebeck coefficient for the benchmark 0.4 M ferri-/ferrocyanide system is 1.4 mV K^{-1} .²⁰ However, this has recently been surpassed by a 0.01 M solution of *tris*(2,2'-bipyridine) Co^{III} bis(trifluoromethanesulfonyl)amide (Tf_2N), which achieves up to $2.19 \pm 0.02 \text{ mV K}^{-1}$ in 2-methoxypropionitrile (MPN).¹⁹ The origin of

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Materials Chemistry C Accepted Manuscript

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Magnetic, Photophysical and Thermal Properties of Complexes of Iron(II) with Structurally Different Schiff Bases

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(Received: ; Accepted:) AJC-0000

Three Fe(II) complexes of structurally different Schiff bases, $[\text{Fe}(\text{L}1)_2](\text{BF}_4)_2$ (1), $[\text{Fe}_2(\text{OOC}(\text{CH}_2)_6\text{CH}_3)_2(\text{L}_2)(\text{H}_2\text{O})_2]$ (2) and $[\text{Fe}_2(\text{OOC}(\text{CH}_2)_6\text{CH}_3)_2(\text{L}_3)(\text{H}_2\text{O})_2] \cdot 2\frac{1}{2} \text{H}_2\text{O}$ (3), were synthesized and characterised for potential uses as spin crossover and low bandgap materials with metallomesogenic properties. Complex 1 was obtained in a one-pot reaction involving $\text{Fe}(\text{BF}_4)_2$ with L1, while compounds 2 and 3 were obtained by step-wise reactions involving $[\text{Fe}(\text{OOC}(\text{CH}_2)_6\text{CH}_3)_2(\text{EtOH})]$ with H₂L2 and H₂L3, respectively. At room temperature, compound 1 has a low-spin Fe(II) atom while both compounds 2 and 3 have two high-spin Fe(II) atoms. The values for the optical bandgap (E_g) were 1.8 eV for compound 1, 1.9 eV for compound 2 and 2.3 eV for compound 3. These complexes were thermally stable, with decomposition temperature of 260 °C for compound 1, 205 °C for compound 2 and 250 °C for compound 3. Complexes 1 and 2 exhibited mesomorphisms while 3 was not mesomorphic.

Keywords: Iron(II), Schiff base, Spin crossover, Bandgap, Metallomesogen.

INTRODUCTION

Fe(II) complexes made up of N-donor ligands are widely investigated as spin crossover (SCO) materials. This is because the valence electronic configuration of Fe(II) ($3d^6$) may be reversibly switched between low spin (LS, t_2g^6) and high spin (HS, $t_2g^4e_g^2$) state by external stimuli, such as temperature, pressure and light irradiation^{1–6}. More recently, Fe(II) complexes are attracting attention as potential photosensitizers in dye-sensitized solar cells (DSSC)^{7–9}, to replace the more

H₂L3, respectively. A common feature of these complexes was the presence of linear 16-carbon alkyl chains, introduced in order to lower their melting temperatures¹⁰ and to induce mesomorphism (s)^{21,22}.



