Supporting Information

for

Solvent Triggered *cis/trans* Isomerism in Cobalt-Dioxolene Chemistry: Distinguishing Effect of Packing on Valence Tautomerism

Anangamohan Panja,*[†] Narayan Ch. Jana,[†] Antonio Bauzá,[‡] Antonio Frontera,*[‡] Corine Mathonière*^{,§,}

[†]Postgraduate Department of Chemistry, Panskura Banamali College, Panskura RS, WB 721152, India

[‡]Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain

[§]CNRS, UPR 9048, ICMCB, Pessac, F-33600, France. Fax: +33 5 40 00 26 49; Tel: +33 5 40 00 26 82

(A.F.);

Univ. Bordeaux, ICMCB, UPR 9048, Pessac, F-33600, France

*Corresponding Author E-mail: ampanja@yahoo.co.in (A.P.); toni.frontera@uib.es corine.mathoniere@icmcb.cnrs.fr (C.M.).

Table of Contents:

Figure S1. Powder X-ray diffraction patterns	S 3
Figure S2. UV-vis spectra of 1 and 2 in different solvents.	S4
Figure S3. cis/trans isomerism in MeOH at 45 °C	S5
Figure S4. IR spectra of 1 and 2	S 6
Figure S5. ¹ H NMR spectra of 1 and 2	S7
Figure S6. Time dependent cyclic voltammograms	S 8
Figure S7. TGA and DTA plots of original samples	S9
Figure S8. IR spectra of 2 as synthesized and after heating at 380 K	S10
Figure S9. TGA and DTA plots of ex-situ dried samples	S11
Figure S10. DFT optimized high-spin structures of 1 and 2	S12



Figure S1. Powder X-ray diffraction patterns of 2 (red) and recrystallized product of 1 from acetone (green) compared with the simulation (black for 2 and blue for 1) obtained from single crystal data.



Figure S2. UV-vis spectra in different solvents showing stability of 1 (in ethanol; green spectrum) and 2 (in acetone, pink spectrum). In other solvents (tetrahydrofuran, pyridine, acetonitrile) 1 is converted in 2. Spectra were recorded just after dissolution.



Figure S3. Time course UV-vis spectral profile showing conversion of *cis* isomer (1) to *trans* isomer (2) in MeOH solvent at 40 °C. The spectra were recorded at 30 min time interval.



Figure S4. IR spectra of **1** and **2**. The peaks marked with \$, # and * denote the C–O stretching for dioxolene ligand, C–N stretching for pyridyl group and C=O stretching for acetone.



Figure S5. ¹H NMR spectra of **1** (Top) and **2** (Bottom) in DMSO-d₆.



Figure S6. Time dependent cyclic voltammograms of 1 in DMF at ≈ 1 mM. Potentials were referenced to the ferrocene/ferrocenium couple. At the time of dissolution (a); after 1 min (b); after 2 min (c); after 5 min (d).



Figure S7. TGA and DTA plots for complexes 1 (top) and 2 (bottom).Marked weight losses corresponding to one MeOH in 1 and two acetone and two water molecules in 2.



Figure S8. IR spectra of **2** as synthesized (red) and after heating at 380 K (black). The peaks marked with , # and * denote the C–O stretching for dioxolene ligand, C–N stretching for pyridyl group and C=O stretching for acetone.



Figure S9. TGA plots for *ex-situ* dried complexes 1 (top) and 2 (bottom).



Figure S10. BP86/def2-TZVP optimized high spin structures of complexes 1 and 2. The relative energies are indicated. Distances in Å.