

A functional hybrid polyoxometalate framework based on a ‘trilacunary’ heteropolyanion $[(P_4W_6O_{34})_2Co_2Na_2(H_2O)_2]^{18-}$ †

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Full Synthesis

Na₂WO₄·2H₂O (8.25 g, 25 mmol), was dissolved in 100 ml 1M NaCl and the pH was adjusted to 3.5 using 4M nitric acid. N, N'-bis(2-hydroxyethyl)piperazine (4.75 g, 27 mmol) is then added followed by 85% H₃PO₄ (2.05 g, 17.7 mmol). This solution is then stirred until all white precipitate redissolves, and Co(NO₃)₂·6H₂O (2.18 g, 7.5 mmol) is added as solid. At this point a large amount of purple precipitate forms, and the solution is then heated to 75 °C and stirred vigorously until all this purple precipitate dissolves. A small amount of CoHPO₄ is then separated by centrifugation after cooling to room temperature, with a final pH of 6.1. A small amount of (H₂bhep)₃Na₄[B-α-P₂W₁₈Co₄O₆₈]·15H₂O is separated after 1 day. Pale purple crystals form over a two weeks period. (Yield = 800 mg, 0.18 mmol, 8.68 % based on W) Elemental analysis for (H₂bhep)₂Na₁₀[P₈W₁₂Co₂Na₂(H₂O)₂O₆₈{Co₂(H₂O)₄}]·8H₂O (%), C₁₆H₆₈N₄Na₁₂Co₄O₈₆P₈W₁₂; Calc; C 4.13, H 1.47, N 1.20, Na 6.00; found: C 4.35, H 2.07, N 1.41, Na 5.92. Characteristic IR bands (KBr): 3445 (br), 1637 (m), 1467 (wk), 1384 (sh), 1124 (wk), 1056 (m), 1019 (w), 939 (m), 894 (m), 841 (m), 701 (m), 528 (w), 457 (w), 411 (w) cm⁻¹.

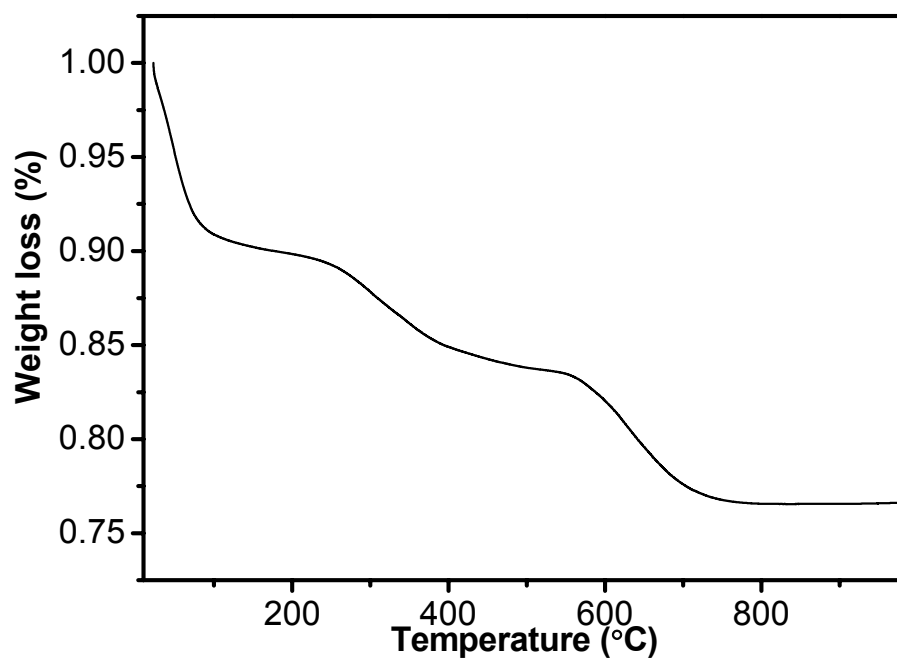


Figure S1(a) TG curve of compound 1.

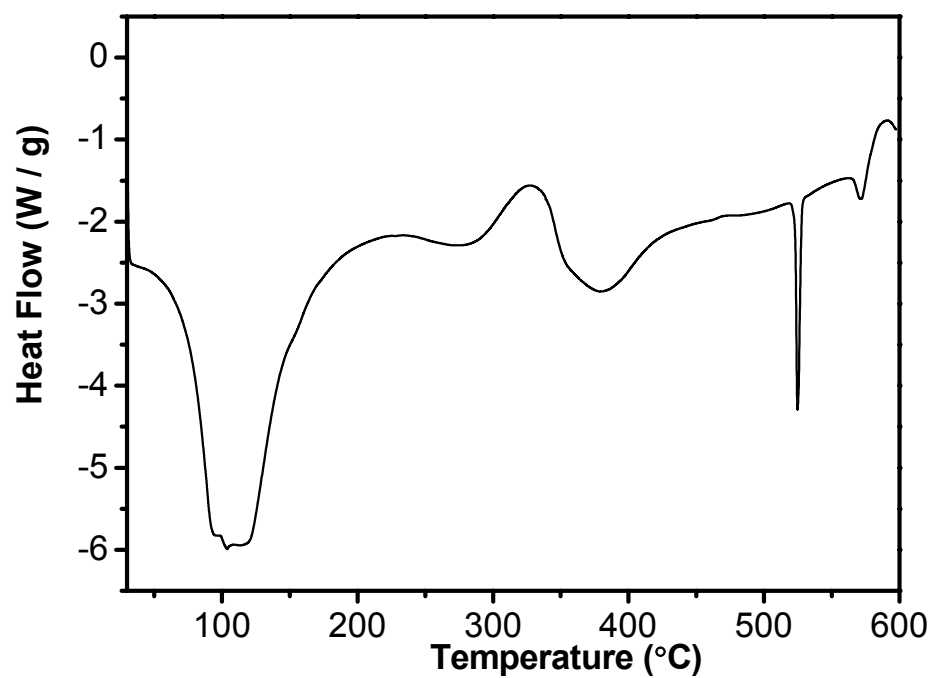


Figure S1(b) DSC curve of compound 1.

UV-Vis Absorption Spectra of the Pink and Blue crystals of Compound 1.

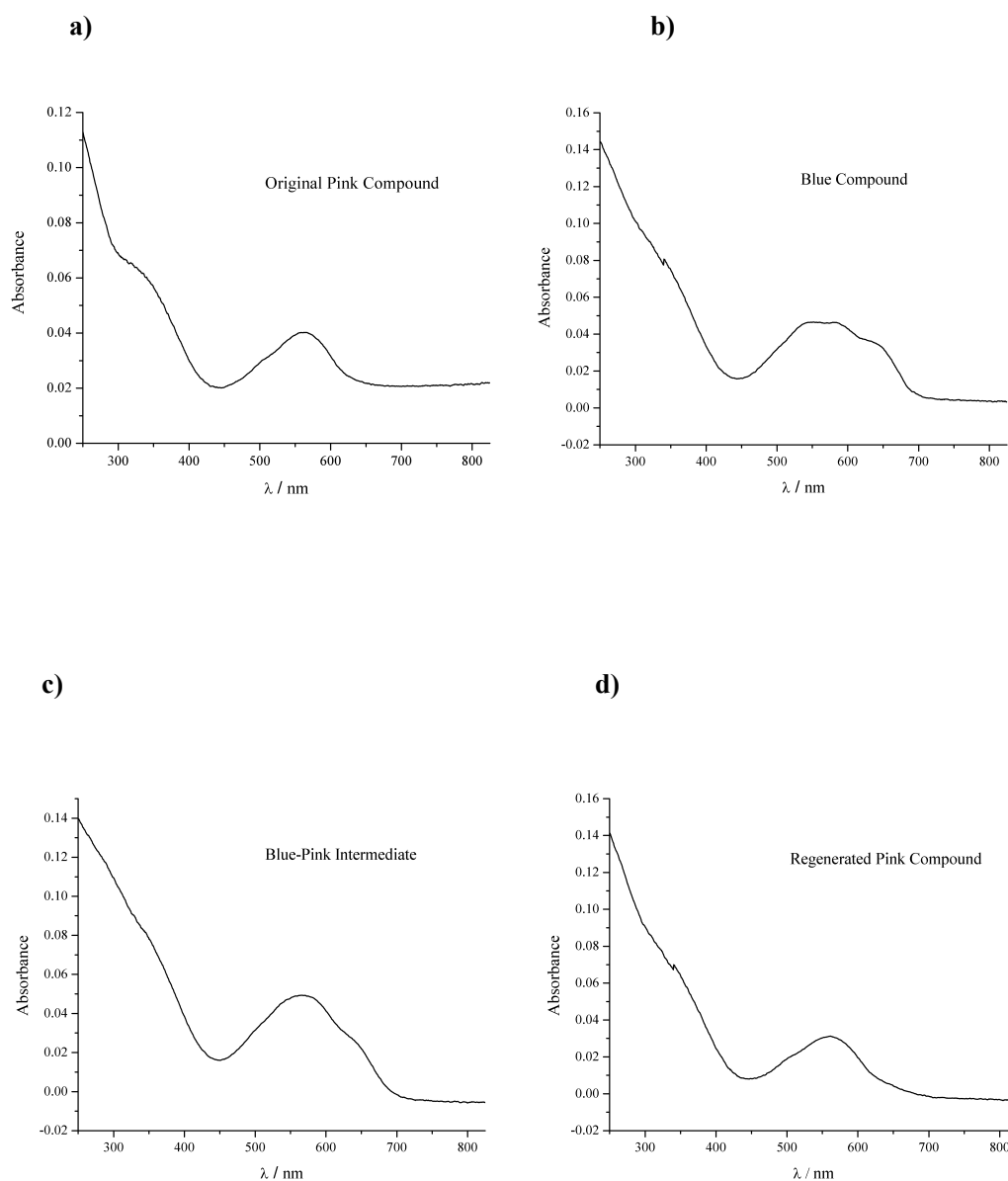


Figure S2(a-d) UV-Vis spectra of compound 1.

The UV-Vis spectra of the powdered samples of the pink and blue samples of compound 1 were measured and the spectra are shown above (**Figures S2 a** and **b** respectively). As expected, these two compounds showed considerable difference in their d-d absorption in the 450-700 nm region. For instance, the broad absorption shown by the pink compound at ~ 560 nm is split into two (538 and 584 nm) in the case of blue compound. Also a new absorption peak at ~ 640 nm is appears in the UV-Vis spectrum of the

blue compound.

To confirm the reversibility of the pink-blue conversion, we did experiments in which the blue compound was exposed to an atmosphere of water vapour in a closed sample vial. During this process it was observed that, the blue compound slowly turns back to pink and we measured the electronic spectrum of a bluish-pink intermediate coloured compound obtained after ~ 1h (**Figure S2 c**), which clearly showed that the transition is not complete. However after exposing the blue sample to water vapour overnight, the transformation was found to be complete (**Figure S2 d**) giving a spectrum that is almost identical to that of the original pink compound (**Figure S2 a**).