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ARTICLE

Turn-On Luminescence based Discrimination of Protic Acids using a Flexible Layered Metal-Organic Coordination Polymer

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Micro-sized metal-organic coordination compound, [Co(OBA)(H₂O)₂] (OBA = 4,4'-oxybis(benzoate), **1**), has been synthesized on gram scale by solvent evaporation method. Two-dimensional structure of the micro-crystals has been confirmed by comparing with the previously reported hydrothermally synthesized compound. The compound was systematically characterized by PXRD, TGA, DSC, IR and SEM studies. The compound shows reversible hydration behaviour and structural flexibility by changing the inter-layers distances. The compound changes its colour to dark blue from the bright pink after heating at 150 °C for 1 hour. The dehydrated blue compound shows weak luminescence centered at 382 nm upon excitation at 273 nm. Luminescence based titration with the addition of traces amount of aqueous solution of various acids with different *pK_a* values such as hydrochloric acid (HCl), nitric acid (HNO₃), sulphuric acid (H₂SO₄), oxalic acid (COOH)₂, formic acid (HCOOH), acetic acid (CH₃COOH) in dehydrated compound (**1'**) dispersed in acetonitrile show differential luminescence turn-on according to their *pK_a* values. Similar behaviours have also been observed for amino acids based on their isoelectric point (*pI*).

Introduction

The clever blend of the principles of supramolecular and coordination chemistry gave rise to a attractive variety of solids that are now being known as metal-organic coordination polymers (MOCPs).¹ MOCPs are relatively a new class of hybrid crystalline materials with diverse structural characteristics constructed by the connectivity of metal ions or metal clusters and organic ligands.² The exceptional non-covalent interactions along with good structural robustness and flexibility exhibited by these compounds make them attractive for research.³ MOCPs have shown a variety of potential applications such as gas storage,⁴ gas separation,⁵ catalysis,⁶ magnetism,⁷ drug delivery,⁸ bio-imaging⁹ and proton conductivity.¹⁰ Many of the important MOCPs compounds have three-dimensional structures, and the preparation of two-dimensional ones is also significant because some of them can replicate the behaviour of naturally occurring clays.¹¹ The two-dimensional compounds can also take part in variety of host-guest chemistries such as photopolymerization reactions, catalysis, etc.¹² Solvent molecules can play a important role in the control of crystal structure and the physical and chemical behaviour of the MOCP compounds.¹³

Luminescence behaviour of MOCPs has become an active area of research based on various potential applications.¹⁴ Details investigations point to the observation of two types of luminescent properties in MOCP: (i) intra-ligand and (ii) ligand sensitized metal centre luminescence. Very recently, significant progress has been made in the uses of both of these types of luminescence property of MOCPs for sensing of small molecules,¹⁵ metal ions¹⁶ and explosives.¹⁷

Luminescence based methods for the sensing of pH¹⁸ and the determinations of *pK_a* values¹⁹ have also reported using various

materials such as organic polymer, mesoporous thin film, DNA-conjugated polymer composite, inorganic complexes, semiconductor quantum dot, silica nano-particles etc. Nevertheless, their wide spread use is limited owing to multistep processing, requirement of expensive chemicals, stability and lack of molecular organization. Recently few Zr and lanthanide based MOCPs have been used for the pH sensing based on their luminescence properties,²⁰ but there are no reports of discrimination of protic acids according to their *pK_a* values using MOCP.

Based on the above considerations, we have prepared micro crystals of a two-dimensional Co-based MOCP [Co(OBA)(H₂O)₂] [(OBA = 4,4'-oxybis(benzoate)], **1**, through simple solvent evaporation methods on gram scale. Powder X-ray diffraction studies indicate that **1** has the same structure as the hydrothermally synthesized compound reported earlier by Natarajan and co-workers.²¹ The compound **1** has bright pink colour in day light and upon dehydration at 150 °C for 1 hour it changes to dark blue colour. The dehydrated compound (**1'**) retains its blue colour in various water miscible solvents but changes to pink only in presence of water. **1'** shows weak blue emission upon exposure to UV light. **1'** in acetonitrile show high luminescence turn-on behaviour in presence of trace amount of 0.001 N of aqueous solution of various protic acids such as HCl, HNO₃, H₂SO₄, (COOH)₂, HCOOH and CH₃COOH. The degrees of luminescence turn-on in presence of these acids are according to the *pK_a* values (highest turn-on for lowest *pK_a* value). Similar luminescence turn-on behaviour have also been observed in the case of three amino acids, L-aspartic acid, L-glutamic acid and L-alanine based on their isoelectric points (*pI*). Enhancement in luminescence according to their hydrogen ion concentration (*pK_a/pI*) in presence of trace amount of these aqueous acid solutions gives a clear indication of strong molecular level interaction between MOCP and the hydrogen

ions. This is the first observation, to our knowledge, where a MOCP is used for the discrimination of protic acids according to their pK_a/pI values. In this article, we present the gram scale synthesis and luminescence based discriminating behaviour of various protic acids using the dehydrated compound, **1'**.

Experimental Section

Materials

The chemicals needed for the synthesis of the metal-organic coordination compound, are $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, 98%), 4,4'-oxybis(benzoic acid) (Sigma-Aldrich, 99%) and NaOH (Merck, 97%) were used as received. The chemical used for the luminescence experiments, hydrochloric acid (HCl) (35%), nitric acid (HNO_3) (69%), sulphuric acid (H_2SO_4) (98%), oxalic acid ($(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) (99%), formic acid (HCOOH) (85%), acetic acid (CH_3COOH) (99%), sodium chloride (99%), sodium nitrate (99.5%), sodium sulphate (99%), were used as received from Merck without further purification. Sodium oxalate, sodium formate and sodium acetate, were prepared using their corresponding acids and NaOH. The amino acids used for the luminescence experiments, L-alanine (Ala) (99%), L-aspartic acid (Asp) (98%) and L-glutamic (Glu) (99%), were used as received from Sigma-Aldrich without further purification. The solvents used for the luminescence experiments, acetonitrile (99%), methanol (99.5%), ethanol (99.9%), acetone (99%), DMF (99%), DMSO (99%), were used as received from Merck without further purification. The water used was double distilled and filtered through a Millipore membrane.

Synthesis and initial characterizations

Compound **1** was prepared by simple solvent evaporation reaction. For this, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.97 g, 4 mM) was dissolved in 20 ml of water in a 100 ml beaker. In another 100 ml beaker, 4,4'-oxybis(benzoic acid) (1.04 g, 4 mM) and NaOH (0.33 g, 8 mM) were dissolved in 20 ml of water. Both the solution mixture was heated at 100°C for 10 min. Then the homogeneous solution of 4,4'-oxybis(benzoic acid) and NaOH was poured into the cobalt salt solution and the resulting solution mixture was kept in a hot plate with continuous stirring at 80°C for 3 hours. After that, the mixture was continuously heated at 80°C for 12 hours without any stirring. The final product, containing large quantities of dark pink colored homogenous micro crystals, was filtered, washed with deionized water under vacuum, and dried at ambient conditions (Yield 85 % based on Co). Elemental analysis calcd (%) for **1**: C 47.84, H 3.42; found: C 47.65, H 3.33. The products were analyzed by PXRD and the PXRD patterns being entirely consistent with the simulated XRD pattern generated based on the structures determined using the single-crystal XRD data of $[\text{Co}(\text{OBA})_3(\text{H}_2\text{O})_2]$ (CCDC: 897211) (see ESI, Fig. S1).

Instrumentations

The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Miniflex diffractometer with $\text{Cu K}\alpha$ radiation within the 2θ range of $5\text{--}50^\circ$. The IR spectrums were recorded on a KBr pellet using JASCO FT/IR-6300 Fourier Transform Infrared Spectrometer. The thermogravimetric analysis (TGA) was carried out using Perkin-Elmer Diamond instrument in nitrogen atmosphere (flow rate = 20 mL/min) in the temperature range of RT- 800°C at a heating rate $10^\circ\text{C}/\text{min}$. The differential scanning calorimetric (DSC) measurement was performed in nitrogen atmosphere using TA Instrument, Q2000 in the temperature range of $30\text{--}500^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

$^\circ\text{C}/\text{min}$. The morphologies and the sizes of the synthesized compound were investigated using scanning electron microscope (QUANTA FEG250, FEI). High temperature magnetic studies of compound **1** were performed using Lakeshore Vibrating Sample Magnetometer.

Photoluminescence based measurements

The photoluminescence properties of **1'** dispersed in acetonitrile were investigated at room temperature. The dispersions were prepared by introducing 5 mg of **1'** into 100 mL solvent and ultrasonic agitation for 30 minutes. Photoluminescent spectra were measured using a Fluorolog Horiba Jobin-Yvon spectrometer. The analytes were added into the dispersion using micro pipette.

Results and Discussion

Structure, morphology and thermal behaviour

To describe and discuss the properties of **1'**, it is important to discuss briefly about the structure of **1**. Here, the Co^{2+} ions are linked to the carboxylate units forming a one dimensional wire-like structure, which are connected by the OBA unit forming a two-dimensional layer structure. Hydrogen bond interactions between the coordinated water of one layer and carboxylate oxygens of another layer gives rise to a supra-molecularly organized three-dimensional structure (Figure 1).

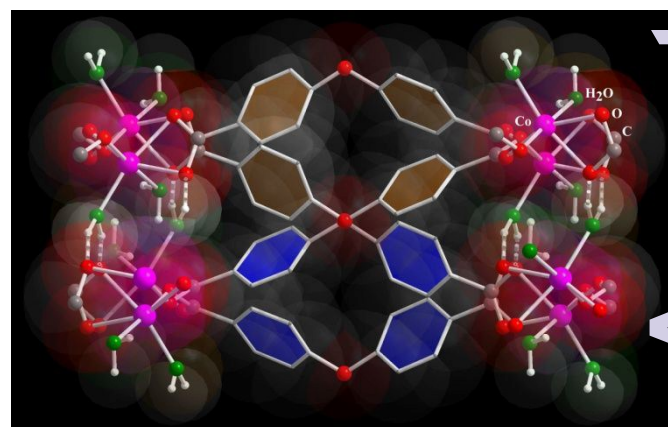


Fig.1: Arrangement of two layers in compound **1**. Dotted lines represent the hydrogen bond interactions.

The size and the morphologies of compound **1** were studied using scanning electron microscopy. Powder grains are of plates shaped in micro size regime (Figure 2).

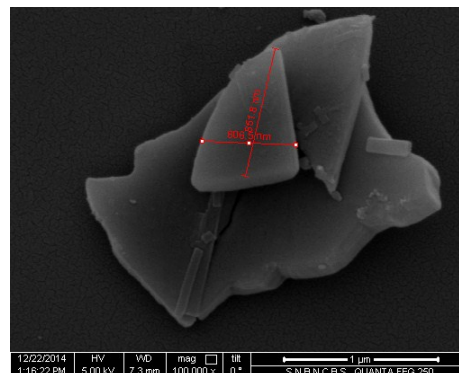


Fig.2: SEM image of compound **1**

TGA shows that **1** release coordinated water molecules in the range of 125 - 155 °C (observed weight loss 9.5%, calculated weight loss 10.25%) followed by the decomposition of the framework in the range of 375 - 460 °C (Figure 3). The DSC data show two endothermic peaks centered at 148 °C (calculated 1.84 Kcal/mole of water) and 431 °C corresponding to removal of water molecules and decomposition of organic ligand, respectively (Figure 3). To understand the dynamics of the water molecules, **1** was heated at 150 °C for 1h in an oven. The heated sample changed its colour from pink to blue due to the removal of the coordinated water molecules (Figure 4). The changes of colour indicate the changes of coordination geometry from octahedral to tetrahedral around Co^{2+} metal ions.

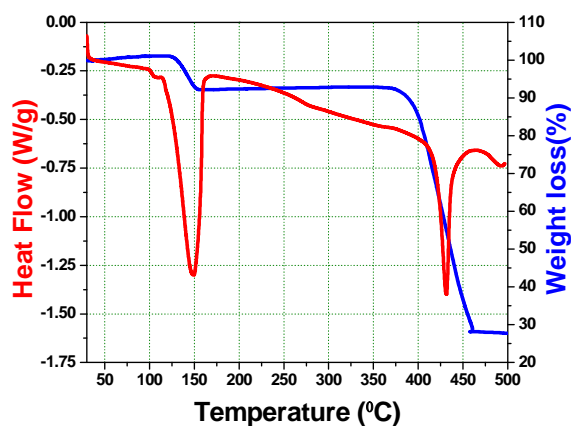


Fig.3: TGA and DSC studies of compound **1**.

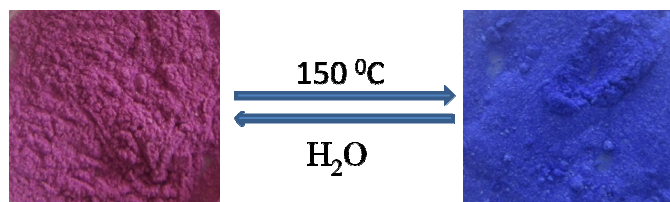


Fig.4: Photograph of original and dehydrated compound.

The dehydration was further confirmed by IR spectroscopy as the broad band due to water molecules in the range of 3000-3500 cm^{-1} disappeared after the sample heated at 150 °C for 1 hour (see ESI, Fig. S2).

To check the reversibility of the water molecules removal, the dehydrated compound (**1'**) were kept in open air for various time interval. The powder XRD patterns of all the samples were compared with the XRD pattern of the original **1** and the dehydrated one (**1'**) (see ESI, Fig. S3). The powder XRD pattern of **1** heated at 150 °C/1h indicates a shift of the two main peaks towards higher 2θ angles from $2\theta = 8.6$ to 8.8° and 13.1 to 13.7° (Figure 5). The main peaks appear to return back towards the originally observed 2θ values when the dehydrated sample was mixed with minute quantity of liquid water; but the reverse transition (uptake of H_2O) appears not complete even after keeping the sample exposed to atmosphere for 3 days. This indicates that the coordinated water molecules may be reversibly adsorbed.

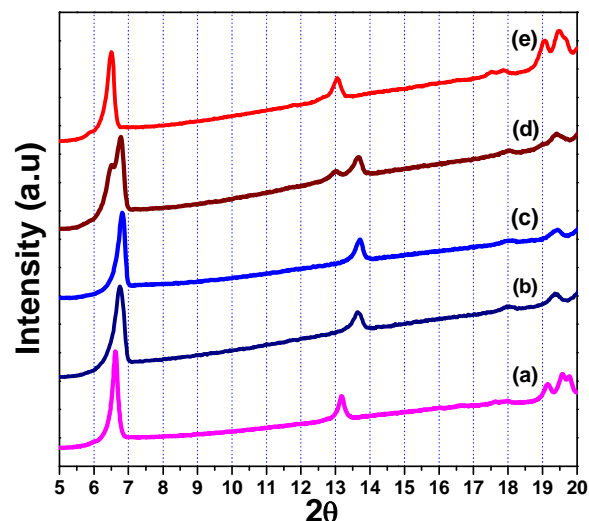


Fig.5: The ex-situ heated powder X-ray diffraction patterns of the compound **1**: (a) compound **1**, (b) the sample heated 150 °C for 1 h, (c) dehydrated sample left under atmospheric condition for 1 day, (d) dehydrated sample left under atmospheric condition for 3 days, (e) the dehydrated sample after mixing with minute quantity of water.

The changes of the coordination geometry around the Co^{2+} ions have studied using solid-state visible spectroscopy (Figure 6). The original compound and rehydrated one shows almost identical spectra. On the other hand, a spectrum of the dehydrated compound (blue one) is completely different. This support the formation of four coordinated Co^{2+} centres after the dehydration from the six coordinated Co^{2+} centres in original compound and its reversibility after rehydration.

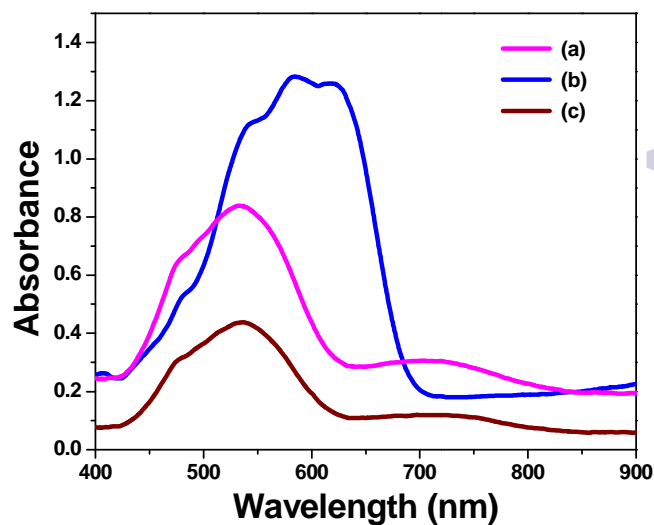


Fig.6: Visible spectra of the powdered sample: (a) compound **1**, (b) dehydrated compound, (c) rehydrated compound. Note the similarity between the spectra of original and rehydrated compound.

The powder X-ray diffraction patterns and visible spectra of the dehydrated compound (**1'**) suggest that the inter-layers distances between the two dimensional metal-organic frameworks are reduced after the removal of the coordinated water molecules. As a result the distances between the OBA ligands of two different adjacent layers are expected to reduce. The reductions of the distances between the

OBA ligands have significant role for the luminescence properties. The stability of dark blue coloured dehydrated compound (**1'**) were also tested in various water miscible solvents such as methanol, ethanol, acetone, DMF, DMSO, acetonitrile and mixture of water and acetonitrile by immersing the blue dehydrated compound in these liquid solvent (see ESI, Fig. S4). The dehydrated compound (**1'**) remains blue in colour in all the cases except in water and the mixture of water and acetonitrile. This indicates that only in presence of water the dehydrated blue compound changes to pink colour. Powder X-ray diffraction pattern of **1'** (blue compound) after immersing in acetonitrile for 24 hrs followed by drying in open air and its comparison with original **1'** confirmed the stability of the dehydrated state (see ESI, Fig. S5).

To understand the magnetic behaviour after the dehydration, magnetic susceptibility measurement has been carried out on powdered sample in high temperature. As can be seen from Figure 7, the magnetic susceptibility value has been reduced drastically in the range of 425 - 475 K. The changes can be correlated with the changes of the coordination geometry during the dehydration. In octahedral coordination geometry with $t_{2g}^5 e_g^2$ electronic configuration of high spin Co^{2+} systems have significant orbital contribution due to the presence of four electrons in degenerate t_{2g} level. Whereas in tetrahedral geometry with $e^4 t_2^3$ electronic configuration of Co^{2+} systems do not have orbital contribution in total magnetic moment due to the half filled t_2 level and full filled e level. Hence, the reduction of magnetic susceptibility in that range further supports the changes of coordination geometry during the dehydration. Magnetic susceptibility measurements have also been studied separately for **1** and **1'** in the low temperature range (80-325 K) (see ESI, Fig. S6). In low temperature, **1** show slightly higher values of magnetic moment compared to **1'** due to the differential orbital contribution.

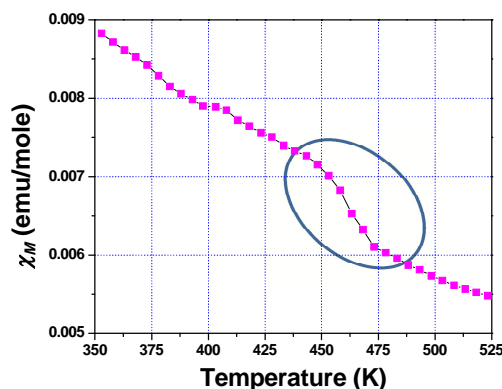


Fig.7: Temperature variation of molar magnetic susceptibility (χ_M) in high temperature range (350-525 K). The encircled portion of plot shows the large changes of magnetic susceptibility.

Luminescence studies

The dehydrated blue compound (**1'**) when dispersed in acetonitrile exhibited weak emission centered at 382 nm upon excitation at 273 nm (see ESI, Fig. S6). The emission observed are due to intra-ligand transitions ($\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ transitions) of the OBA ligands. The emissions of **1'** are also sensitive to the changes of the solvents. It shows emissions at 371, 389, 402, 405 and 410 nm, respectively, for DMSO, ethanol, acetone, methanol and DMF upon excitation at 273 nm (see ESI, Fig. S7). To explore the ability of **1'** to differentiate protic acids using trace amount of their aqueous solution of ultra low concentration, luminescence titrations were performed with the

incremental addition of acid solutions to **1'** dispersed in acetonitrile. Figure 8 shows changes in the luminescence intensity with the increasing addition of 0.001 N HCl ($pK_a = -6.3$) solutions (upto 0.500 % v/v). The emission of **1'** on UV exposure was intensified upon the addition of HCl solution, which is nearly 13 times of the initial luminescence intensity. The luminescence quantum yield has been calculated using L-tyrosine as standard. The observed values are 0.045 and 0.4, respectively, for before and after addition of the 0.001 N HCl solutions (0.500% v/v) in acetonitrile. Similar luminescence based titrations were also performed with other protic acids with diverse pK_a values such as nitric acid (HNO_3 , $pK_a = -1.64$), sulphuric acid (H_2SO_4 , $pK_1 = -3$, $pK_2 = 1.92$), oxalic acid ($(COOH)_2$, $pK_1 = 1.23$, $pK_2 = 4.19$), formic acid ($HCOOH$, $pK_a = 3.7$) and acetic acid (CH_3COOH , $pK_a = 4.7$) and pure water ($pK_a = 15.7$) (see ESI, Fig. S8-S13).

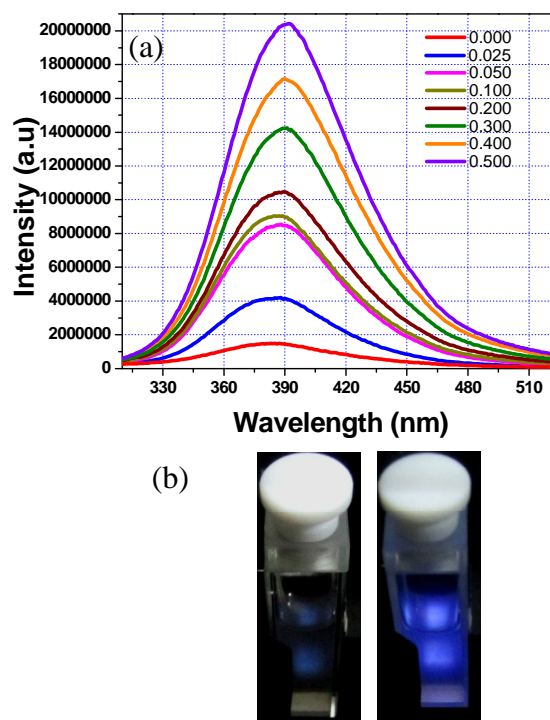


Fig.8: (a) Emission spectra of **1'** dispersed in acetonitrile upon incremental addition of 0.001 N HCl solutions (0.025-0.500% v/v). The excitation wavelength (λ) is 273 nm. The volume of the aqueous solution with respect to the volume of acetonitrile solution in the medium is indicated in the legend as % v/v. (b) Images showing the original luminescence of **1'** (left) and the turn-on one in presence of 0.5 % v/v of aqueous solution of 0.001 N HCl (right).

Luminescence turn-on behaviours have been observed in all of these protic acids solutions and the degrees of turn-on efficiencies are according to the acids dissociation constants (pK_a values). The changes of luminescence intensity (turn-on) in the case of all protic acids after the addition 0.5% v/v of aqueous acid solutions are shown in figure 9 as bar diagram with respect of I/I_0 values. These results indicate luminescence behaviour of **1'** can be used for the differentiation of protic acids according to their pK_a values.

Similar luminescence titrations with the corresponding sodium salts solutions show less turn-on behaviours. This indicates the role of hydrogen ions in the aqueous solution (see ESI, Fig. S14-S19).

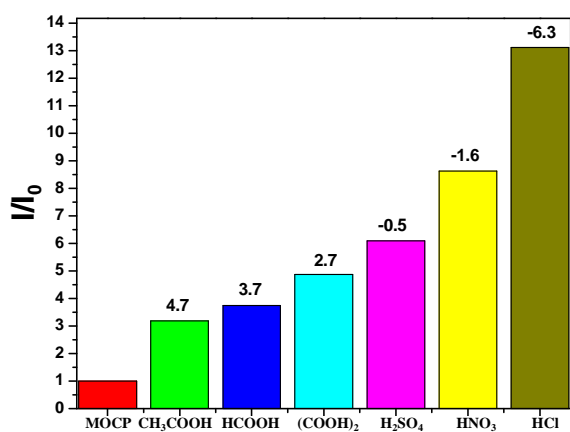


Fig.9: Plot of I/I_0 of **1'** and all the protic acids. I_0 and I are luminescence intensity in absence of acid solution and presence of 0.500 % v/v of 0.001 N acids solution, respectively. The pK_a value of each acid is mentioned in top of bar. In the case of sulphuric acid and oxalic acid average pK_a values are given.

Encouraged by the results of the common protic acids, the phenomenon has been extended for the amino acids. For these three amino acids have been chosen, L-aspartic acid, L-glutamic acid and L-alanine (see ESI, Fig. S20-S22). In these cases, the luminescence turn-on behaviours are according to the values of isoelectric points (pI) (Figure 10). L-aspartic acid, L-glutamic acid and L-alanine show 3.36, 3.05 and 2.71 fold enhancement in luminescence intensity upon the addition of 0.500% (v/v) addition.

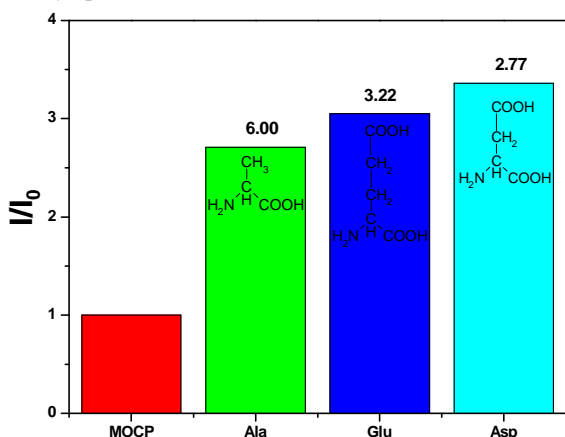


Fig.10: Plot of I/I_0 of **1'** and all the amino acids. I_0 and I are luminescence intensity in absence of amino acid solution and presence of 0.500 % v/v of 0.001 N amino acids solution, respectively. The pI value of each amino acids are mentioned in top respective bar.

To understand the observed luminescence turn-on behaviour in presence of aqueous solution of acids, the structural transformation from the blue dehydrated state to hydrated pink state is important. This transformation helps for efficient luminescence behaviour by increasing the inter-ligand (inter-OBA) distances of the compound.^{3c} The process has been shown schematically in Figure 11. The hydrogen bonding between coordinated water and organic ligands of pink state help to exceed the critical radius between two OBA ligands for coulombic energy transfer, thereby favouring the radiative deactivation of ligand-based excited states. Whereas in blue state the self-quenching of intra-ligand emission becomes

important factor for the observation less intense luminescence. In acidic solution, the higher hydrogen ions concentration in the system further help to form the stable pink compound by increasing the higher hydrogen bonding effect. The acids with lower pI values/ pI values in aqueous medium can increase the hydrogen ions concentration in medium, which effectively help to increase the luminescence intensity.

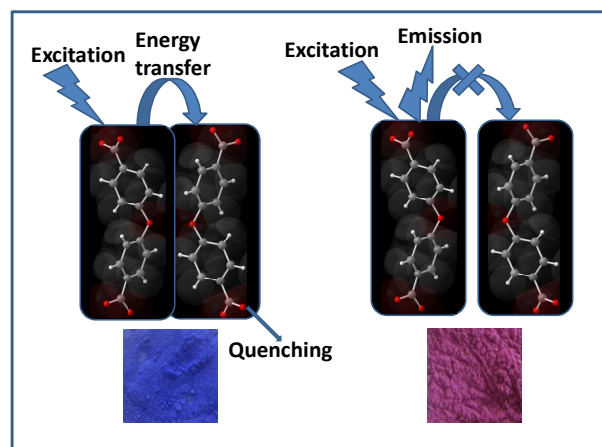


Fig.11: Schematic of luminescence behaviour of blue and pink compounds through the changes of inter-ligands distances.

Conclusions

In conclusion, a micro sized layered MOCP has been synthesized on gram scale by simple solvent evaporation reaction. The compound shows exceptional flexibility and reversible hydration behaviour. Luminescence based titrations with the addition of traces amount of various acidic aqueous solutions in dehydrated MOCP dispersed in acetonitrile show differential luminescence turn-on behaviours based on their pK_a values. The compound also show discriminating behaviour in presence of traces amount of aqueous solution of amino acids based on their isoelectric points (pI). Luminescence turn-on behaviour according to their hydrogen ion concentration (pK_a/pI) in presence of trace amount of these aqueous acid solutions gives a clear indication of strong molecular level interaction between MOCP and the hydrogen ions. This is the first observation, to our knowledge, where a MOCP is used for the discrimination of protic acids/amino acids according to their pK_a/pI values.

Acknowledgements

This work was supported by INSPIRE faculty research grant (IFA12-CH-69) and fast track project grant (SB/FT/CS114/2012) of Department of Science and Technology (DST), Government of India. NS thanks CSIR, Government of India for fellowship.

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[†]Electronic Supplementary Information (ESI) available: Details of the experimental data. See DOI: 10.1039/c000000x/

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