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Aggregation induced emission of excited state intramolecular proton transfer compounds: Nanofabrication mediated white light emitting nanoparticles

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ABSTRACT: Excited state intramolecular proton transfer (ESIPT) compounds, 2-(2-((2-hydroxybenzylidine)amino) phenoxy) benzonitrile (1) and 2-(4-((2-hydroxy-4-methoxy benzylidine)amino) phenoxy) benzonitrile (2) exhibited aggregation induced enhanced emission (AIEE) in the solid state and nanofabrication mediated white light emission. The strong intermolecular interactions (H-bonding, C-H... π and π ... π) restrict the free rotation and rigidify the fluorophores, 1 and 2, in the crystal lattice that lead to enhanced fluorescence in the solid state of 1 (yellow, $\lambda_{max} = 535$ nm, $\Phi_f = 38$ %) and 2 (greenish-yellow, $\lambda_{max} = 525$ nm, $\Phi_f = 21$ %). Surprisingly, nanofabrication of 1 and 2 produced meta-stable white light emitting nanoparticles ($\Phi_f = 24$ % (1), 19% (2)) that slowly converted into stable yellow (1) or greenish-yellow (2) fluorescent nanoparticles with increasing time. The time dependent fluorescence, morphological and metal ion interacting studies indicate the formation of soft nanoparticles in which both blue fluorescent cyanophenoxy and yellow/greenish-yellow fluorescent salicylidene

group behave independently. **1** and **2** nanoparticles undergo morphological change from spherical to plates with increasing time. Thus simple ESIPT molecules showed solid state fluorescent and nanofabrication induced tuneable fluorescence particularly white fluorescent meta-stable nanoparticles.

Introduction

Organic solid state fluorescent materials have played significant role in developing modern optoelectronic devices such as light emitting diodes, flexible display, organic lasers, photovoltaic cells and sensors.¹⁻⁷ Particularly, small organic materials and nanostructures with tuneable fluorescence are important for developing multiple color emitting devices. However, aggregation caused quenching (ACQ) remains a big challenge for solid state fluorescence since that promoted non-radiative decay process caused by strong intermolecular vibronic interactions and excimer formation.⁸ Hence various approaches including use of twisted molecular conformation and supramolecular complexation have been explored for generating organic solid state fluorescence systems.⁹⁻¹²

In recent years, a new class of organic functional materials that exhibit unusual aggregation-induced enhanced emission (AIEE) in the solid state has emerged as an important topic both in the field of fundamental research and device applications.¹³⁻¹⁴ The AIEE molecules are non-fluorescence or weakly fluorescent in the solution but show strongly enhanced fluorescence in the aggregated/solid state by rigidifying fluorophore and restricting intramolecular rotation. Tetraphenylethylene, cyanostilbene, triphenylethylene and triarylamine derivatives are some of the organic molecules employed for generating AIEE materials.¹⁵⁻²⁰ Organic fluorescent compounds that exhibit excited state intramolecular proton transfer (ESIPT)

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mechanism constitute another interesting class of functional materials because of their unique four-level cyclic proton-transfer reactions.²¹ The ESIPT compounds exhibit large Stokes shifts and unique fluorescence that made them as potential candidates for wide application in molecular switches, laser dyes, sensors and UV photostabilizers.²²⁻²⁴

Tuneable organic solid state fluorescence often realized via systematic modulation of structures, polymorphism, nanofabrication, controlling supramolecular interactions and inclusion of guest molecules.²⁵⁻³³ AIEE and ESIPT mechanism has also been utilized for fabricating organic materials with tuneable emission.³⁴⁻³⁶ AIEE responsive single molecule with twisted molecular conformation could show multi-color emission due to external stimuli induced conformational change or different molecular packing in the aggregated state.³⁷⁻⁴¹ The tuneable multi-color fluorescence of some AIEE and ESIPT materials have also lead to white-light emission.⁴²⁻⁴³ The simultaneous generation of three primary color (red, green and blue) or at least any two color with equal intensity covering wide visible spectrum would be ideal for white-light emitter. White light emitting organic molecular assemblies in nanostructures, solution and solid state have often been realized using multiple components via Forster resonance energy-transfer (FRET) between donor and acceptor. However, white light emission from single small organic fluorescent molecules are rarely reported.⁴⁴⁻⁴⁶ Recently, Maity et al. reported unique ESIPT couple AIEE in a single organic molecule for generating multiple emission including white light emission.47

In this manuscript, we report AIEE from simple ESIPT compounds, **1** and **2**, and nanofabrication induced tuneable fluorescence including white light emission and fluorescence sensing of Cu²⁺ and Co²⁺ metal ions. Single crystal analysis revealed strong intermolecular interactions (H-bonding, C-H... π , π ... π) in the crystal lattice of **1** and **2** that restrict free rotation

and rigidify the fluorophores. This leads to strong enhancement of fluorescence in the solid state. **1** and **2** showed yellow (λ max = 535 nm, Φ_f = 38 %) and greenish-yellow (λ max = 525 nm, Φ_f = 21 %) emission, respectively. Nanofabrication of **1** and **2** in water produced rare meta-stable white light emitting nanoparticles that slowly transform into yellow/greenish yellow emitting nanoparticles. SEM studies revealed morphological change of **1** and **2** nanoparticles from spherical to plates with increasing time and support the fluorescence change. Further, selective fluorescence quenching of salicylidene group by Cu²⁺ and Co²⁺ metal ions demonstrate the formation of soft nanoparticles in which cyanophenoxy and salicylidene groups are behaving independently. The tuneable fluorescence particularly white light emission of simple ESIPT molecules could be potential interest in optoelectronic applications.

Materials and methods

2-fluoro-nitrobenzene, 4-fluoro-nitrobenzene, 2-cyanophenol, NaBH₄, Pd/C, salicylaldehyde and 2-hydroxy-4-methoxy benzaldehyde was obtained from sigma-Aldrich and used as received. The solvents were obtained from Merck India. All chemicals are used as received. The metal ion solutions used for the colorimetric sensor experiments were prepared in Mill-Q water. Ultrapure water produced using a Milli-Q apparatus (Millipore), was used in all experiments.

Synthesis of 1 and 2:

Schiff base ESIPT molecules, **1** and **2** was synthesized following our reported procedure (Scheme S1).⁴⁸ Typically, salicylaldehyde (1.1mmol) dissolved in ethanol (20 ml) was added drop-wise into ethanol (5 ml) solution of 2-(2-cyanophenoxy)aminobenzene (1mmol) under stirring at room temperature. The resultant reaction mixture was refluxed for 5 h. The product was precipitated out upon cooling the reaction mixture to room temperature. The precipitate was filtered, washed with ethanol and dried under vacuum. 2 has also been synthesized in a similar

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procedure but by using 4-methoxysalicylaldehyde (1.1mmol) and 4-(2cyanophenoxy)aminobenzene in ethanol solution.

1: Yield = 85 %. m.p. 171-173 °C. ¹H NMR (CDCl₃) δ 12.419 (s, 1H (OH)), 8.674 (s, 1H (imine H)), 7.617-7.640 (d, 1H), 7.448-7.453 (d, 1H), 7.427-7.434 (t, 1H), 7.408-7.413 (d, 1H), 7.309-7.332 (m, 4H), 7.175-7.192 (m, 1H), 7.072-7.110 (t, 1H), 6.885-6.922 (m, 2H), 6.754-6.777 (d, 1H). ¹³C NMR (CDCl₃) δ 164.77, 161.10, 159.49, 147.03, 141.14, 134.19, 133.92, 133.57, 132.64, 127.98, 126.58, 122.68, 122.21, 121.27, 119.06, 119.01, 117.28, 115.93, 115. 60, 102.81.

2: Yield = 90 %. m.p. 116-118 °C. ¹H NMR (CDCl₃) δ 13.601 (s, 1H (OH)), 8.674 (s, 1H (imine H)), 7.661-7.676 (d, 1H), 7.512-7.516 (t, 1H), 7.472-7.497 (m, 3H), 7.262-7.306 (m, 3H), 6.892-6.913 (d, 1H), 6.492-6.516 (t, 2H), 3.85 (s, 3H). ¹³C NMR (CDCl₃) δ 164.19, 163.82, 161.71, 159.86, 153.55, 145.67, 134.40, 134.09, 133.73, 123.11, 122.73, 121.05, 117.08, 116.06, 113.18, 107.07, 103.90, 101.22, 55.61.

Nanoparticles fabrication of 1 and 2: The stock CH_3CN solution (10 ml) of 1 and 2 (10⁻³ M) was prepared and stored. 100 µl of this solution was rapidly injected into 20 ml of water under vigorous stirring at room temperature. The stirring was allowed to continue for another 30 minutes. The samples were subjected absorption, fluorescence and microscopy studies immediately as well as after 24 h. The nanoparticles of 1 and 2 were collected on the aluminium foil surface and dried under vacuum for microscopy analysis. Spectroscopic analysis of the nanoparticles was carried out while keeping the sample directly in the solution. The effect of temperature, pH, presence of different ions (cations/anions) in the water and stirring speed has been explored on the formation of nanoparticles and fluorescence change.

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Microscopy characterization: The morphologies and sizes of the nanoparticles were examined using field emission scanning electron microscopy ((FE-SEM) (JSM-6701F, JEOL Japan INC) with an accelerating voltage 30 kV and filament current of 20 mA for 45 seconds. The samples are stuck onto a double-face conducting carbon tape mounted on a brass stub. Prior to analysis, the samples were coated with a thin layer of gold.

Structural analysis: Single crystal of 1 and 2 was coated with paratone-N oil and the diffraction data measured at 100K with synchrotron radiation ($\lambda = 0.62998$ Å) on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program⁴⁹ was used for data collection (detector distance is 63mm, omega scan; $\Delta \omega = 3^{\circ}$, exposure time is 2 sec per frame) and HKL3000sm (Ver. 703r)⁵⁰ was used for cell refinement, reduction and absorption correction. The crystal structure of 1 and 2 was solved by the direct method with SHELX-XT (2014/4) program and refined by full-matrix least-squares calculations with the SHELX-XL (2014/7) program package.⁵¹ All non-hydrogen atoms except some atoms with high thermal anisotropies and all the solvent atoms were refined anisotropically. The hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C,N) or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective atoms. CCDC-1414929 (1) and 1414930 (2) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EX, UK.

Spectroscopy and characterization: Absorption and fluorescence spectra were recorded using Perking Elmer Lambda 1050 and Jasco fluorescence spectrometer-FP-8200 instruments. Fluorescence quantum yields (Φ_f) of solid samples were measured using a Horiba Jobin-Yvon

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model FL3-22 Fluorolog spectrofluorimeter with integrating sphere. **1** and **2** solids and nanoparticles were excited at 370 nm for measuring quantum yields. IR spectra were recorded using KBr disks on a Shimadzu affinity spectrophotometer over the range 4000 - 400 cm⁻¹ using KBr as the reference.

Result and Discussion

1 and **2** Schiff base compound was synthesized by condensing corresponding aromatic aldehyde and amine precursors in ethanol as shown in Scheme S1.⁴⁸ The amine precursors were prepared by reaction between 2-cyanophenol and 2-fluoro or 4-fluoro nitrobenzene in presence of K₂CO₃ in DMSO at 110 °C and subsequent reduction of nitro group using NaBH₄ in presence of catalytic amount of Pd/C in methanol. Absorption studies of **1** and **2** showed π - π * transition between 340-345 nm in different solvents (Fig. S1). The absorption maxima of **1** and **2** did not shift significantly in different solvents that ruled-out the solvatochromism. Further, **1** and **2** did not show fluorescence in any solvent that could be due to the free rotation of C-C bond and C=N isomerization.

Interestingly, **1** and **2** showed strong AIEE in the solid state (Fig. 1a). **1** showed yellow fluorescence ($\lambda_{max} = 535 \text{ nm}$, $\Phi_f = 38 \%$) whereas greenish-yellow fluorescence ($\lambda_{max} = 525 \text{ nm}$, $\Phi_f = 21 \%$) was observed for **2** (Fig. 1b). Further, the fluorescence spectra of **1** and **2** showed a small hump at 558 and 500 nm, respectively. The excitation spectra of **1** and **2** in the solid state showed π - π * transition at 370 nm which is 25 nm red shifted relative to absorption maxima in solution. The red shift of absorption peak suggests the J-aggregation of **1** and **2** fluorophores in the solid state. The long stoke shift of **1** (165 nm) and **2** (155 nm) could be due to the ESIPT phenomena of Schiff base unit. To get the insight on the molecular organization, single crystals

of 1 and 2 were grown from methanol and toluene, respectively. The structural analysis of 1 and

2 revealed strong intramolecular hydrogen bond interaction between phenolic hydroxyl and



Fig. 1. (a) Molecular structure with digital fluorescence images and (b) excitation and emission

spectra of 1 and 2. $\lambda exc = 365$ nm.



Fig. 2. (a) Molecular conformation of 1 (a) and 2 (b) in the crystal lattice. C (grey), N (blue), O (red), H (white); H-bonds (broken line). Intramolecular H-bond distances are marked in Å.

imine nitrogen. The Schiff base molecular unit of **1** and **2** adopts perfectly planar conformation in the solid state whereas cyanophenoxy adopts nearly perpendicular orientation (Fig. 2). Further, the weak intermolecular interactions, H-bonding (phenoxy hydroxyl and cyanophenyl hydrogen) and CH... π , in the crystal lattice of **1** lead to the formation of *zig-zag* structure along *c*-axis (Fig. 3a). However **1** did not form any intermolecular interactions in other two directions and are well separated (Fig. S2-3). The intermolecular H-bonding between methoxy oxygen and



Fig. 3. *Zig-Zag* chain of **1** (a), dimer formation (b) and extended H-bond interaction in the crystal lattice (c) of **2**. N (blue), O (red), H (white); H-bonds (broken line). H-bond and C-H... π distances are marked in Å.

cyanophenyl hydrogen and $\pi...\pi$ interactions lead to the formation of dimer with opposite molecular orientation in the crystal lattice of **2** (Fig. 3b). The dimer is further connected in all three directions via H-bonding and $\pi...\pi$ interactions (Fig. 3c, S4). These weak intermolecular

interactions rigidify the **1** and **2** fluorophore in the crystal lattice and exhibit AIEE properties. The off-set stack structural arrangement confirms the J-aggregation of **1** and **2** fluorophores in the solid state.

Further to confirm the AIEE, nanoparticles of 1 and 2 were fabricated using fast precipitation method by swiftly injecting CH₃CN solution of 1/2 (good solvent) into water (poor solvent). 1 in CH₃CN (100 %) and up to 80 % of water solution (20:80 CH₃CN and water) did not show any florescence. However, injecting 1 (25 μ L) into water (100 %) showed the formation of strongly enhanced fluorescent nanoparticles (Fig. 4a). Similarly, 2 also produced strong fluorescent nanoparticles when injecting into water (90% as well as 100 %, Fig. 4b). Surprisingly, the fluorescence spectra of 1 and 2 exhibited dual emission peak, blue and yellow/greenish vellow fluorescence with nearly equal intensity. Both 1 and 2 showed a new peak at 410 nm along with molecular crystals emission at 532 nm (1)/523 nm (2). The appearance of blue and yellow/greenish yellow emission in the nanoparticles of 1 and 2 (100 % water) lead to white light emission ($\Phi_f = 24 \%$ (1), 19 % (2)), a phenomenon rarely observed in a simple single organic fluorescent compound. It is noted that equal intensity of blue, green and red fluorescence or at least either two is required for observing white emission.⁵² The CIE color coordinates of white emission were calculated from fluorescence spectra (0.275, 0.306 (1); 0.232, 0.365 (2)). The ideal CIE coordinates for pure white light is (0.33, 0.33). Single organic fluorophores emit dual fluorescence when the structure contains different color emitting group or by halochromic effect that produced several emitting species.^{47,53} For example, different degree of protonation in dithienophosphole-based donor-acceptor conjugated fluorophore⁵³ and disturbing the conjugation by protonation in amino-trimethylammonium oligophenylene vinylene lead to white light emission.⁵⁴ Similarly, the evolution of weak supramolecular interaction in the aggregates



Fig. 4. Nanoparticles evolution of study of 1 (a) and 2 (b) by measuring fluorescence spectra. Digital images of nanoparticles fluorescence is shown in the inset. $\lambda_{exc} = 365$ nm.

of fluorene-based gold(1) complex resulted in single component white light emitting materials.⁵⁵ The molecular structure of **1** and **2** contain both blue emitting cyanophenoxy and green/greenish yellow emitting salicylidene Schiff base group (Fig. 1a). The blue emission from cyanophenoxy group was confirmed by synthesizing 2-phenoxycyanobenzonitrile that showed blue fluorescence at 432 nm in the solid state (Fig. S5). The greenish-yellow/yellow fluorescence could be due to salicylidene Schiff base group. In solid state of **1** and **2**, both blue and yellow/greenish-yellow emitting groups are held together by supramolecular interactions that produced only single fluorescence peak and no blue fluorescence was observed. However, it appears that blue and yellow/greenish-yellow emitting units are independent in the initial aggregates and showed dual fluorescence. The nanoparticles morphological studies, time dependent fluorescent and excitation spectra and metal ions sensing that are discussed in the following paragraphs have also support the above hypothesis. The nanoparticles evolution has also been monitored using absorption spectroscopy. It is noted that **1** and **2** in CH₃CN showed absorption λ_{max} at 345 nm. The absorption peak of **1** did not undergo any significant change as

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well as no new peak has been observed up to 90 % water solution (Fig. 5a). However, introducing **1** into 100 % water exhibited a clear red shifted absorption peak at 378 nm (Fig. 5a). The absorption peak of **2** was steadily decreased with appearance of new absorption at 402 nm as increasing water percentage (Fig. 5b). **2** in 90 and 100 % water showed a clear red shifted new absorption at 402 nm and the peak at 345 nm has been completely disappeared. The red shifted absorption suggests the J-aggregation of molecules in the nanoparticles that was evidenced from single crystal X-ray structure (Fig. 3).



Fig. 5. Nanoparticles evolution of study of 1 (a) and 2 (b) by measuring absorption spectra.

The white light emitting nanoparticles of both 1 and 2 are stable for 1 h. After that they slowly changed into yellow (1) or greenish-yellow (2) emitting nanoparticles with increasing time. Hence 1 and 2 white light emitting nanoparticles are meta-stable. Time dependent fluorescence studies were performed for of 1 and 2 nanoparticles to gain the insight on the appearance of dual fluorescence and color change (Fig. 6). The as-fabricated nanoparticles of 1 and 2 (100 % water sample) showed two strong emission with nearly equal intensity; one at 410 nm (blue emission) another at 532 nm (1, yellow) or 522 nm (2, greenish yellow) initially. The nanoparticles solution exhibited clear white emission when excited by UV lamp ($\lambda_{exc} = 365$ nm).

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The intensity of blue emission peak was slowly decreased and yellow or greenish-yellow emission peak has been intensified with increasing time. After 16 h, the blue emission peak has been completely disappeared in both 1 and 2 nanoparticles. The excitations spectra of 1 and 2 nanoparticles have also showed clear shift of peak position with increasing time (Fig. S6). The initial excitation spectrum of 1 nanoparticles showed peak at 378 nm that slowly blue shifted to 370 nm with increasing time (Fig. S6a). Similarly, excitation spectra of 2 showed a peak at 385 nm initially and slowly blue shifted to 370 nm with time (Fig. S6b). It is noted that excitation spectra of 1 and 2 molecular crystals have also showed peak at similar position (370 nm, Fig. 1b). Further, the time dependent excitation spectra showed a small hump at longer wavelength (435 nm) for both 1 and 2 nanoparticles initially along with strong peak at 378 nm (1) and 385 nm (2). The longer wavelength peak might be due to the salicylidene unit. With increasing time, this peak slowly disappeared and merged with main strong peak that clearly broadened with blue shift. The $\lambda_{cut-off}$ for 1 and 2 nanoparticles after 24h is 440 nm and 480 nm, respectively. The excitation spectra of 2-phenoxycyanobenzonitrile, a model compound prepared to study the cyanophenoxy fluorescence, showed a peak at 378 nm (Fig. S5). Thus initially both blue emitting cyanophenoxy and yellow/greenish-yellow emitting salicylidene groups might not be having strong interactions and emit separately. As increasing time, the nanoparticles slowly evolved and produced one single peak of longer wavelength that is matched with bulk materials emission. These studies indicate that 1 and 2 fluorophores adopt different molecular arrangement initially in the nanoparticles that re-organize with time and adopt molecular arrangement similar in the molecular crystals of 1/2. This was further confirmed by PXRD studies that exhibited perfect matching of 1 and 2 nanoparticles (after 24 h) pattern with simulated PXRD pattern from single crystal data (Fig. S7). However, we could not perform PXRD measurement for white light

emitting nanoparticles since it was meta-stable and centrifugation converted into yellow/greenish-yellow emitting particles. FTIR studies of **1** and **2** crystals, powders and nanoparticles are essentially same (Fig. S8). Thus the modulation of fluorescence in the nanoparticles with time is due to the change of molecular arrangement in the nanoparticles evolution. **1** and **2** nanoparticles fabricated at different temperatures (10, 25 and 60 °C) have also showed dual fluorescence with small variations in the intensity (Fig. S9). However, it was observed that nanoparticles fabricated at higher temperature (60 °C) were converted into stable nanoparticles with single emission fast compared to low and room temperature fabrication. Further, it was observed that freezing white light emitting nanoparticles solution has also converted to yellow/greenish-yellow emitting nanoparticles immediately. It is noted that room temperature fabricated **1** and **2** nanoparticles exhibited dual emission with equal intensity whereas longer wavelength emission dominates in the nanoparticles fabricated at lower temperature (S9). Thus applying any external stimuli appear to help the conversion of meta-stable to stable nanoparticles.



Fig. 6. Change of nanoparticles fluorescence intensity and λ_{max} of **1** (a) and **2** (b) with time. Digital images of nanoparticles fluorescence with time is shown in the inset. $\lambda_{exc} = 365$ nm.

Further SEM studies of **1** and **2** nanoparticles with time revealed interesting morphological changes and support the fluorescence modulation. The white light emitting **1** and **2** nanoparticles fabricated initially (100 % water) showed clear spherical morphology with size range between 20-30 nm (Fig. 7a,c). The spherical nanoparticles further assembled into micron sized big balls in **1** whereas strip-like arrangements observed in **2**. The spherical nanoparticles of **1** and **2** undergoes morphological change from spherical nanoparticles to nano plates with increasing



Fig. 7. SEM images of nanoparticles at initial stage (a (1) and c (2)) and after 24 h (b (1) and d (2)). The scale bar in the SEM image is 100 nm.



Scheme 1. Schematic diagram of fluorescent and morphological changes of 1 and 2 nanoparticles with increasing time.

time (after 24 h) in both sample (Fig. 7b,d). 1 exhibited featureless nanoplates with thickness between 40-50 nm and diameter range 100-200 nm. However, 2 showed clear hexagonal nanoplates formation with diameter between 200-300 nm. PXRD confirms the formation of crystalline nanoplates with similar structure to their single crystals (Fig. S7). Although the exact structural arrangement in the white light emitting 1 and 2 spherical nanoparticles is difficult to predict, the above studies clearly suggest that fluorophores adopt different molecular orientation in the soft spherical nanoparticles initially in which both blue and yellow/greenish-yellow emitting groups could emit separately. It is noted that morphology and soft surface of organic functional nanoparticles can modulate the fluorescence.⁵⁶⁻⁵⁸ Initially, when the nanoparticles are soft, there might be only the strong intramolecular hydrogen bonding in the aggregates and the weak intermolecular hydrogen boding (CH... π , C-H...O) might not have been formed (Fig. 3). Hence it appears that there is no energy transfer between blue emitting cyanophenoxy group and yellow or greenish-yellow emitting salicylidene unit (Scheme 1). However, the evolution of weak intermolecular hydrogen bonding converts the soft spherical nanoparticles to hard nanoplates and the rigidified fluorophores exhibited either yellow (1) or greenish-yellow (2) emission. The evolution of weak intermolecular interaction has already been shown to influence on the nanoparticles hardness and optical properties.⁵⁸

The molecular structure of **1** and **2** consist of metal ions interacting phenolic chelating ligand. It is noted that **1** and **2** in solution exhibited selective colorimetric sensing of Cu^{2+} and Fe^{3+} ions via coordination.⁴⁸ The as-fabricated **1** and **2** nanoparticles that exhibited white fluorescence initially due to dual fluorescence (blue and yellow/greenish-yellow) from phenolic chelating salicylidene unit and cyanophenoxy group. The time dependent fluorescence and SEM studies further indicates that both salicylidene and cyanophenoxy group behave independently at initial Page 17 of 27

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stage of nanoparticles evolution. The independent salicylidene unit might interact with metal ions that could be used to further demonstrate the dynamic nature of the nanoparticles. Hence, 1 and 2 spherical white fluorescent nanoparticles were explored for selective fluorescence sensing of metal ions in aqueous solution. Interestingly, addition of Cu^{2+} and Co^{2+} ions into white fluorescent nanoparticles completely quenched the salicylidene unit fluorescence (532 nm (1) or 522 nm (2), Fig. 8). The blue fluorescence peak has not been affected significantly. It is noted that Cu²⁺ addition showed partial reduction in the blue fluorescence intensity in nanoparticles of **1**. Addition of other metal ions did not show significant change in the fluorescence. The selective quenching of fluorescence could be due to the interaction of metal ions with nanoparticles via metal ions interacting phenolic chelating functional groups (Scheme S1). However, addition of metal ions into 1 and 2 nanoparticles after 24 h did not show fluorescence quenching for any metal ions. This might be due to the formation of hard nanoplates. These studies further support the formation of soft spherical nanoparticles initially in which cyanophenoxy and salicylidene unit behave independently and emit both blue and yellow/greenish-vellow emission. The formation of soft spherical nanoparticles might facilitate the metal ions to interact with phenolic chelating functionality. The hard nanoplates completely block the metal ions interaction with chelating functionality. Thus the morphological change of nanoparticles (spherical to plates) accompanies with complete re-organization of fluorophores arrangement and support the fluorescence tuning from white to yellow/greenish yellow. The fluorescence intensity of 1 and 2 nanoparticles decreased gradually with increasing the concentration of Cu^{2+}/Co^{2+} metal ions (Fig. 9, S10-11). However, in contrast to molecular fluorescent probes that often exhibit complete fluorescent quenching at 1:2 or 1:3 metal:ligand ratio depending on the coordination geometry of metal ions,⁵⁹ 1 and 2 nanoparticles required higher concentration of metal ions

 (Cu^{2+}/Co^{2+}) for complete fluorescent quenching. This could be due to the difficulty in the diffusion of metal ions with aggregated nanoparticles and evolution of nanoparticles with increasing time. To get the insight on the complex formation, we have tried to single crystals of Cu^{2+}/Co^{2+} with 1 and 2 by dissolving in DMSO. Although, Co^{2+} did not produce quality single



Fig. 8. Fluorescence spectra of white light emitting nanoparticles of **1** (a) and **2** (b) with different metal ions. Digital images of nanoparticles with different metal ions is shown for 1 (a). crystals to collect the data, Cu^{2+} with **1** and **2** gave good crystals that clearly demonstrate the formation of 1:2 metal:ligand ratio coordination complex (Fig. S12). Further it has also confirmed involvement of salicylidene unit alone in the coordination with metal ions. Based on this result, we propose the formation of 1:2 coordination complexes for Co^{2+} also with **1** and **2** (Scheme S1). The interference studies indicate that Cu^{2+}/Co^{2+} could quench the fluorescence **1** and **2** nanoparticles in presence of other metal cations (Fig. S13). However, the reason for selective coordination of Cu^{2+}/Co^{2+} with **1** and **2** ligands are not clear at present. Combining single crystal structure of **1** and **2**, **1** and **2** with Cu^{2+} , selective interaction of white fluorescent nanoparticles with metal ions, morphological and fluorescence change, it can proposed that

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initial non-planar salicylidene unit in the white fluorescent nanoparticles slowly evolve into planar conformation along with strong intramolecular H-bonding and produced dominant yellow/greenish-yellow emitting nanoparticles. Thus these studies have also clearly demonstrate the dynamic nature of **1** and **2** nanoparticles that produced meta-stable nanoparticles initially and converted to stable nanoparticles with increasing time.



Fig. 9. Change of fluorescence intensity of **1** (a) and **2** (b) nanoparticles (fabricated by injecting 10 μ L of 1 and 2 (10⁻³ M) into 2 mL water) with concentration of Co²⁺ and Cu²⁺ ions.

Conclusion

In conclusion, simple ESIPT compounds, **1** and **2**, exhibited AIEE in the solid state and interestingly nanofabrication induced rare white light emitting meta-stable nanoparticles. Single crystal analysis confirmed the restriction of free rotation and rigidification of fluorophores in the solid state via strong intermolecular interactions (H-bonding, C-H... π , π ... π). The rigidification of fluorophores in the solid state lead to enhanced fluorescence for **1** (yellow, $\lambda_{max} = 535$ nm) and **2** (greenish-yellow, $\lambda_{max} = 525$ nm). Interestingly, **1** and **2** produced meta-stable white light emitting nanoparticles in water that showed blue and yellow or greenish-yellow dual fluorescence from phenoxybenzonitrile and salicylidene unit separately. The white fluorescent

meta-stable nanoparticles were slowly converted into corresponding bulk materials fluorescence with increasing time. Time dependent fluorescence, morphological and metal ions interaction studies indicate the formation of soft nanoparticles in which blue fluorescent cyanophenoxy and yellow/greenish-yellow fluorescent salicylidene group produce fluorescence independently. The soft spherical nanoparticles converted into hard nanoplates with increasing time that matched with the bulk materials through evolving supramolecular interactions in the nanocrystals. The selective quenching of salicylidene fluorescence in the dual fluorescent meta-stable nanoparticles by Cu^{2+}/Co^{2+} metal ions support the separation of both groups at initial nanoparticles. Hard nanoplates did not show any fluorescence quenching. Thus, simple ESIPT molecules showed solid state florescence and nanofabrication mediated white fluorescent meta-stable nanoparticles.

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Supporting Information

Absorption spectra, crystallographic table for 1 (CCDC No. 1414929) and 2 (CCDC. No. 1414930) and fluorescence spectra are available in the supporting information.

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Aggregation induced emission of excited state intramolecular proton transfer compounds: Nanofabrication mediated white light emitting nanoparticles

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ESIPT compounds exhibited aggregation induced enhanced emission and unusual nanofabrication induced meta-stable white light emitting that exhibited morphological, fluorescence and metal ion interaction changes with increasing time.

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