Supporting document

Encapsulation of Multi-Stimuli AIE Active Platinum(II) Complex: A Facile and Dry Approach for Luminescent Mesoporous Silica

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Experimental

Materials: Potassium tetra chloroplatinate(II), 2-phenylpyridine, 2-ethoxyethanol, ethylenediamine, tritylchloride and mesostructured silica were purchased from Sigma Aldrich Chemical Company Ltd. The other used solvents and chemicals were procured from Merck.

Characterizations: ^{1}H NMR and[13]C NMR spectra were recorded in a 400 MHz Brucker NMRspectroscope. UV-Vis absorption spectra were recorded in a Shimadzu Spectrophotometer (model UV-1800 and 2550). Steady state Photoluminescence (PL) spectra were recorded on Horiba JobinYvon Spectro fluorometer(FluoroMax-4). The solid state quantum yield of the thin film sample was measured using a calibrated integrating sphere in a Gemini Spectrophotometer (model Gemini 180). Surface area of mesostructured silica and encapsulated mesostructured silica were measured with the Smart Instrument Co. Pvt. Ltd instrument (model number SMARTSORB-92/93). High-resolution MS (HRMS) was carried out with a (TOF MS ES+ 1.38 eV) VG Analytical (70-S) spectrophotometer and Q-Tof micro mass spectrophotometer.

Fabrication of thin-film of 3 on substrate for PL measurement: 10^{-3} M solution of **3** (in DCM) was prepared. Two drops of the solution were placed on thin glass substrate (2x2cm^2) and the solvent was allowed to evaporate slowly.

Preparation of a series of MeOH/H$_2$O solution of 3 for PL measurement and support to AIE behavior:

10^{-5} M stock solution of **3** was prepared in methanol. Ten 5 ml glass tubeswere taken and labeled them as 0%, 10%, 20%, 30%, 40%, 50%, 60%,70%, 80% and 90%. 0.5 mL of stock solution was added to each of the flask. Then, volume was filled to 5 ml through addition of 0 ml, 0.5 ml, 1 ml, 1.5 ml, 2 ml, 2.5 ml, 3.0 ml , 3.5 ml, 4 ml and 4.5 ml water to 0%, 10%, 20%, 30%, 40%, 50%, 60% ,70%, 80% and 90%,labeled flasks, respectively.

Computational Details:

The Density Functional Theory (DFT) based computations for **3**wascarried out using Gaussian09[1] program suit. The required structures were generated with Gauss View[2] visualization program. All the calculations were performed at B3LYP (The Becke three parameter exchange functional[3] and the Lee-Yang-Parr correlation functional[4]) level of theory. The particular choice for B3LYP method was based on the accuracy of calculations at this level reviewed through literature. The initial structures were optimized at same level of theory (*i.e.*, B3LYP), where Pt atom was defined at LanL2DZ(with effective core potential, ECP[5]) basis sets and all electron 6-31G (d,p) basis sets[6] were used for lighter atoms. Use of LanL2DZ basis set with ECP was a common practice for systems containing atoms of higher atomic numbers (in case of present calculations it is Pt) because the formalism approximates chemically inert core electrons to be frozen which significantly reduces the computational cost of*Ab* initio calculations without compromising the accuracy much. Subsequently, frequency analysis was performed on the respective structure and absence of any imaginary frequency confirmed the global energy minima in the potential energy surface (i.e., most stable structure) for the complex. The solvent parameters are incorporated through SCRF calculations *via* IEFPCM[7] model for dichloromethane.

Syntheses and characterizations:

Compounds **1** and **2** were synthesized by following the reported literature[8, 9].

General Synthesis of [Pt(C^N)(CH^N)(Cl)], 1: It was synthesized by following the method as described in the literature[9]. ^{1}HNMR spectra of **1** , [^{1}HNMR (400 MHz, Chloroform-d) a=δ 9.63 (d, J = 6.0 Hz, 1H), b= δ 9.26 (d, J= 5.7 Hz, 1H), c= δ 8.10 (d, J = 5.2 Hz, 2H), d= δ 7.96 (t, J = 7.8 Hz, 1H), e= δ 7.74 (t, J = 7.6 Hz, 1H), f= δ7.64 (s, 1H), g= δ 7.52 (d, J = 7.8 Hz, 2H), h= δ 7.36 (dt, J = 20.8, 6.9 Hz, 4H), i= δ 7.08 (t, J = 6.7 Hz, 1H),7.03 – 6.97 (m, 1H), j= δ 6.89 (t, J = 7.4 Hz, 1H), k=6.22 (t, 1H), l= δ 6.20 (d, 1H)]. ^{13}CNMR spectra of **1**, [^{13}CNMR (101 MHz, CDCl$_3$) a=δ 167.16, b= δ 162.31, c= δ 154.35, d= δ151.21, e= δ 144.20, f= δ 141.03, g= δ 139.80, 138.39, 137.67, h= δ 130.81, 129.75, 129.56, 129.27, 128.98,127.83, 127.32, 127.21, i= δ 123.83, 123.17, 123.05, 121.69, j= δ 118.03].

Synthesis of N^1-tritylethane-1,2-diamine, 2: It was synthesized by following the method as described in the literature[8].^{1}HNMR (400 MHz, CDCl$_3$) δ 7.55−7.48 (m, 5H), 7.35−7.27 (m, 7H), 7.25−7.17 (m, 3H), 2.83 (t, J = 6.0 Hz, 2H), 2.23 (t, J = 6.0 Hz, 2H), 1.63 (s, 3H).

General Synthesis of [Pt(C^N)(N^NCPh$_3$)Cl], 3: 0.00048 mmol of **1**, 0.00072mmol of **2** were mixed in 2-ethoxy ethanol and refluxed it overnight at 100^{0}C. Then, the solvent was evaporated under reduced pressure and the crude product was collected and product was purified by column chromatography (60-120 mess of silica gel). Yield, 69%.^{1}H NMR (400MHz, CDCl$_3$) δ 9.49 (dd, J = 5.9, 0.9 Hz, 1H), 7.77 (td, J = 8.0, 1.6 Hz, 1H), 7.52 (m, J = 7.4, 6.0 Hz, 7H), 7.40 (m, J = 5.9, 3.2 Hz, 1H), 7.36 – 7.19 (m, 10H), 7.14 – 7.00 (m, 3H), 4.66–4.30; ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.53, 150.89, 145.41, 145.08, 139.98, 138.26, 129.98, 128.76, 128.58, 128.08, 126.64, 123.83, 123.43, 122.08, 118.20, 70.98, 4844.47. (t, 2H), 2.54 – 2.36 (t, 2H).
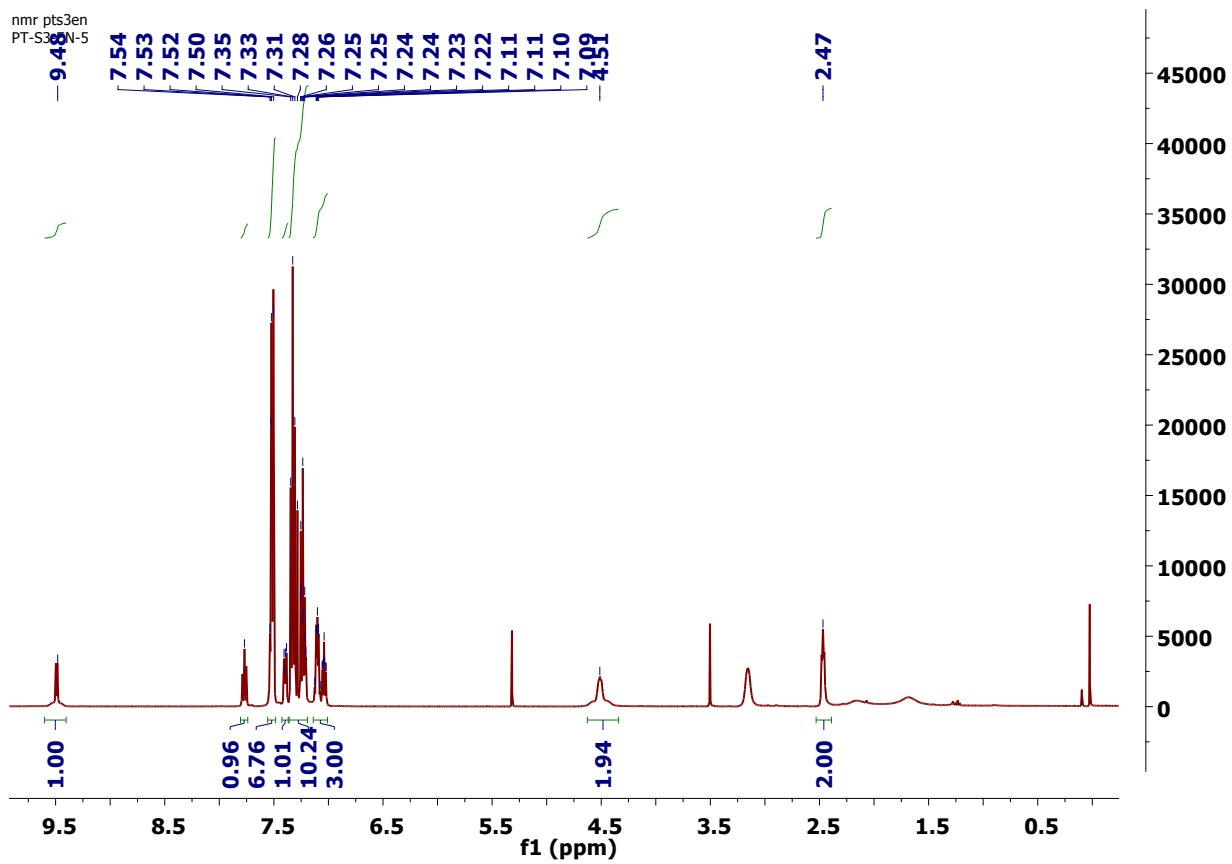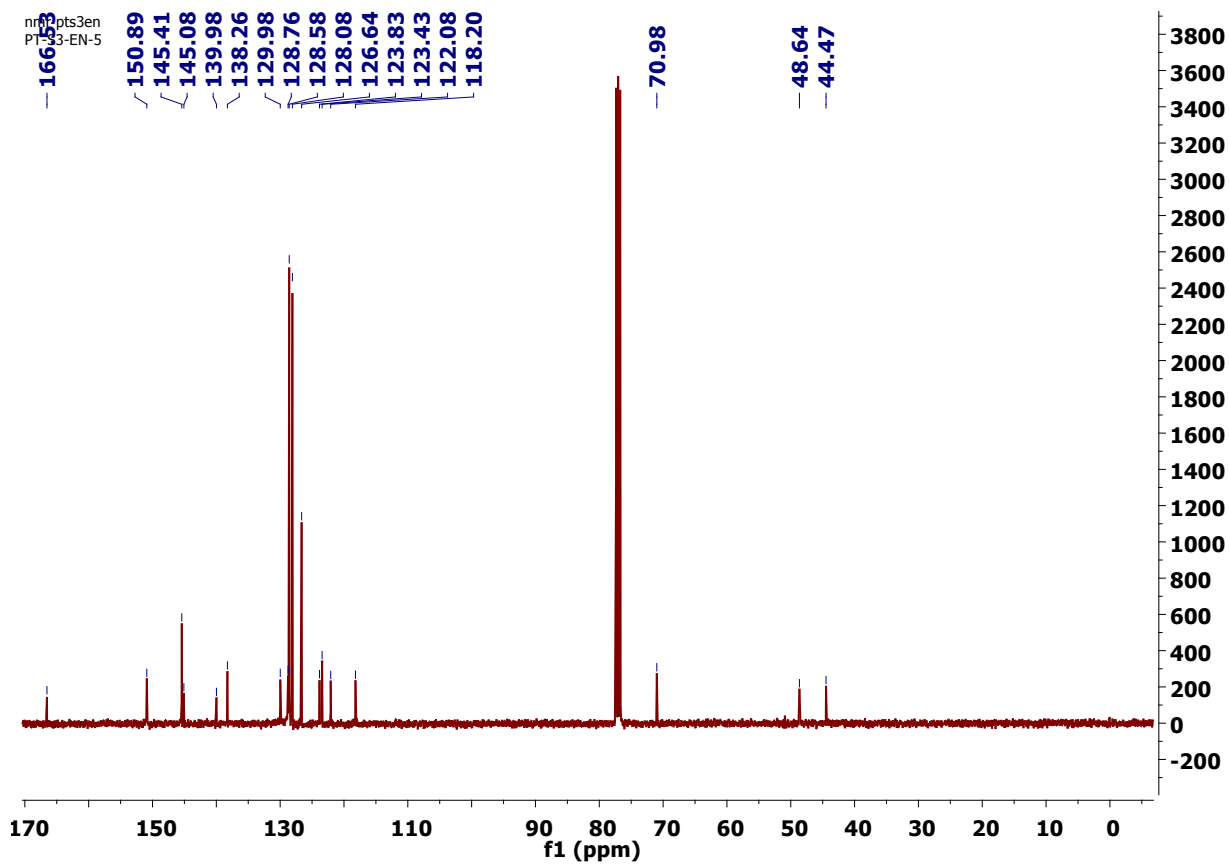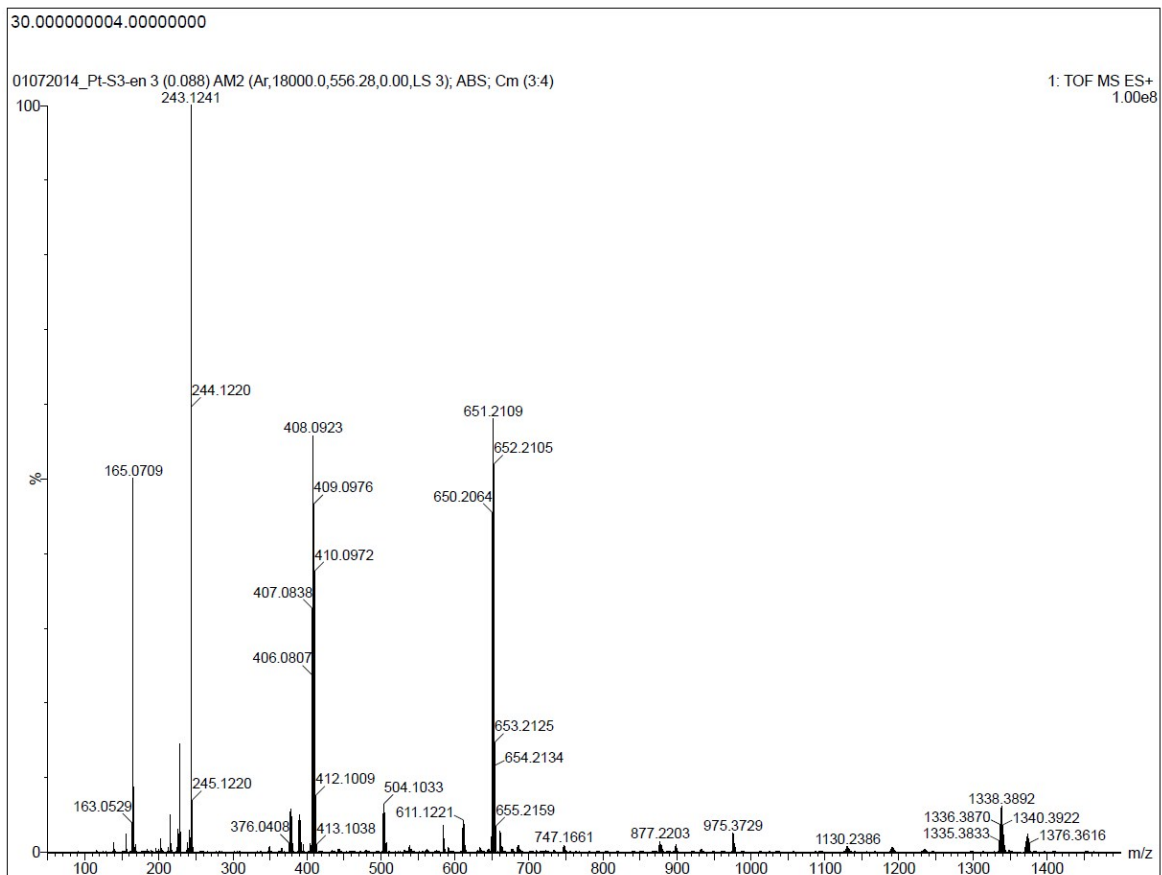
Fig. S1 ¹HNMR spectrum of **3**

Fig. S2 ^{13}CNMR spectrum of **3**
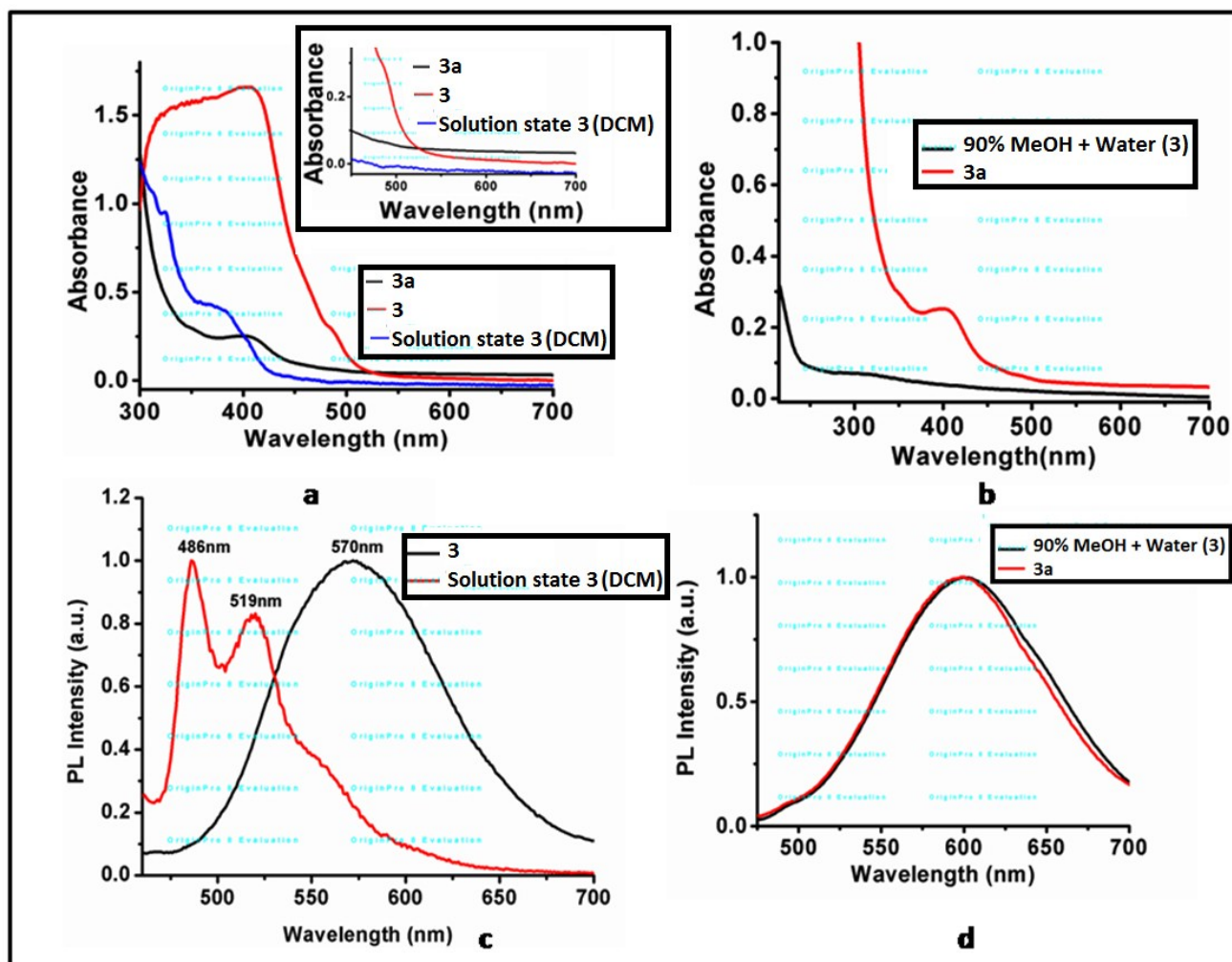
Fig. S3 Mass spectrum of **3**

Fig. S4 (a) Absorption spectra of **3** (solid), **3a** (solid) and **3** in DCM; (b) Comparative absorption spectra of **3a** (solid) and nanoaggregates of **3** from MeOH/water; (c) Emission spectra of **3** in solid and solution (DCM); (d) Emission spectra of **3 (**at 90% MeOH and water) and **3a** (solid) in various states (for the case of solution phase, absorption and emission 10^{-5}M DCM solution was used).

(a)

LUMO

HOMO

HOMO-1

HOMO-2

(b)
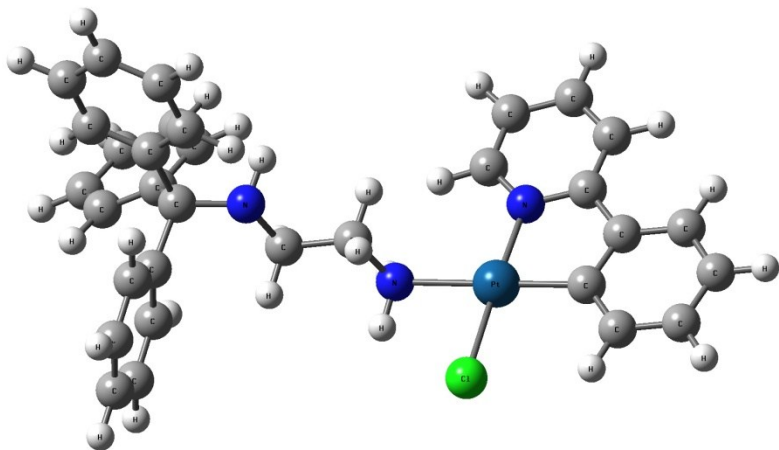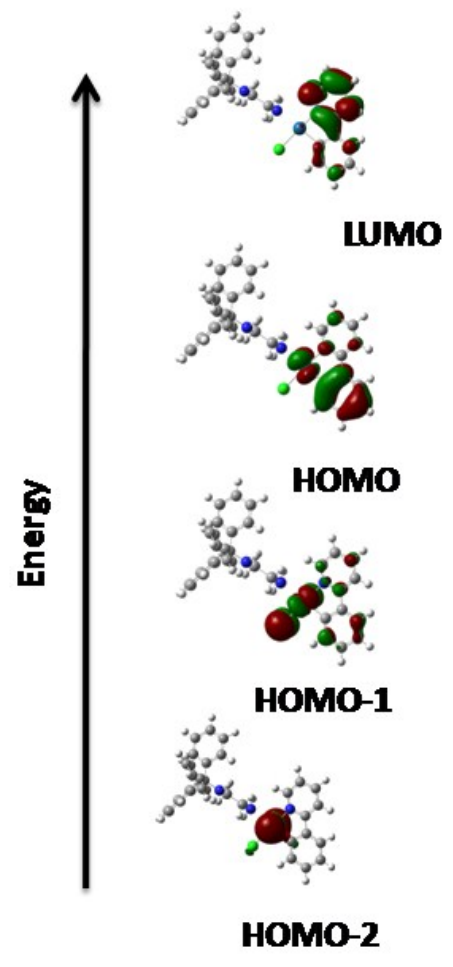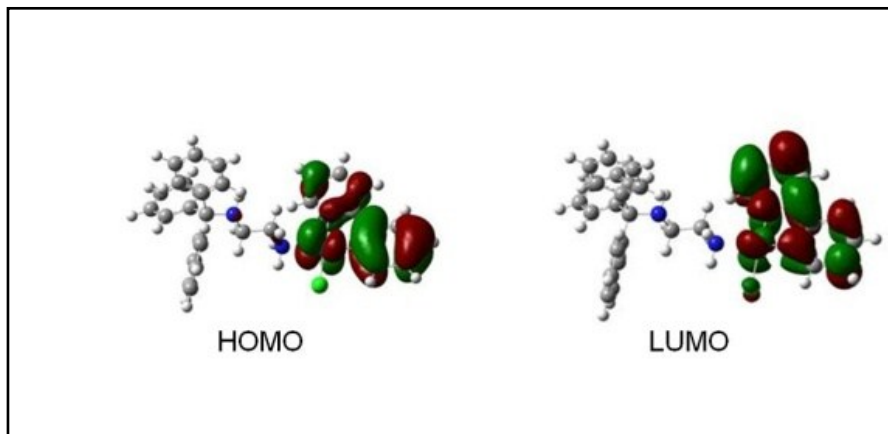
HOMO   LUMO

(c)

Fig. S5 (a) Optimized structure of **3** at B3LYP/6-31G(d,p)Ú LanL2DZ level; (b) TD-DFT based transition energy calculations and the electron distribution in the following orbitals (HOMO, LUMO, HOMO −1 and HOMO − 2) of **3**; (c) DFT based ground state optimized HOMO and LUMO orbitals of **3**.
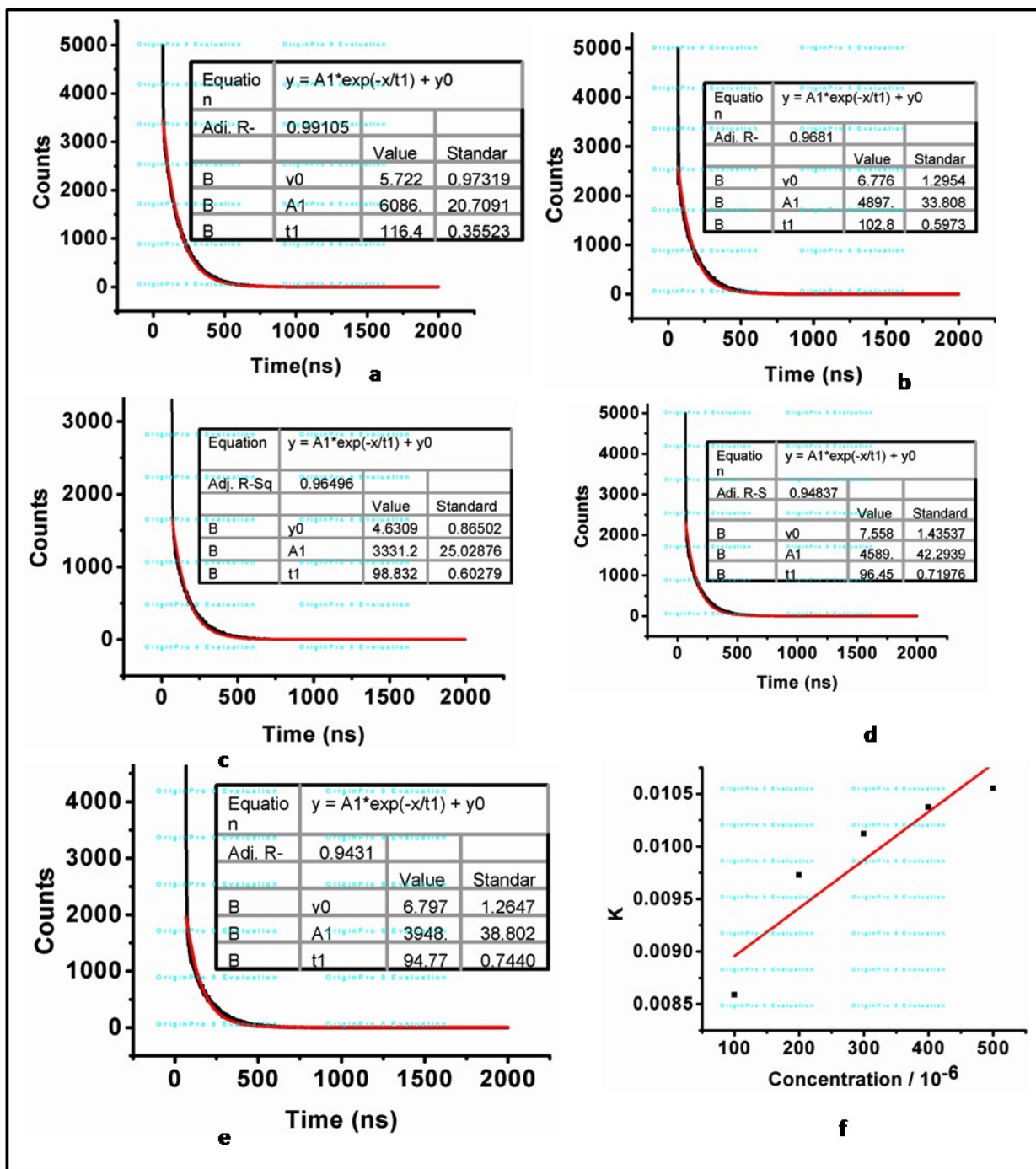
Fig. S6 (a) (b) (c) (d) & (e) show lifetime decay curve of **3** in the range of concentration, 1×10^{-4} - 5×10^{-4} M (Life time, for a = 116.6ns ; for b = 102.8; for c = 98.8; for d = 96.4; for e = 94.7). (f) It shows plot of the measured luminescence decay constants (Y-axis) versus concentration (X-axis) of **3**.
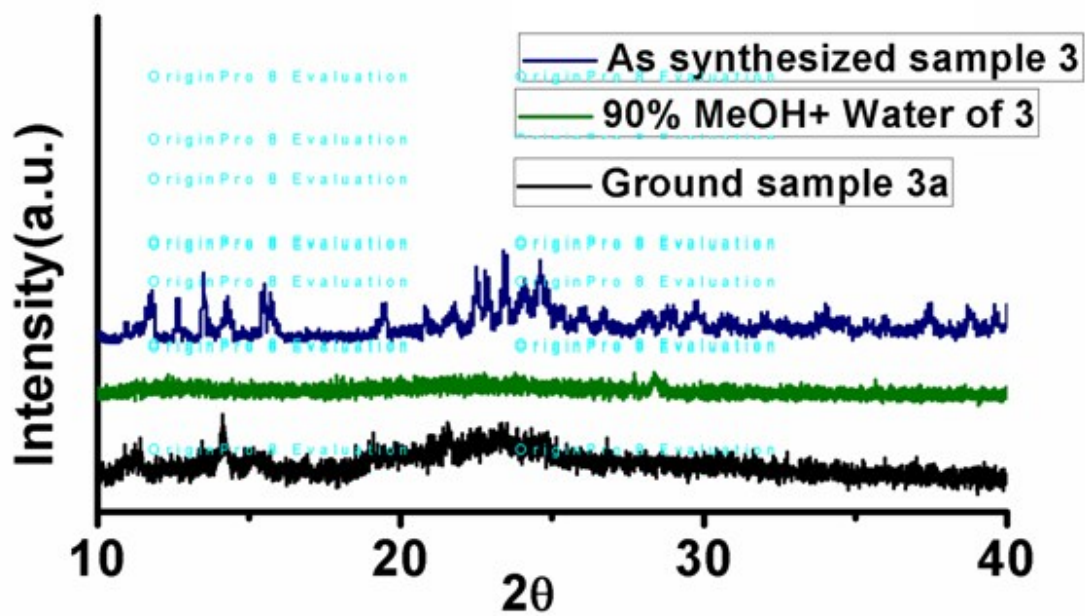
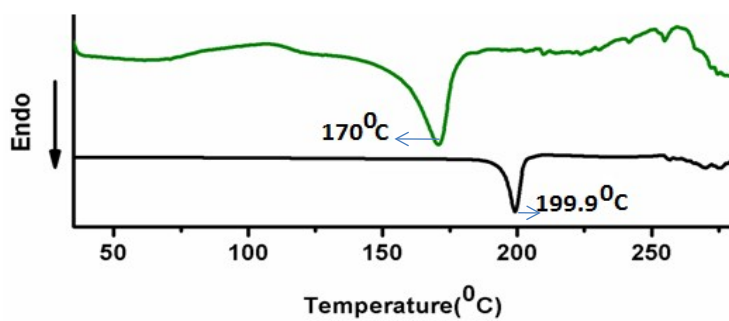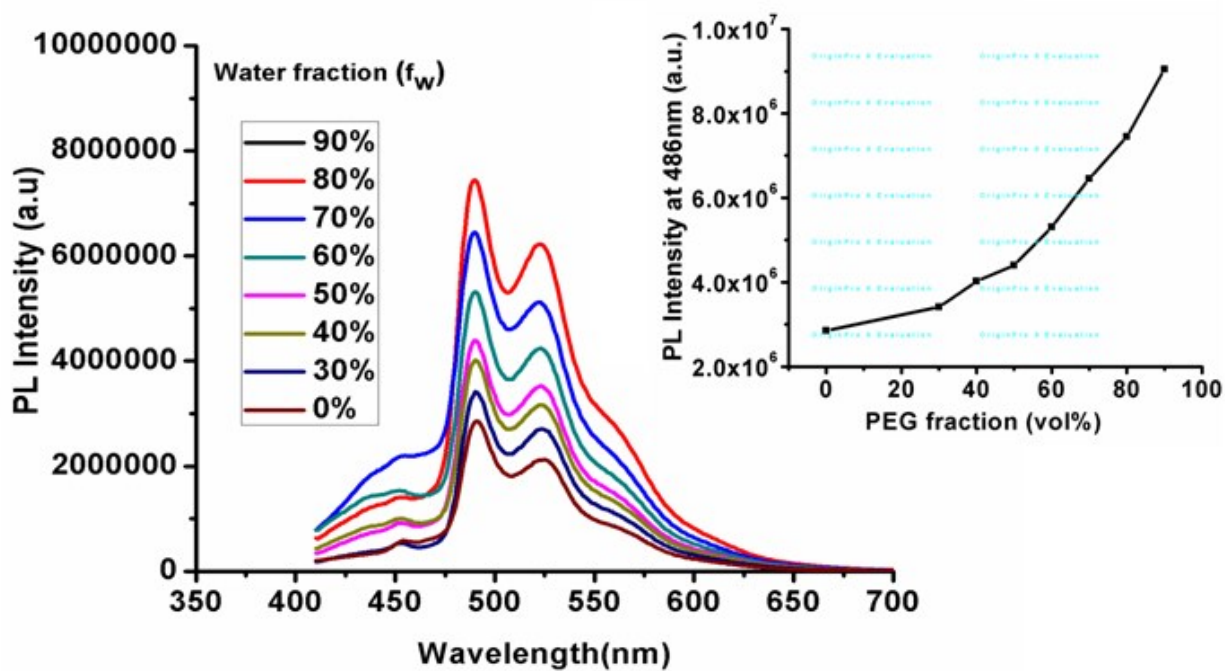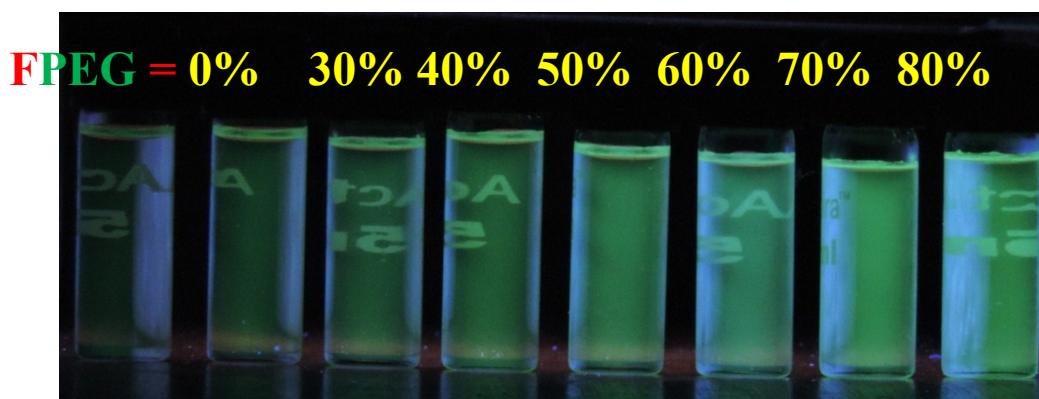**Fig. S7** Powder XRD of **3** in various states

Fig. S8 DSC curve of **3** before grinding (black) and after grinding (green)

a

b

Fig. S9 (a) PL spectra of **3** in methanol/Poly(ethyleneglycol) (PEG) mixed solvents with different fraction of water (f_w) with excitation at 365 nm (Insets, depict the changes of PL peak intensity with different f_w) (λ_{max}= 486nm); (b) Luminescent images of **3** (irradiated with an ultraviolet light at 365 nm) in PEG−Methanol mixed solvents with the concentration kept at 1×10^{-5} M.

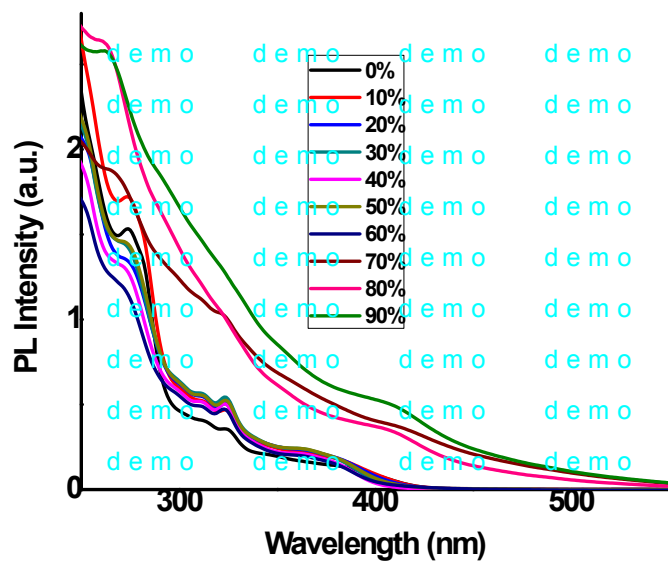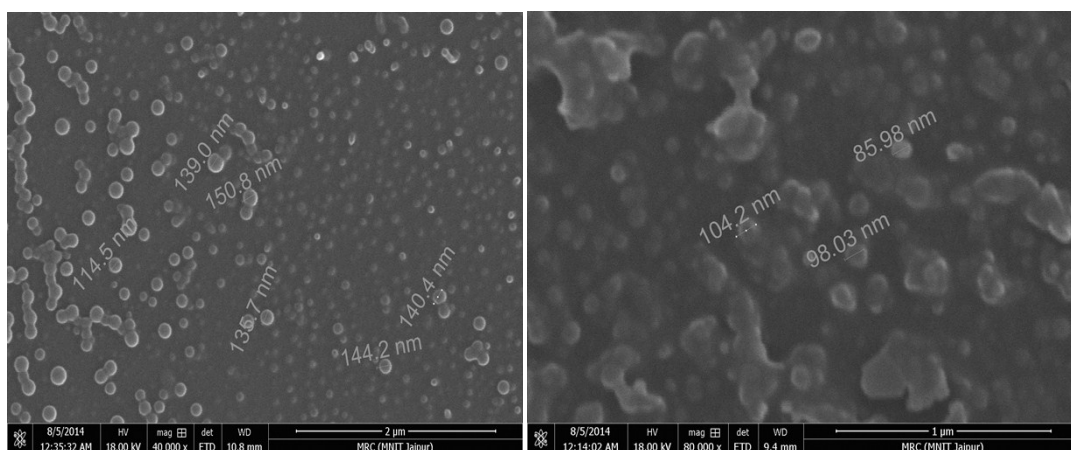**Fig. S10** Absorption spectrum of **3** with increasing fraction of water in a MeOH/water mixture (0-90%).

a   b

Fig. S11 FESEM images of (a) 70% water in MeOH/water and (b) 90% water in MeOH/water mixtures of **3.**
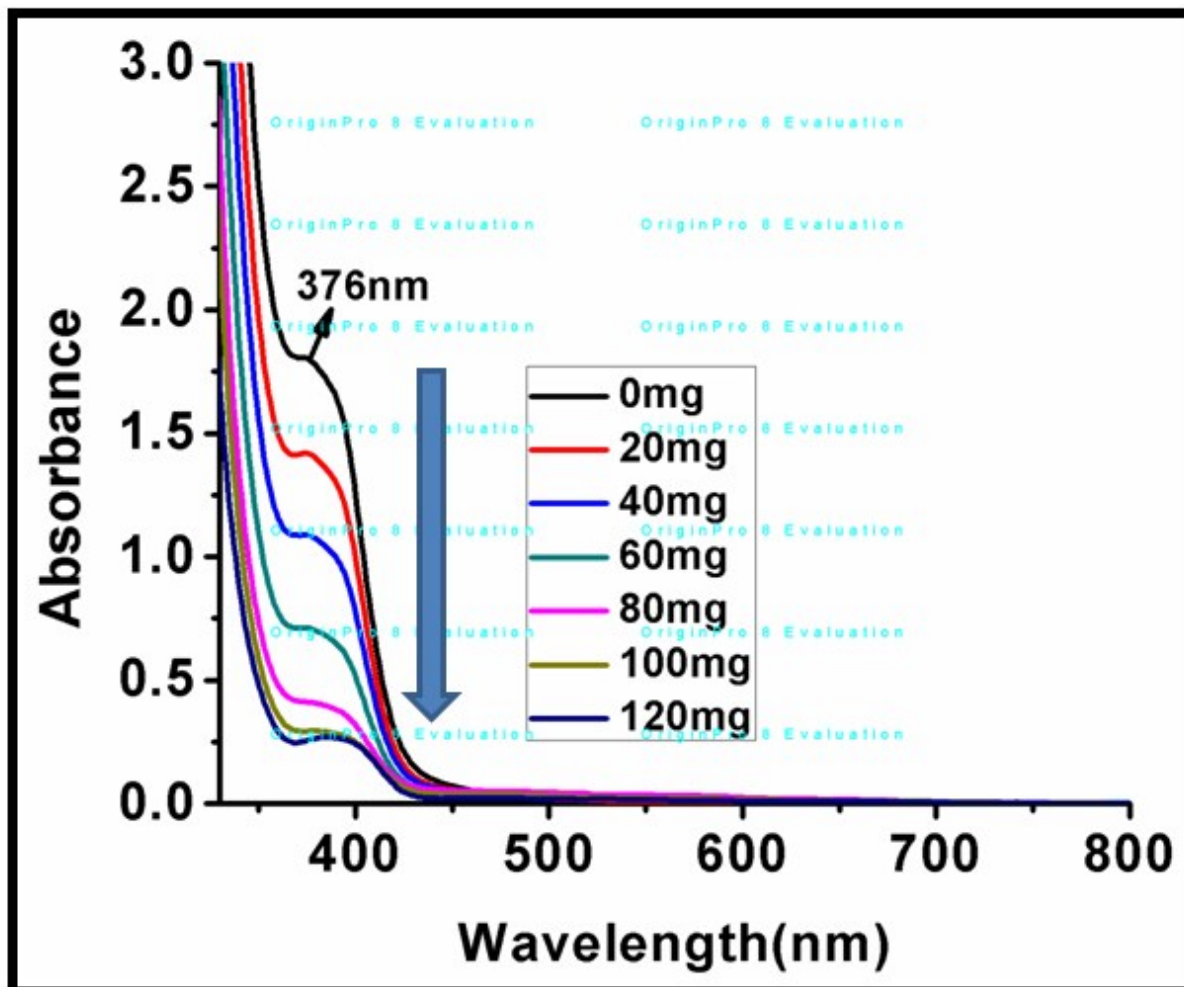

Fig S12. Absorbance spectra of **3** with gradual increasing amount of MS silica into DCM (0 to 120mg) showing decreasing order of absorbance at λ_{max} = 376 nm.

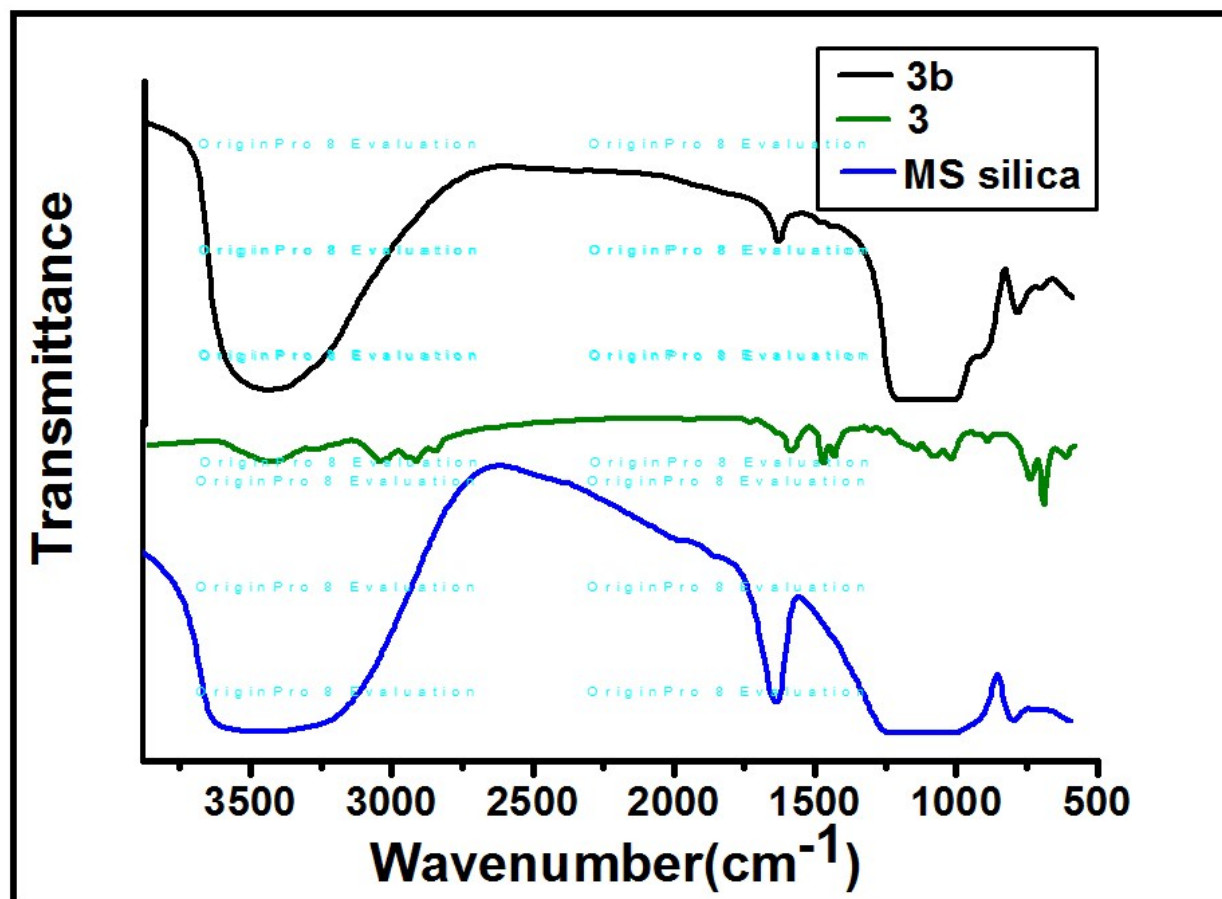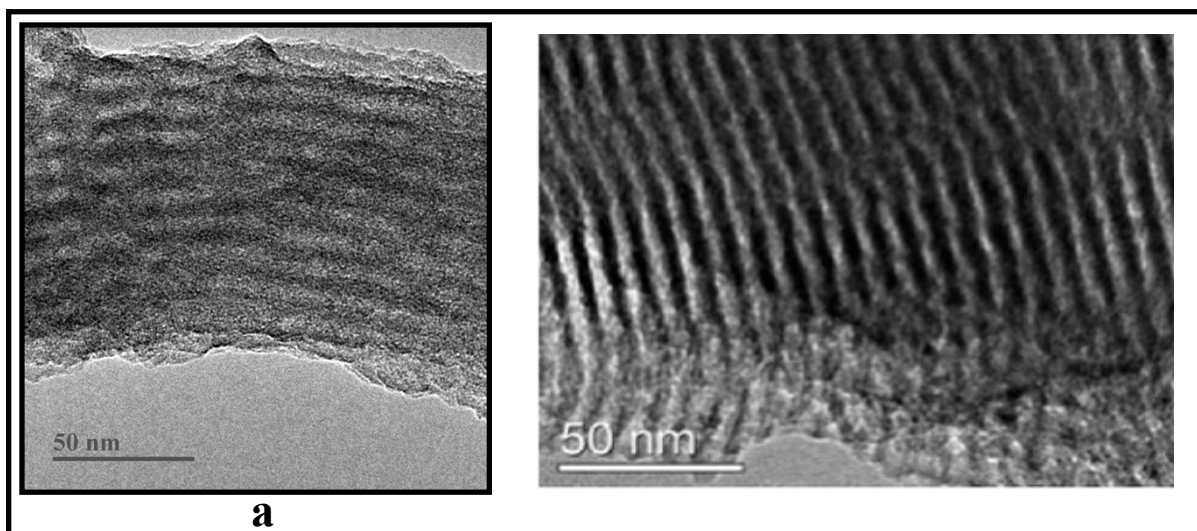**Fig. S13** FTIR spectrum of **3b**, **3** and bare MS silica.

Fig. S14 HRTEM images of (a) **3** encapsulated into the pores of MS silica (b) bare MS silica[10]

Table S1: Vertical excitation energies calculated for the lowest lying singlet and triplet states for **3**.

State	ΔE	Oscillator strength (f)	Assignments
T_1	2.69 eV (462 nm)	0	HOMO-3→LUMO (7%)
			HOMO-3→LUMO+1 (3%)
			HOMO-1→LUMO(6%)
			HOMO→LUMO (74%)
T_2	3.18 eV (390 nm)	0	HOMO-3→LUMO+1(5%)
			HOMO-1→LUMO(71%)
			HOMO→LUMO(14%)
S_1	3.23 eV (384 nm)	0.0150	HOMO-1→LUMO(2%)
			HOMO→LUMO(94%)
S_2	3.51 eV (353 nm)	0.0056	HOMO-2→LUMO(97%)

Table S2: Major contribution of metal and ligand atomic orbitals (AO) into FMO and their corresponding energy values.

State	FMOs	Major Orbital Contribution	Energy (eV)
Ground state	HOMO	36% d(Pt), 41% p (phenyl pyridine)	−5.82
	HOMO-1	53% d(Pt), 26% p (phenyl pyridine)	−6.15
	HOMO-2	75% d(Pt), 19% s (Pt)	−6.20
	LUMO	54% p (phenyl pyridine)	−1.80
	LUMO+1	57% p (phenyl pyridine)	−1.15

Table S3: Textural data (measured by N_2 adsorption-desorption isotherms) of the porous materials estimated by BET experiment

	Surface Area (m^2/g)
Mesostructured silica	750
Complex **3** encapsulated mesostructured silica	387

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