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Supporting information for article:

Stimuli-responsive aggregation-induced fluorescence in a series of biphenyl-based Knoevenagel products: Effect of substituent active methylene group on π–π interaction

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1 Experimental Section

1 Materials

Biphenyl-4-carboxaldehyde, malononitrile, ethylcyanoacetate and 2, 2-dimethyl-1, 3-dioxane-4, 6-dione (Meldrum's acid) were purchased from Sigma-Aldrich and used without further purification.

S1. Synthesis of biphenyl derivatives (1a-1c)

A 1:1 mixture of biphenyl-4-carboxaldehyde and active methylene compound (malononitrile/ ethylcyanoacetate/ 2, 2-dimethyl-1, 3-dioxane-4, 6-dione) in presence of catalyst X(Sarma *et al.*) was stirred in ethanol at room temperature for 2.5 h. The precipitated product from the reaction mixture was filtered and recrystallized from ethanol.

S2. Instrumentation

Absorbance and fluorescence measurements of the samples were recorded in Shimadzu UV-1800 and Hitachi F-7000 spectrophotometers (Japan) respectively. The UV-visible diffuse reflectance spectra (DRS) absorption spectra for the solid samples are recorded in 2600-SHIMADZU spectrophotometer. The time-resolved fluorescence decay is measured in a picosecond time-resolved fluorimeter, FSP920 Eddinburg Instruments. pH measurements were carried out with model PH-035 (ATC) pH meter (Japan). Morphology of the pristine samples and powder materials of products **1a** and **1b** are recorded on field emission scanning electron microscope (FESEM), Sigma-300, ZEISS. X-ray reflections were collected on a Bruker SMART APEX II CCD equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Data integration was done using SAINT. Intensities for absorption were corrected using SADABS. Structure solution and refinement were carried out using Bruker SHELXTL. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. C−H hydrogens were fixed using the HFIX command in SHELXTL. Crystallographic.cif files are deposited with the CCDC (Nos. 1908695-1908697) and may be accessed at www.ccdc.cam.ac.uk/data. X-ray data are summarized in Table 1. PXRD measurements were performed on a Rigaku Ultima IV X-ray powder diffractometer operating a CuKα X-ray source, equipped with a Ni filter to suppress K_β emission and a D/teX Ultra high-speed position sensitive detector, and measurements were performed at room temperature, with a scan range 2θ = 5−50°, step size of 0.02°, and scan rate of 2° min^{-1}.

S3. AEE experiments

Compounds **1a** and **1b** are soluble in most commonly available organic solvents but insoluble in water. They are first dissolved in ethanol (10^{-3} M) followed by addition of various percentage of water

and kept for 30 min at room temperature. After 30 min the fluorescence measurements of the samples were carried out.

Determination of fluorescence qauntum yield (Φ)

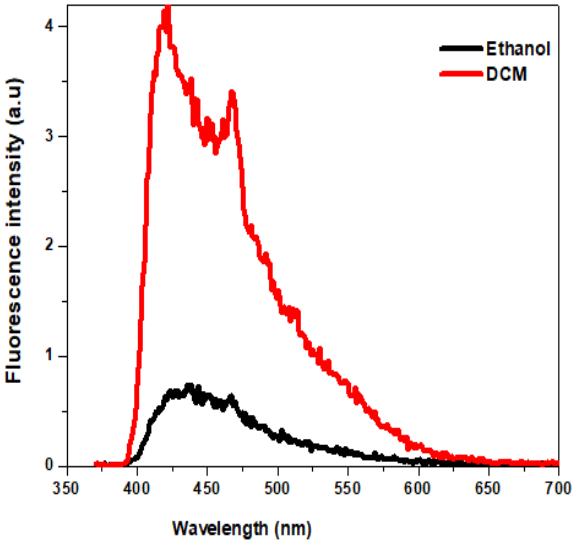
Quantum yield (Φ) of the samples are measured by optical dilution method with a standard reference of quinine sulfate (Φ_R=0.55, quinine sulfate in 0.05M sulphuric acid) and determined by using the following equation

$$\Phi_S = \Phi_R \times (B_R/B_S) \times (\eta_S/\eta_R)^2 \times (D_S/D_R)$$

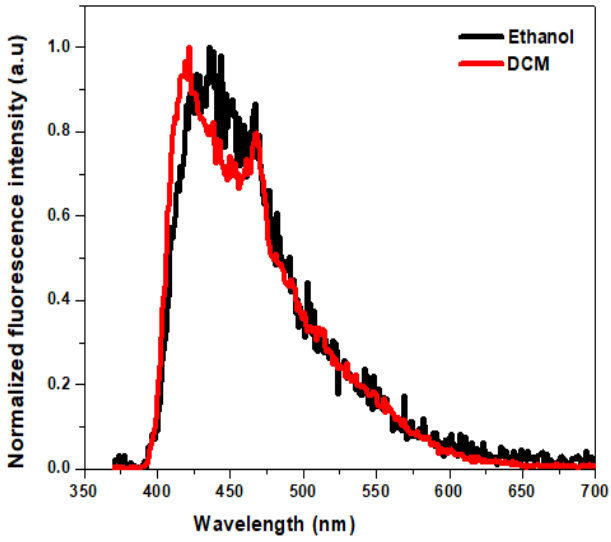
S and R refer to the sample and reference standard solution respectively, η is the refractive index of the solvents, D is the integrated fluorescence intensity and B is the excitation intensity. The excitation intensity B is determined by using the equation, $B=1-10^{-AL}$, where A is the absorbance and L is the optical path length (L= 1cm in all cases). The refractive indices of the solvents are using from standard source.

S4. Fluorescent pH sensing experiments

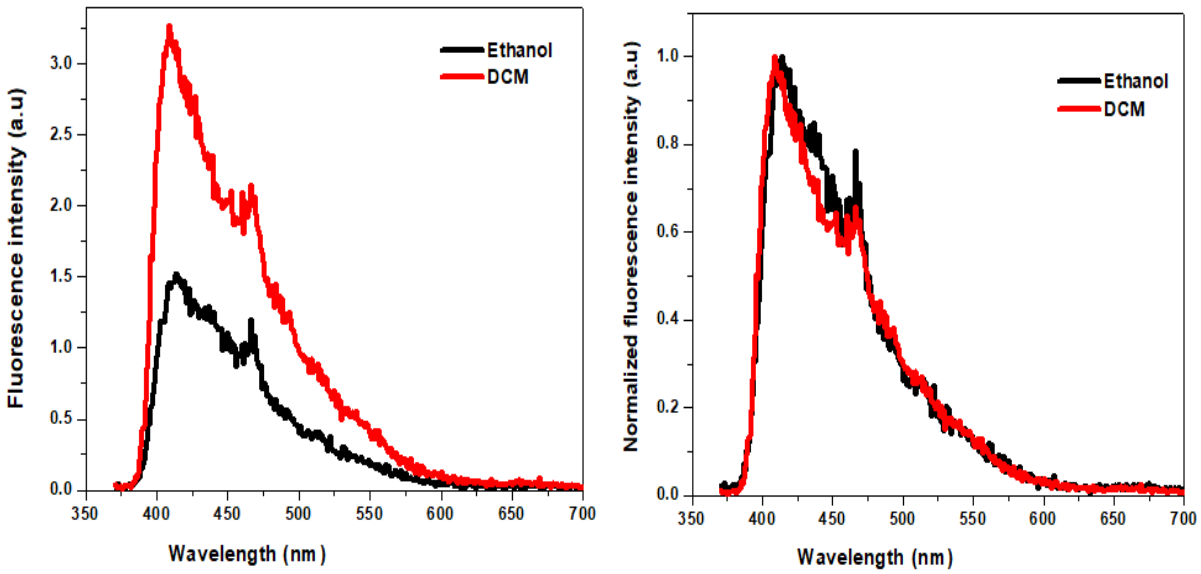
The pH sensing experiment is carried out in mixed solvent system of ethanol/ aqueous Britton-Robinson buffer (B-R) solution **(**mixture of 0.04 M H_3BO_3, 0.04 M H_3PO_4 and 0.04 M CH_3COOH). The pH from 2 to 12 is adjusted with 0.2 M NaOH. The fluorescence measurement of the samples under different pH was carried out after keeping for 30 min at room temperature.



(a)

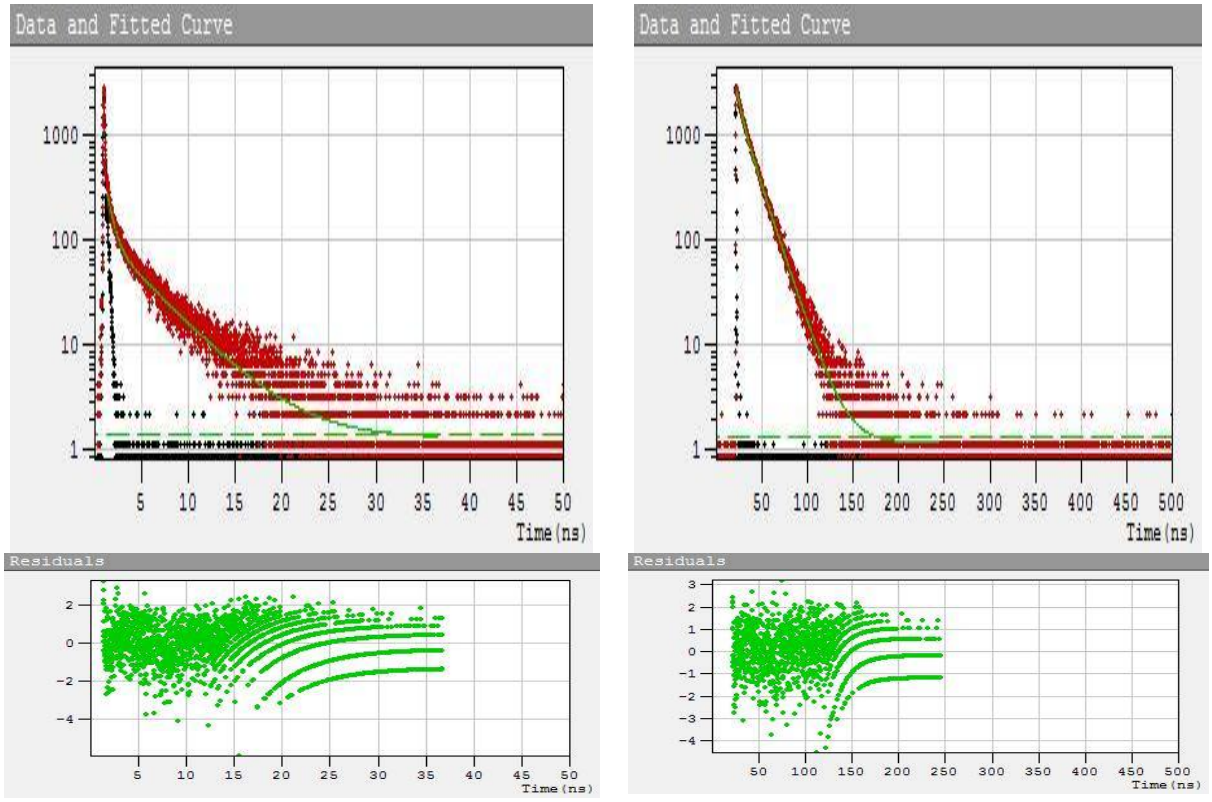


(b)



(c) (d)

Figure S1 Fluorescence spectra of compound **1a** in (a) ethanol and dichloromethane (DCM) and their corresponding (b) normalized spectra; Fluorescence spectra of **1b** in (c) ethanol and DCM, (d) their corresponding normalized spectra.



(a) (b)

χ^2: 1.024

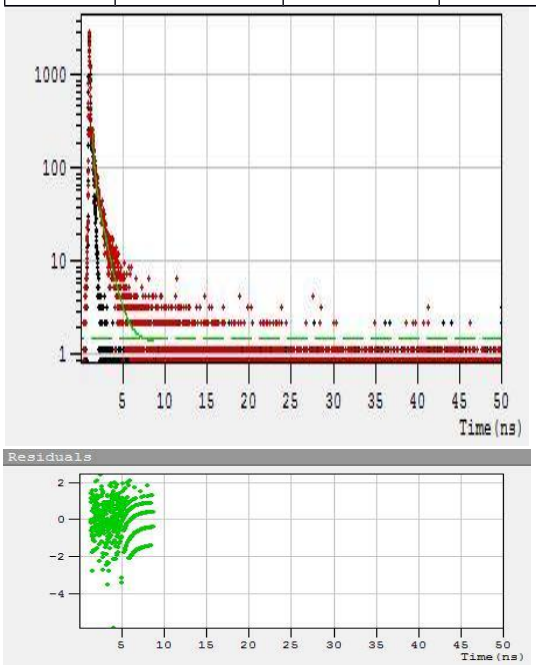
	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0209	0.0175	49.347	44.728	0.616	0.043
2	0.0028	0.0008	50.653	14.894	4.695	0.002
					τ_{av}=1.69 ns	

(c)

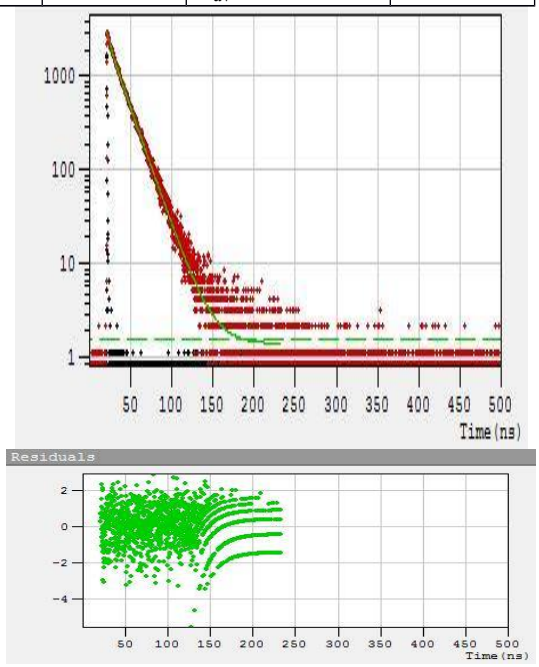
χ^2 : 1.062

(d)

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	1079.9241	22.9580	17.193	0.379	5.828	0.004
2	1833.0353	25.2643	82.807	1.143	16.539	0.0003
					τ_{av}=15. 87ns	



(e)



(f)

χ^2: 1.055

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.5301	0.1861	84.496	24094.8281	0.030	8.510
2	0.0031	0.0001	15.504	0.904	0.949	0.024
					τ_{av}=0.0328 ns	

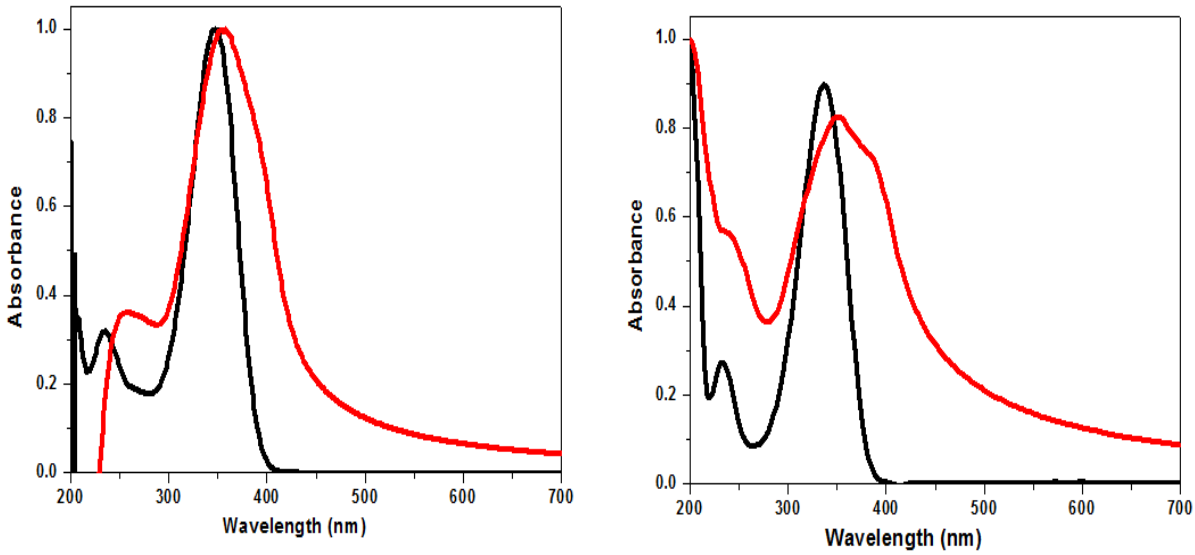
(g)

χ^2: 1.080

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	532.5170	18.6918	5.790	0.216	4.929	0.011
2	2458.6191	19.2650	94.210	0.739	17.372	0.0002
					τ_{av}=17.164 ns	

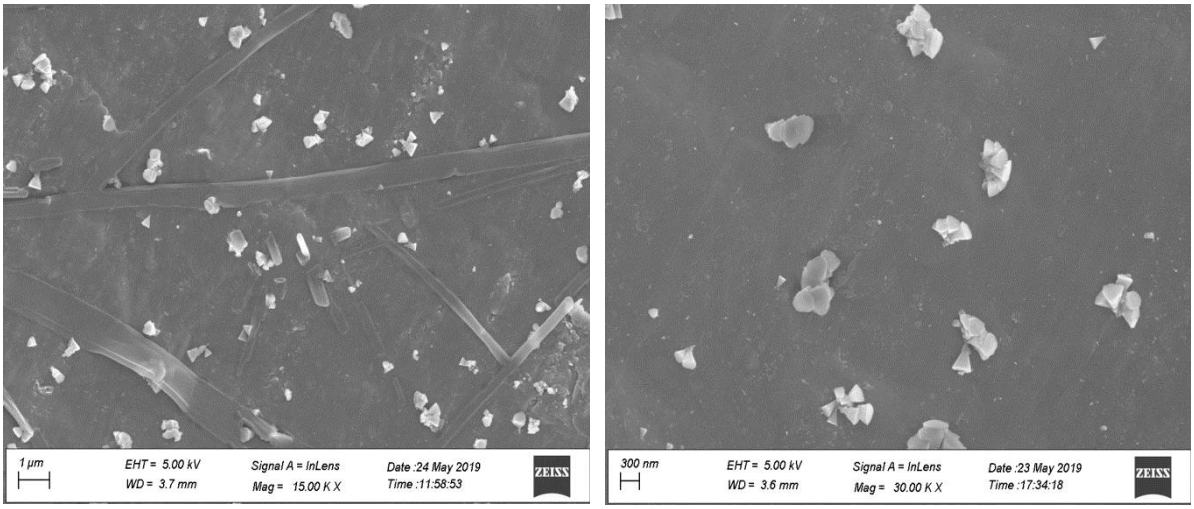
(h)

Figure S2 Fluorescence lifetime decay profile and residual plot of compound **1a** in (a) ethanol and (b) ethanol/H_2O (10^{-3} M, f = 95%, f = percentage of water); (c) and (d) corresponding fluorescence lifetime table; compound **1b** in (e) ethanol and (f) ethanol/H_2O (10^{-3} M, f = 95%, f = percentage of water); (g) and (h) corresponding fluorescence lifetime table.



(a) (b)

Figure S3 (a) UV-visible spectra of **1a** in ethanol (10^{-3} M, black line) and ethanol/ H_2O (10^{-3} M, f = 95%, red line) (b) UV- spectra of **1b** in ethanol (10^{-3} M, black line) and ethanol/ H_2O (10^{-3} M, f = 95%, red line).



(a) (b)

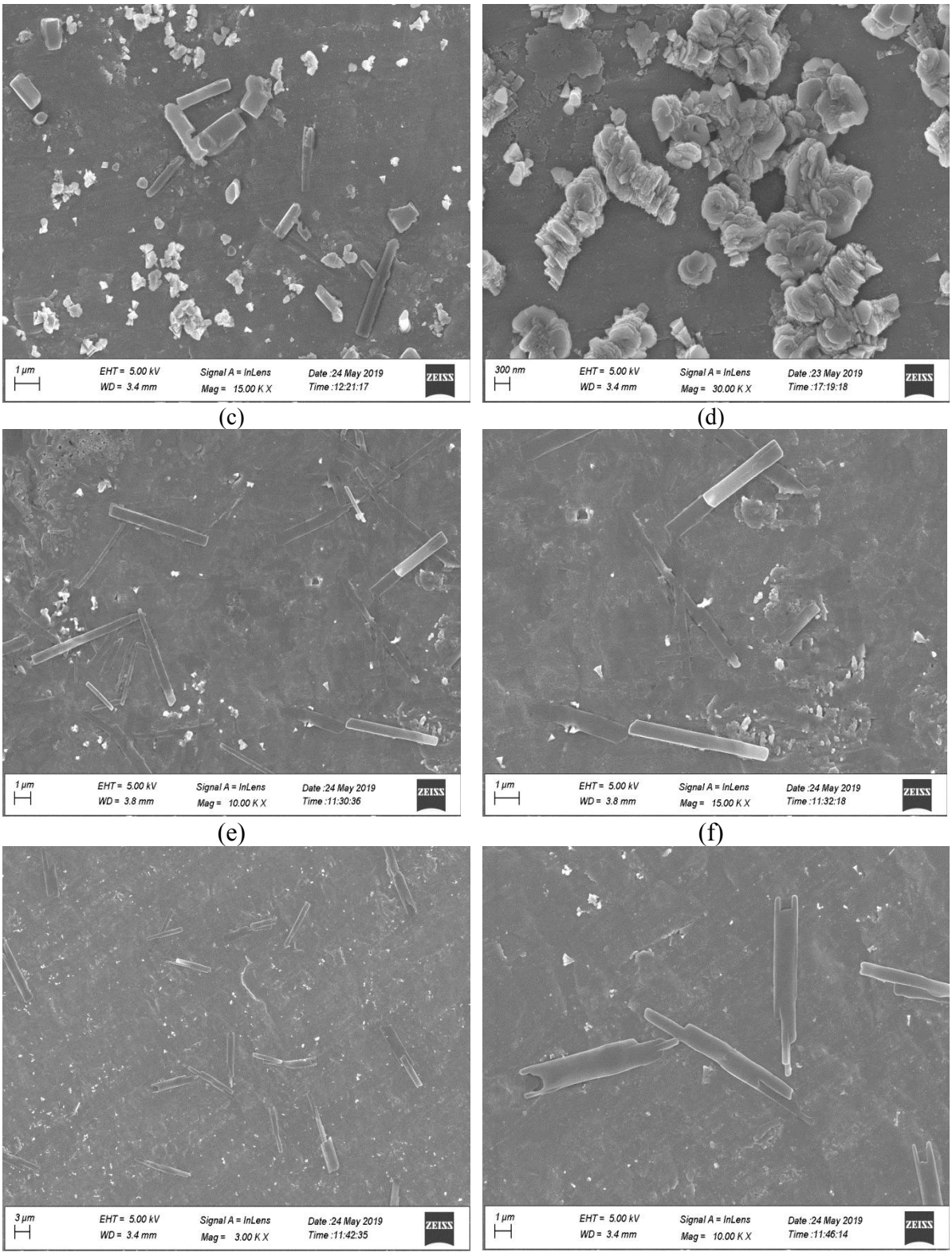
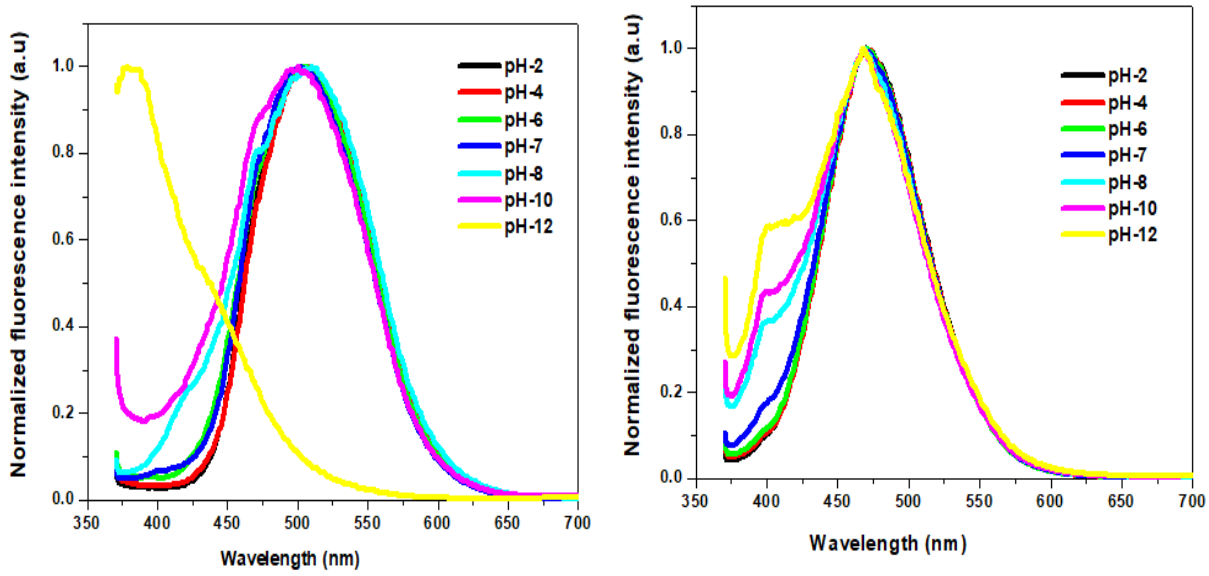


Figure S4 FESEM images of **1a** (a) and (b) ethanol/H_2O (10^{-3} M, f = 0%, f = percentage of water) under different maginification (c) and (d) ethanol/H_2O (10^{-3} M, f = 95%, f = percentage of water) under different maginification. FESEM images of **1b** (e) and (f) ethanol/H_2O (10^{-3} M, f = 0%, f = percentage of water) under different maginification (g) and (h) ethanol/H_2O (10^{-3} M, f = 95%, f = percentage of water) under different maginification.



(a) (b)

Figure S5 (a) Normalized fluorescence spectra of **1a** in ethanol/H_2O (10^{-3} M, f = 95%) with variation of pH (b) Normalized fluorescence spectra of **1b** in ethanol/H_2O (10^{-3} M, f = 95%) with variation of pH.

Figure S6 Photograph of the compound **1a-1c** under day light (above) and 365 nm UV light irradiation (below).

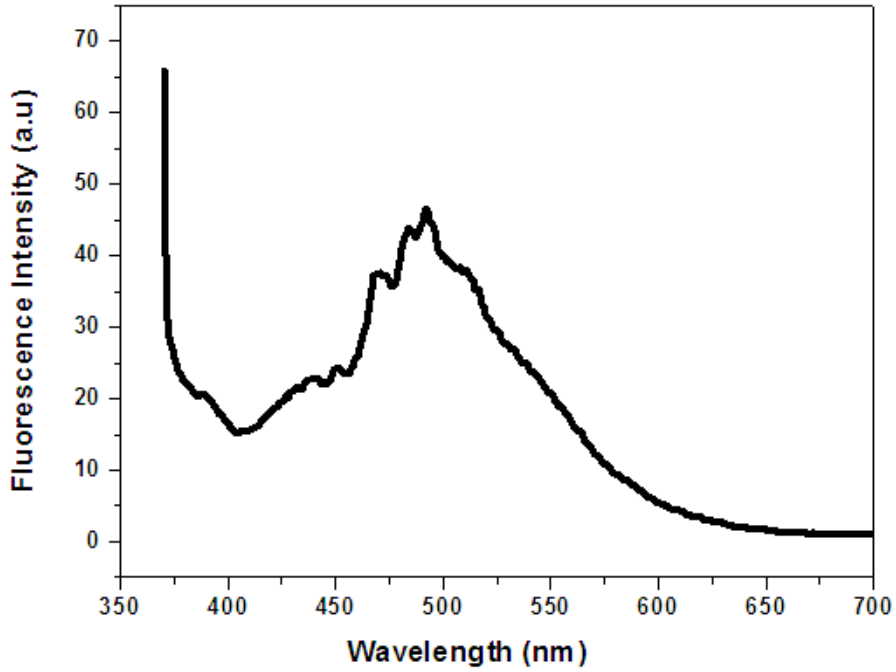


Figure S7 Fluorescence spectra of **1c** under 360 nm excitation wavelength.

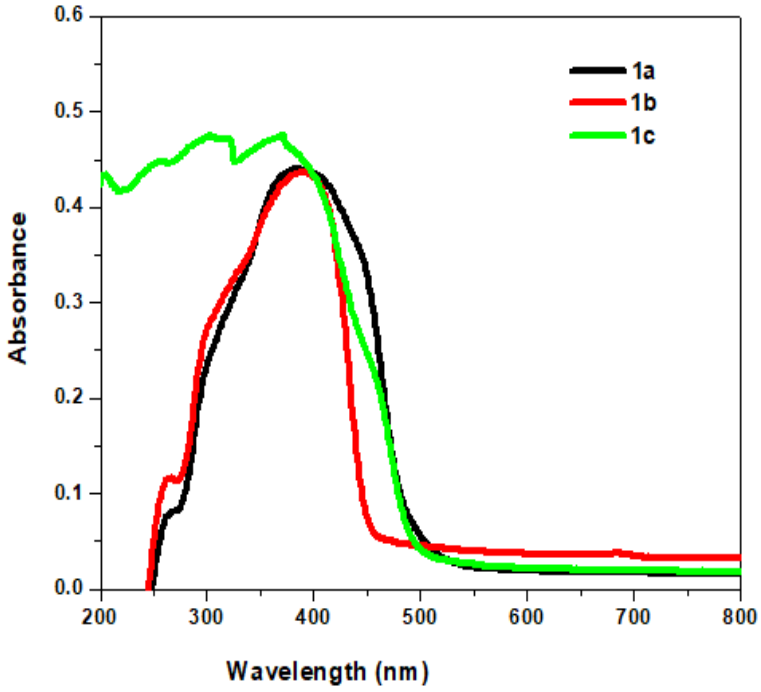
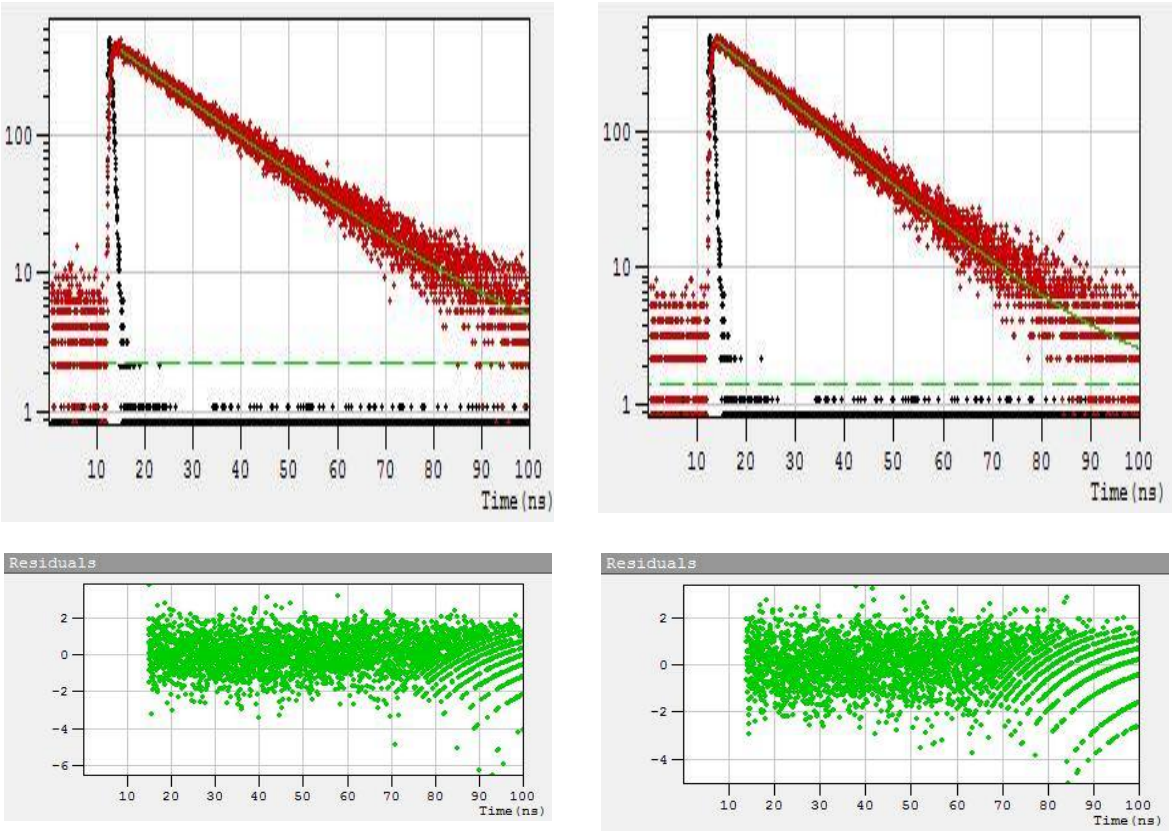


Figure S8 Solid state UV-visible absorbance spectra of **1a**, **1b** and **1c**.



(a) (b)

χ^2 : 1.092

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0260	0.0059	100.000	22.543	17.271	0.0002

(c)

χ^2 : 1.099

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0274	0.0005	100.000	1.796	14.698	0.0002

(d)

Figure S9 Fluorescence decay curve and residual plot of compound (a) **1a** and (b) **1b** in solid state along with their respective fluorescence lifetime table of compound (c) **1a** and (d) **1b**.

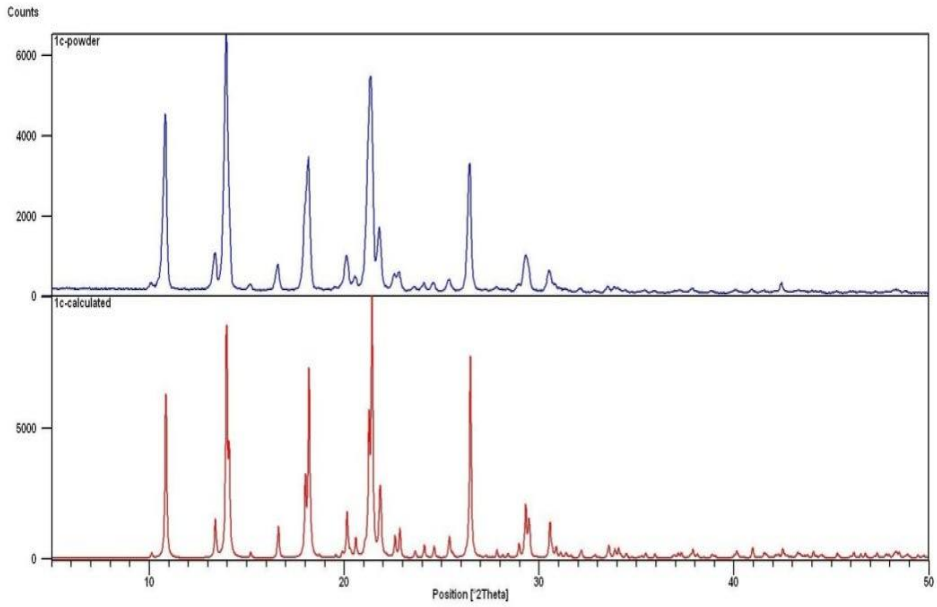
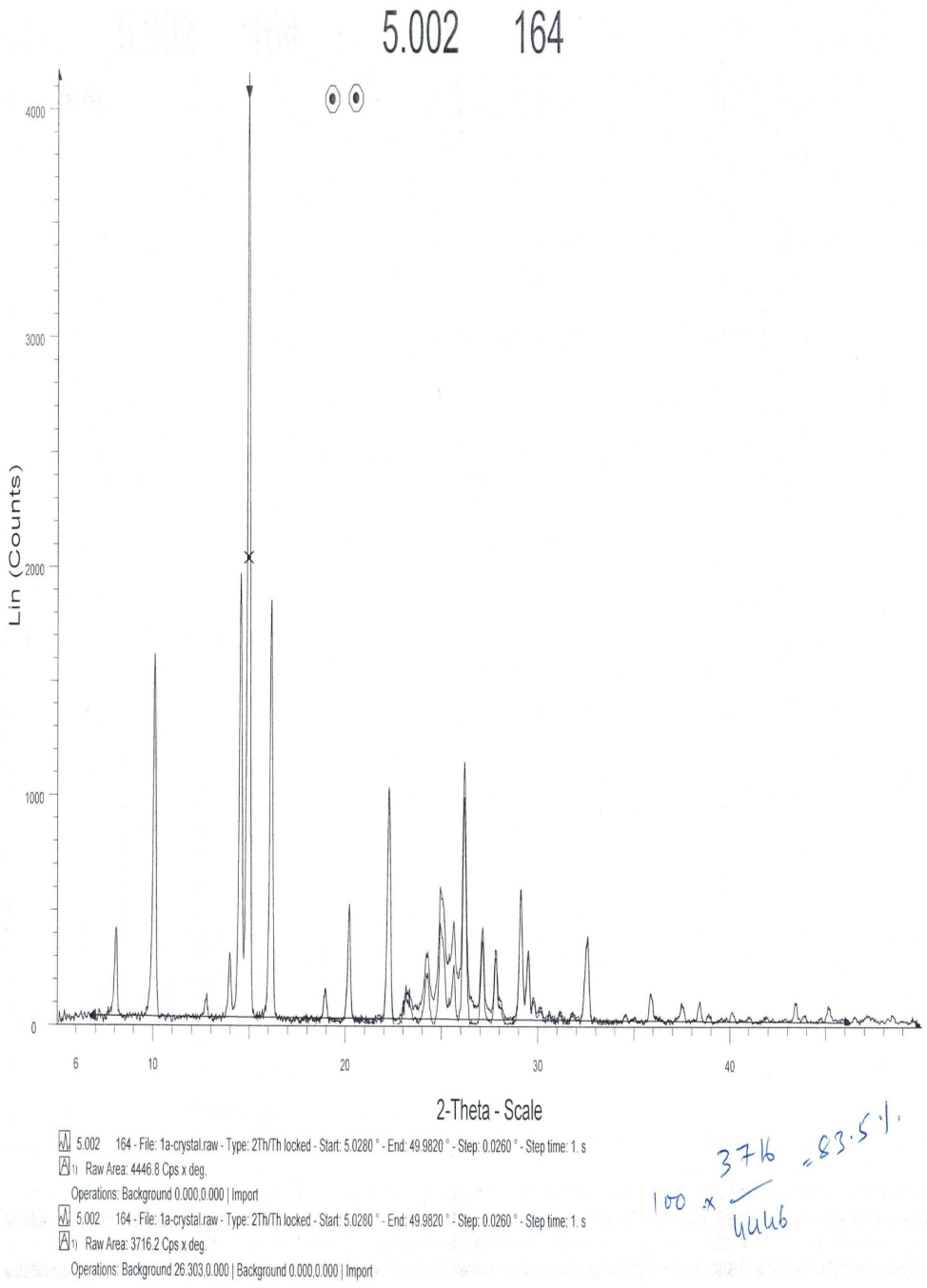
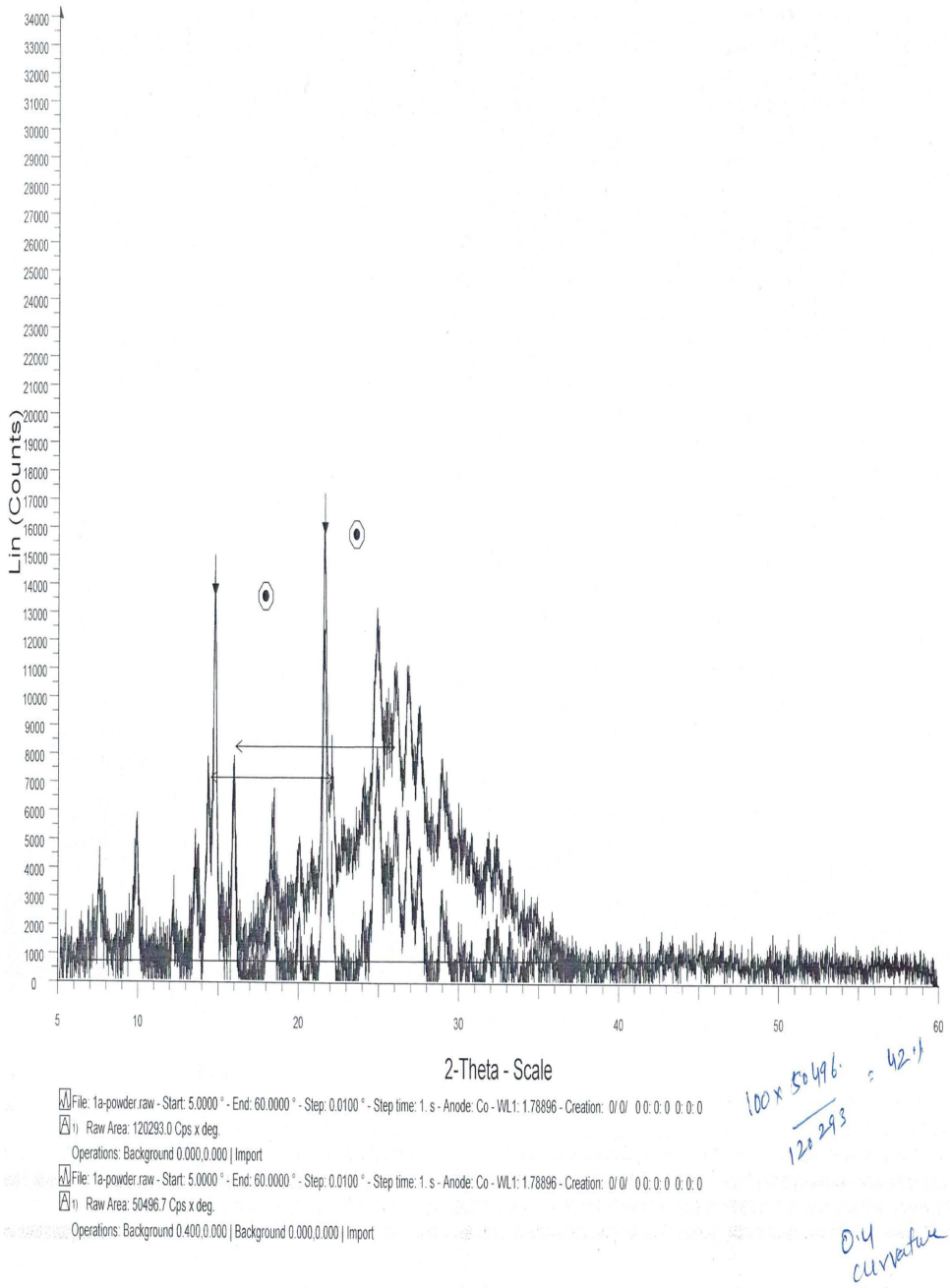


Figure S10 PXRD patterns of compound **1c** experimental PXRD of **1c** matches well with its calculated pattern confirming bulk purity of the sample.

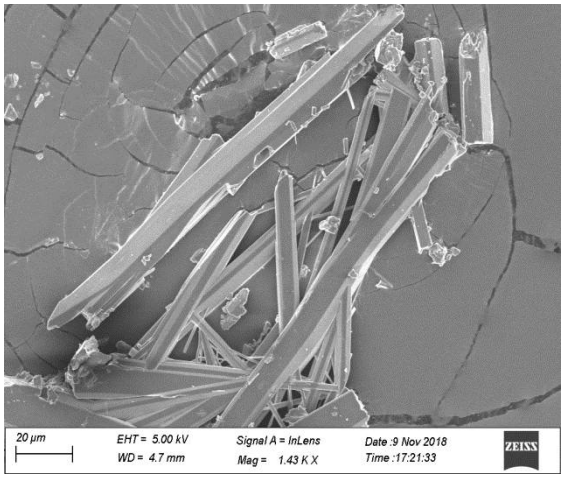

5.002 164
Lin (Counts)
4000
3000
2000
1000
0
6
10
20
30
40
2-Theta - Scale
5.002 164 - File: 1a-crystal.raw - Type: 2Th/Th locked - Start: 5.0280 ° - End: 49.9820 ° - Step: 0.0260 ° - Step time: 1. s
Raw Area: 4446.8 Cps x deg.
Operations: Background 0.000,0.000 | Import
5.002 164 - File: 1a-crystal.raw - Type: 2Th/Th locked - Start: 5.0280 ° - End: 49.9820 ° - Step: 0.0260 ° - Step time: 1. s
Raw Area: 3716.2 Cps x deg.
Operations: Background 26.303,0.000 | Background 0.000,0.000 | Import
100 x 3716/4446 = 83.5 %

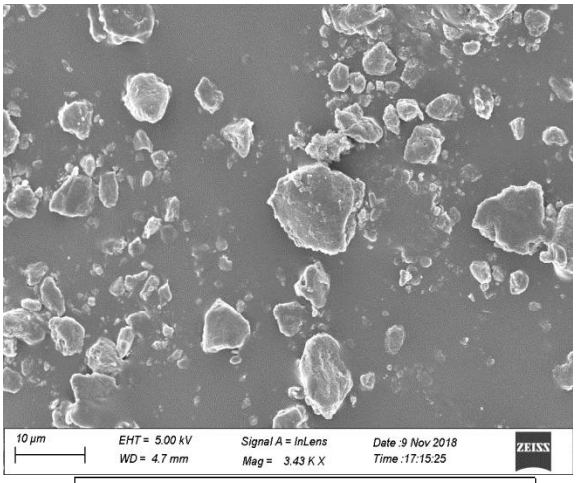
(a)

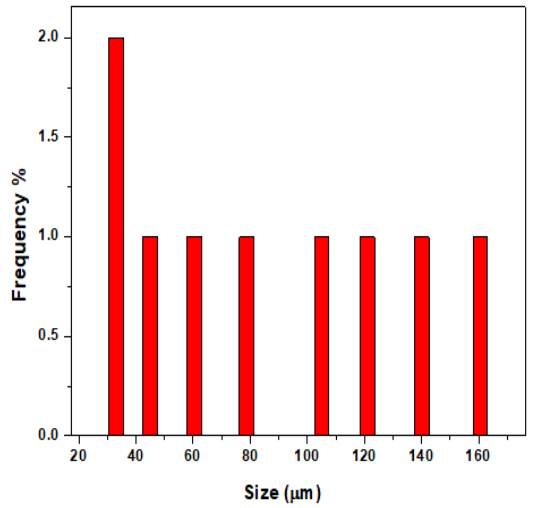


(b)

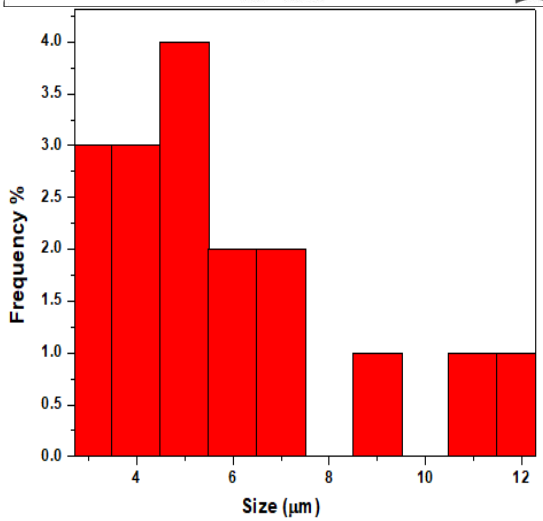
Figure S11 Calculation of degree of crystallinity (DOC) value for compound **1a** (a) crystal and (b) powder samples respectively based on PXRD analysis considering background correction.


20 µm
EHT = 5.00 kV
WD = 4.7 mm
Signal A = InLens
Mag = 1.43 K X
Date :9 Nov 2018
Time :17:21:33
ZEISS

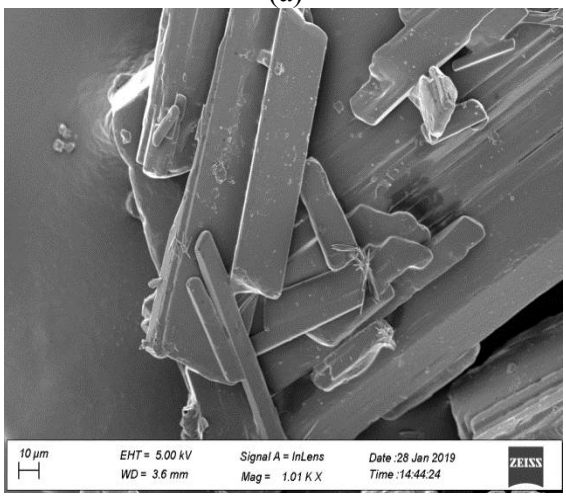

10 µm
EHT = 5.00 kV
WD = 4.7 mm
Signal A = InLens
Mag = 3.43 K X
Date :9 Nov 2018
Time :17:15:25
ZEISS

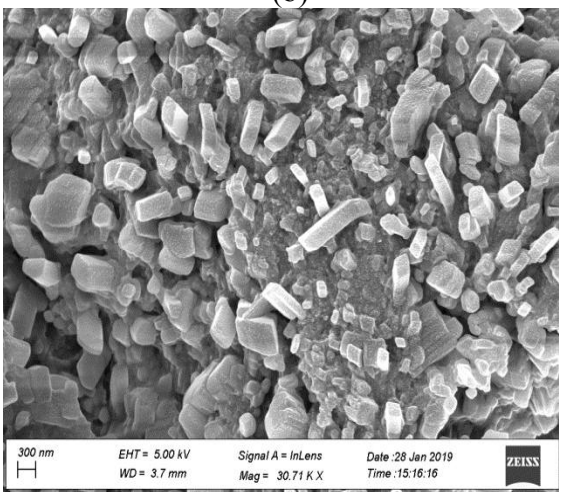

Frequency %
Size (µm)
0.0
0.5
1.0
1.5
2.0
20
40
60
80
100
120
140
160

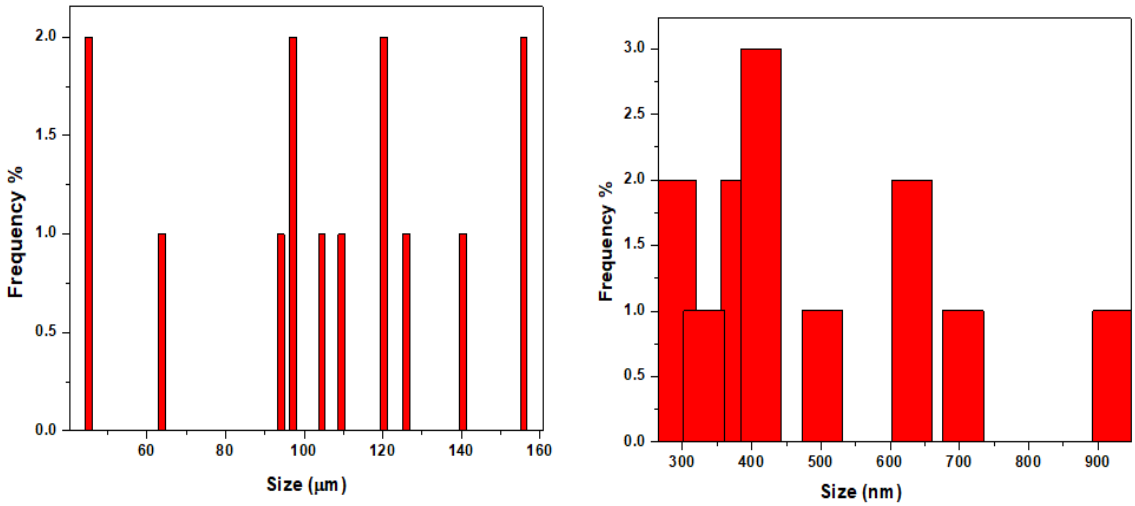
(a)


Frequency %
Size (µm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4
6
8
10
12

(b)

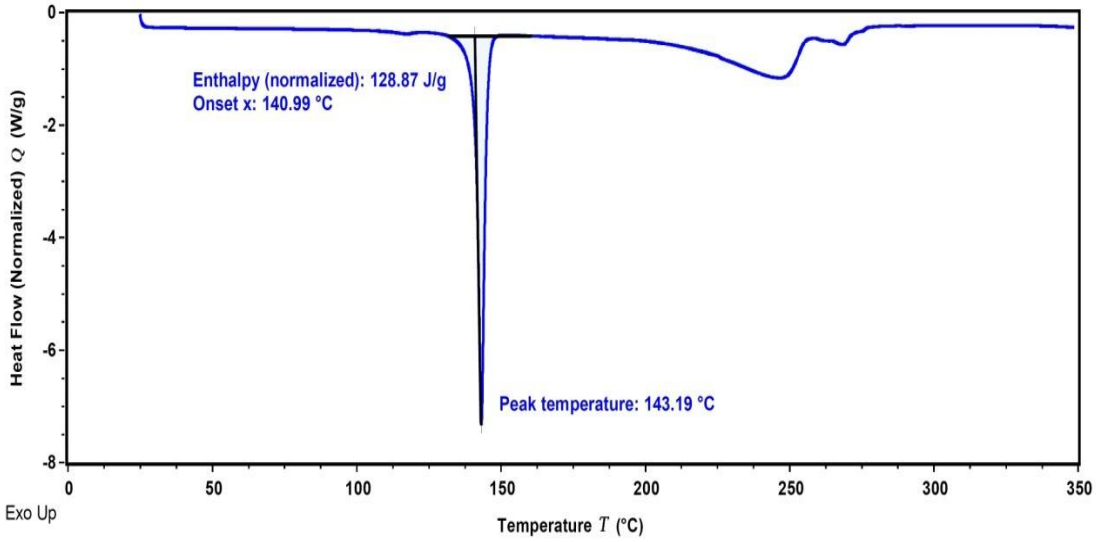

10 µm
EHT = 5.00 kV
WD = 3.6 mm
Signal A = InLens
Mag = 1.01 K X
Date :28 Jan 2019
Time :14:44:24
ZEISS


300 nm
EHT = 5.00 kV
WD = 3.7 mm
Signal A = InLens
Mag = 30.71 K X
Date :28 Jan 2019
Time :15:16:16
ZEISS

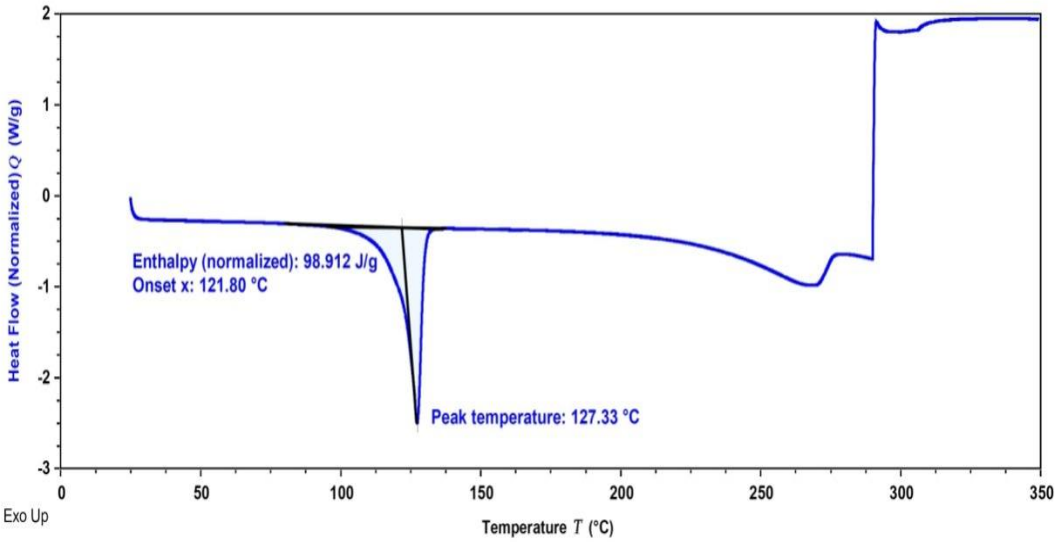


(c) (d)

Figure S12 FESEM images (above) and corresponding particle size distribution (below) of (a) **1a** in crystal form; (b) **1a** in powder form; (c) **1b** in crystal form and (d) **1b** in powder form show crystalline nature.



(a)



(b)

Figure S13 DSC endotherm of compound (a) **1a** and (b) **1b** show single melting endotherm without any phase transition followed by decomposition of the materials at round 250 °C.

Reference

Sarma, P., Sarmah, K. K., Kakoti, D., Mahanta, S. P., Adassooriya, N. M., Nandi, G., Bučar, D.-K., Das, P. J. & Thakuria, R. unpublish work.