

Supporting Information

Protonation Induced Redshift in Fluorescence of Pyridine Derivative as the Potential Anti-counterfeiting Agent

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1. Experimental:

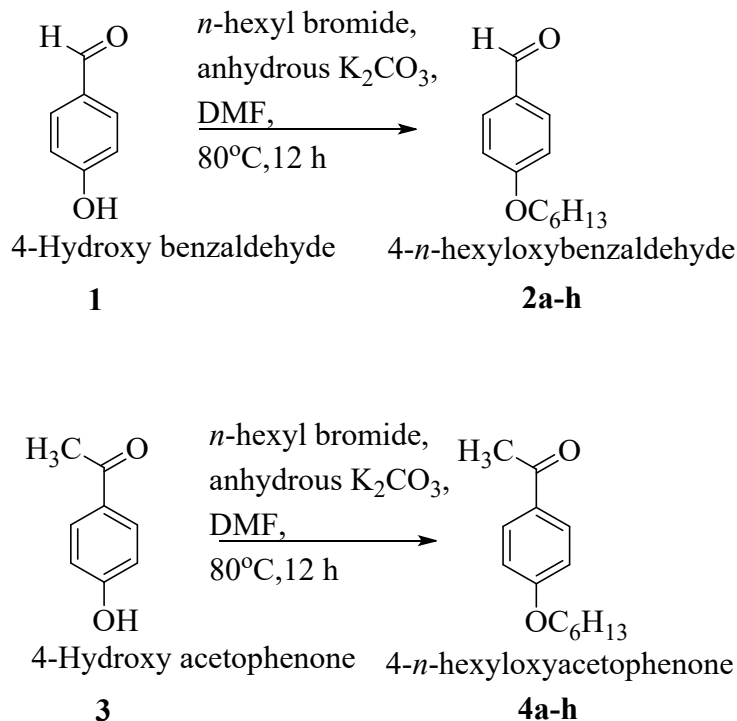
1.1. Materials and methods

n-hexyl bromide, acetonitrile, and trifluoroacetic acid were procured from Spectrochem Pvt. Ltd. Mumbai (India). Ammonium acetate, hexane, methanol, and dimethylformamide were procured from SD-Fine-Chem Ltd, Mumbai (India). Glacial acetic acid was procured from Sigma-Aldrich India, Ethylacetate was procured from Avra synthesis Pvt. Ltd. India. Tetrahydrofuran, chloroform, and dimethylsulphoxide were procured from Rankem, India. Ethanol (99.9%) was procured from Chinachangshu Yangyuan Chemical. Hydrochloric acid (35%) was procured from Himedia Laboratories Pvt. Ltd. India. UV-visible absorption and emission properties were measured by using UV-1800 SHIMADZU UV-spectrophotometer and RF-5301 PC, SHIMADZU spectrophotometer equipped with a Xe-lamp as an excitation source, respectively. Emission and excitation slit widths were kept fixed while recording emission spectra of all the samples. Dynamic light scattering (DLS) experiments were performed to measure the particle size of the **D** aggregates using an Anton-Paar DLS instrument equipped with a 40 mW single-frequency laser diode at a wavelength of 658 nm at 25 °C.

1.2. Synthesis

Step 1: Synthesis of 4-*n*-hexyloxy benzaldehyde (**2a-h**) and 4-*n*-hexyloxy acetophenone (**4a-h**)

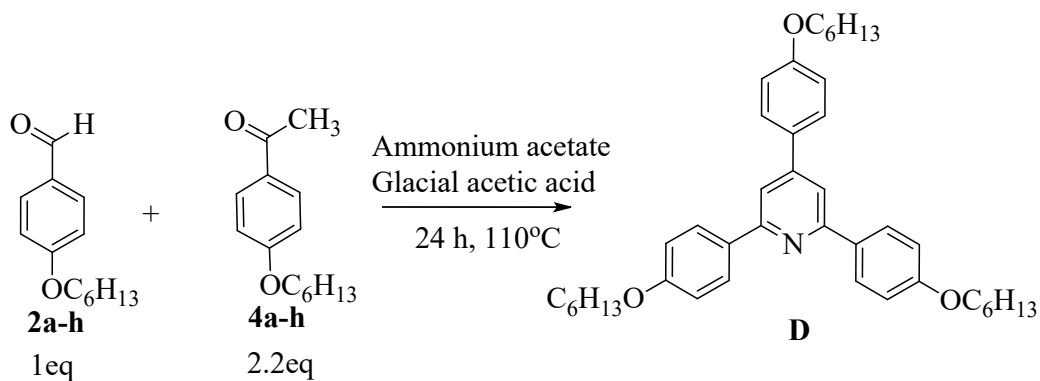
The 4-*n*-hexyloxy benzaldehyde (**2a-h**) and 4-*n*-hexyloxy acetophenone (**4a-h**) were prepared from 4-hydroxybenzaldehyde (**1**) and 4-hydroxyacetophenone (**2**) respectively by reacting with the *n*-hexyl bromide following the standard procedures.^{1,2}



Scheme S1: General synthetic route for **2a-h** and **4a-h**.

Step 2: Synthesis of 2,4,6-*tris*(4-hexyloxyphenyl)pyridine (**D**)

A mixture of 4-*n*-hexyloxybenzaldehyde (**2a-h**, 1 equivalent) and corresponding 4-*n*-hexyloxyacetophenone (**4a-h**, 2 equivalent) was taken in glacial acetic acid and added ammonium acetate (2 equivalent) to it and stirred the reaction mixture at 110 °C for 24 h. After completion of the reaction, reaction mixture was added to the water and organic components were extracted by using DCM solvent. Excess DCM solvent was removed by using a rotary evaporator. Further, the obtained product was passed through the column by using the solvent hexane and diethyl ether in the 98:2 ratio to obtain the pure expected compound (**D**).



Scheme S2: General synthetic route for **D**.

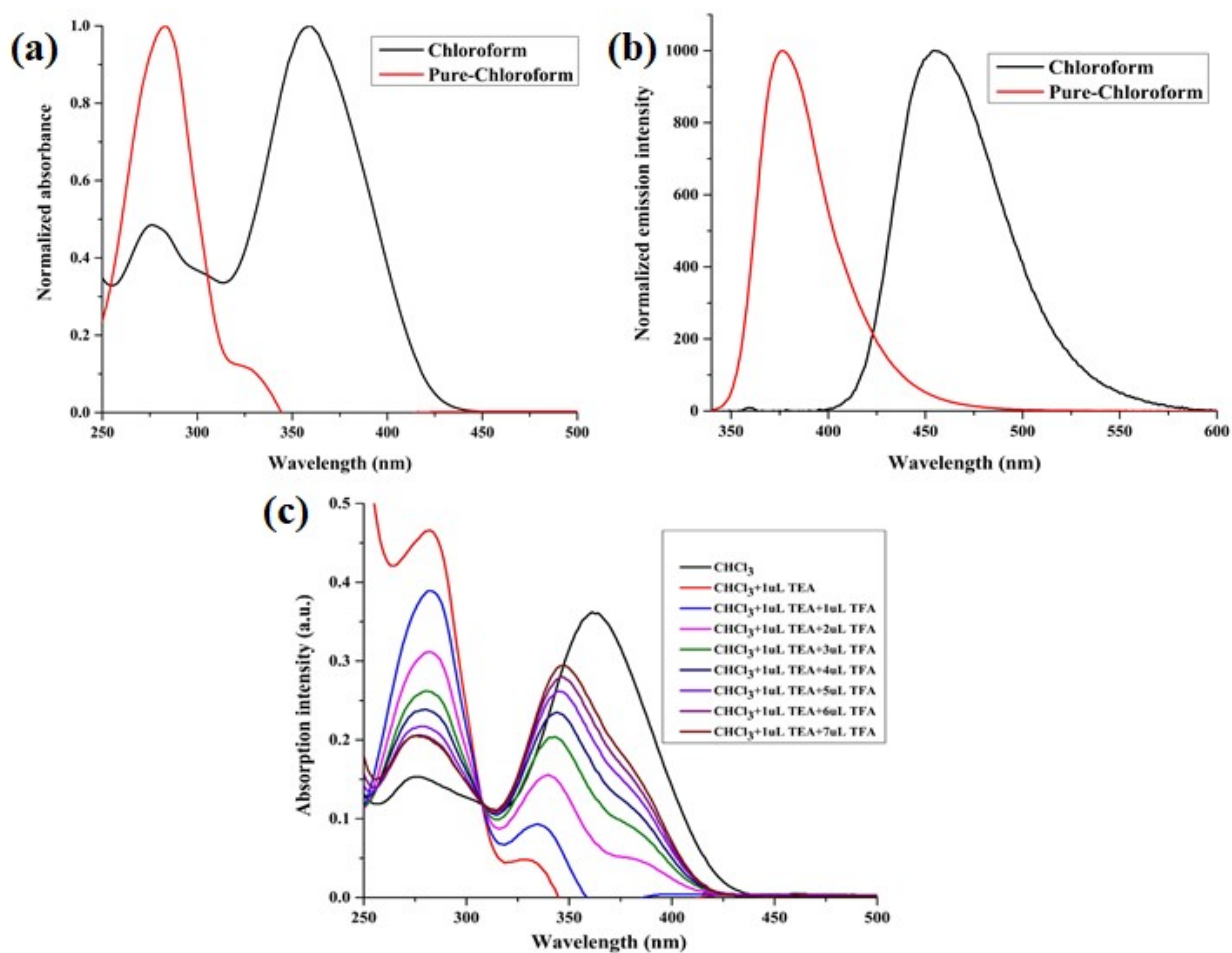


Figure S1: (a) Absorption spectra of sample **D** in chloroform before and after passing through sodium carbonate. (b) Emission spectra of sample **D** in chloroform before and after passing through sodium carbonate. (c) Absorption spectra of sample **D** in CHCl₃+ TEA + TFA.

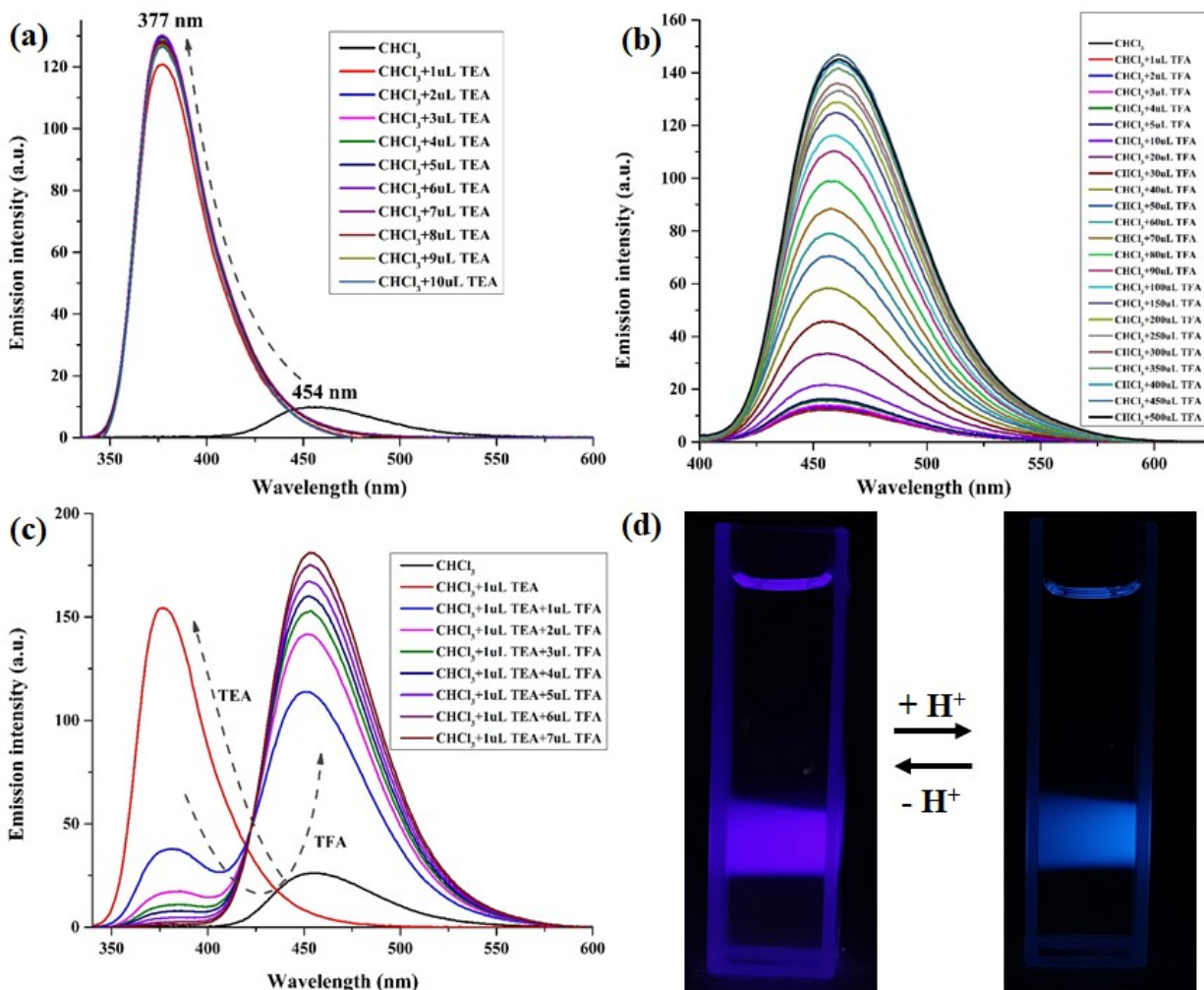


Figure S2: Emission property of sample **D** in (a) CHCl₃+TEA, (b) CHCl₃+TFA, and (c) CHCl₃+TEA+TFA. (d) Photographic images of **D** exhibiting color change with the addition of TFA and TEA, under UV light.

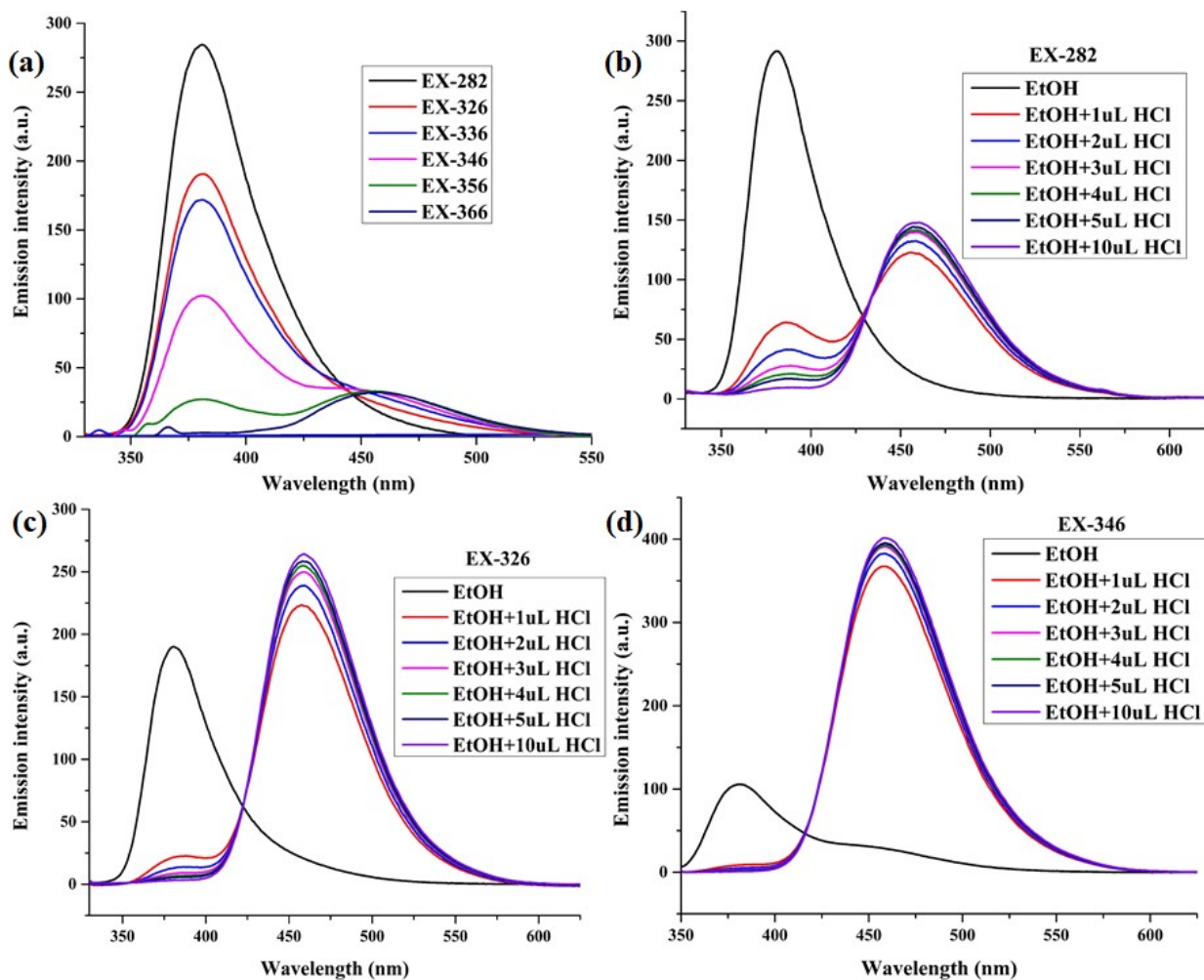


Figure S3: Emission property of sample D in (a) ethanol with different excitation wavelengths (b) EtOH + HCl (Ex: 282), (c) EtOH + HCl (Ex: 326), and (d) EtOH + HCl (Ex: 346).

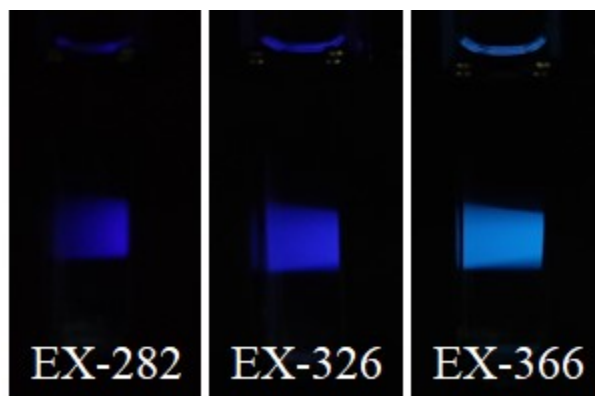


Figure S4: Photographic images of emission of sample D in ethanol with different excitation wavelengths.

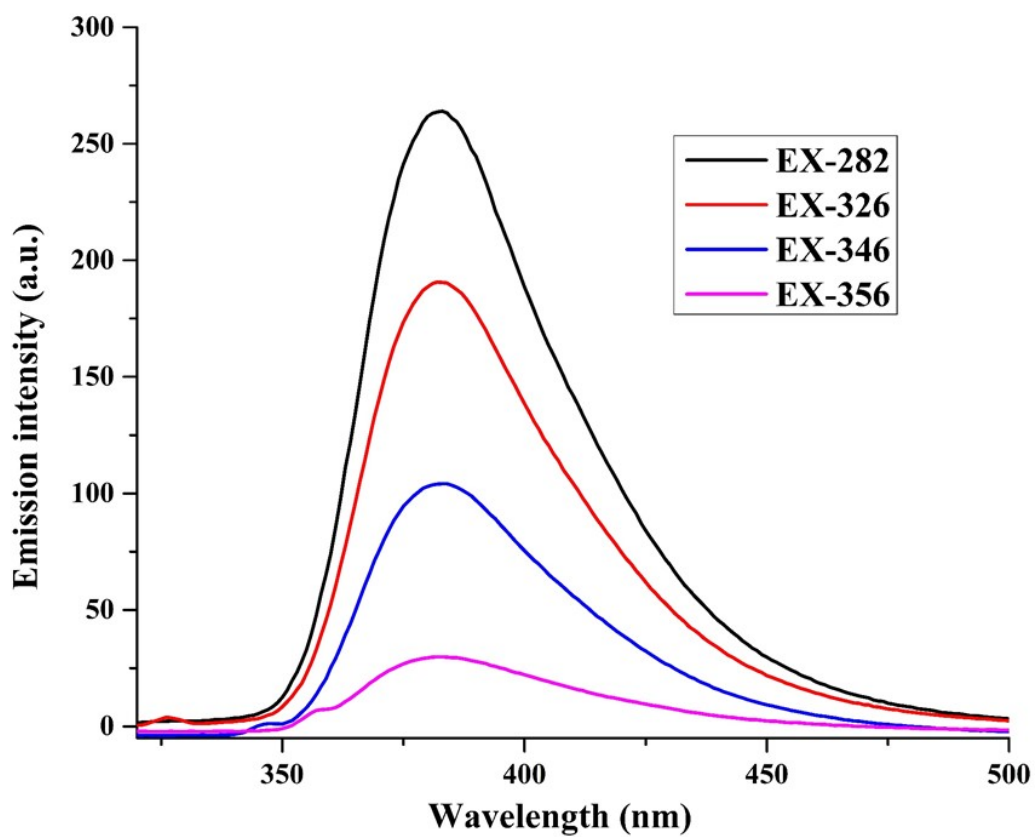


Figure S5: Emission property of sample D in methanol solvent with different excitation wavelength.

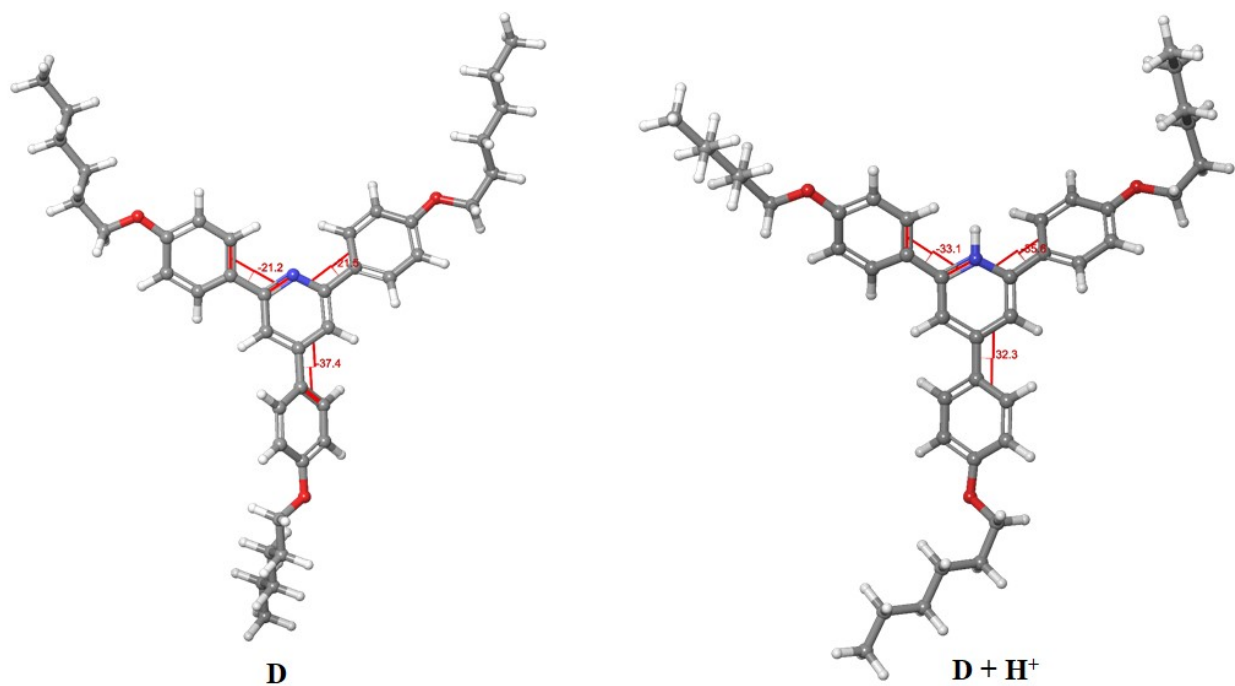


Figure S6: Optimized geometry of sample **D** in neutral form and in protonated form (**D + H⁺**).

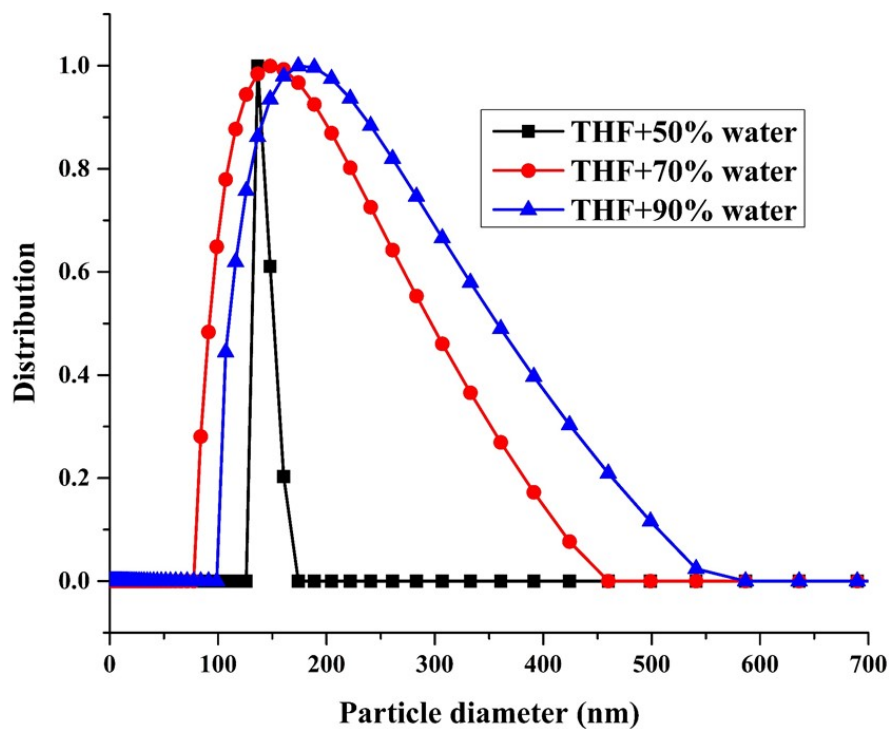


Figure S7: Particle size distribution curves for the **D** in THF+50% water, THF+70% water, and THF+90% water.

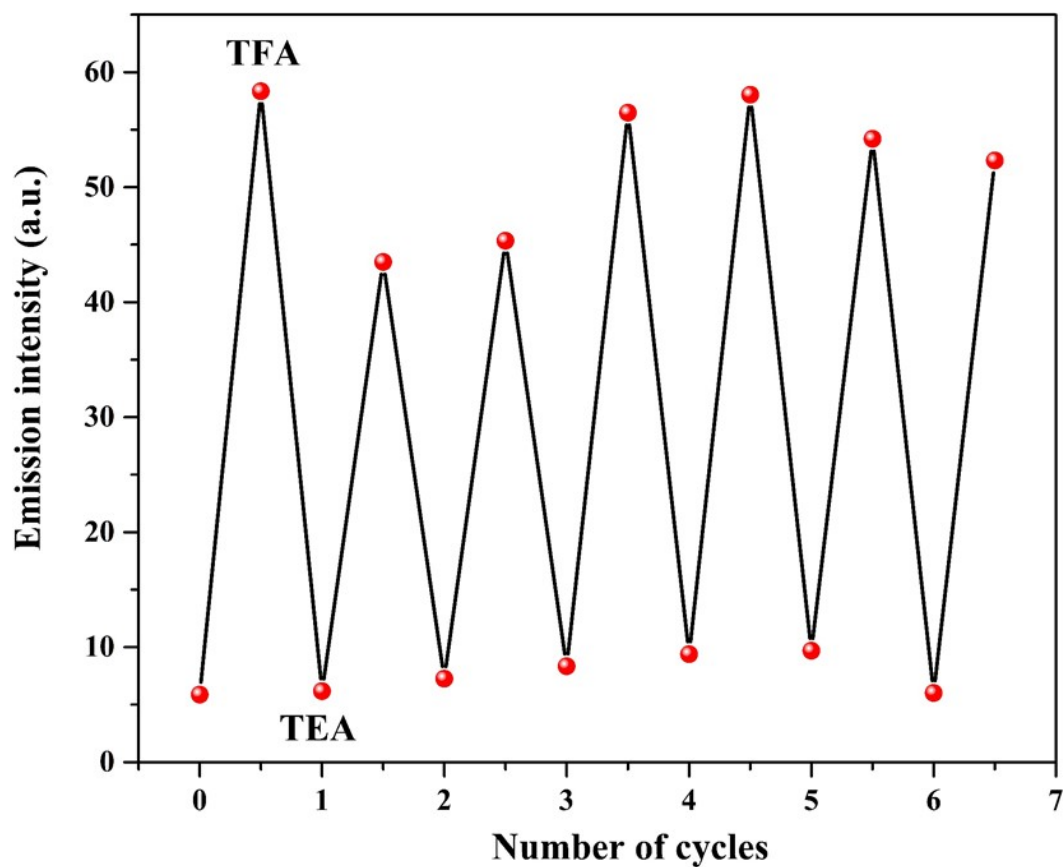


Figure S8: Fluorescence intensity of sample **D** coated paper as a function of the TFA-TEA cycle numbers. The fluorescence intensity was examined at the wavelength of 483 nm by using excitation wavelength of 328 nm.

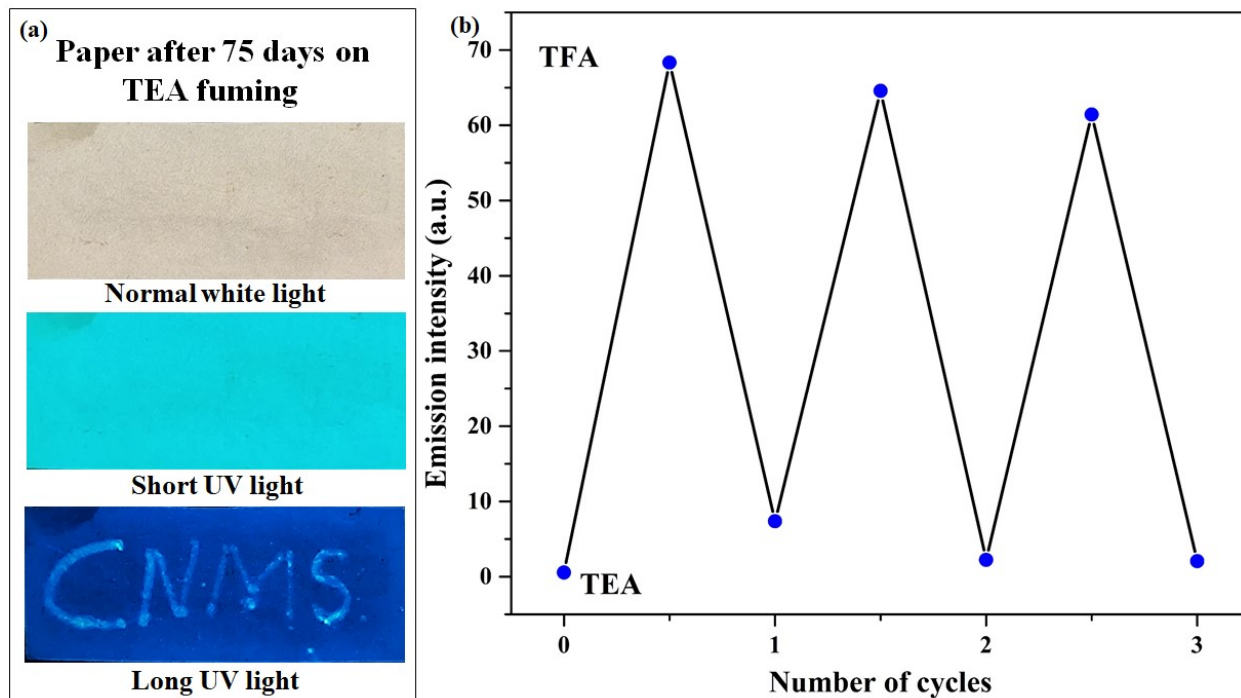


Figure S9: (a) Photographs of word “CNMS” after 75 days on TFA fuming under normal white light, short UV and the long UV light. (b) Fluorescence intensity of sample **D** coated paper as a function of the TFA–TEA cycle numbers after 75 days. The fluorescence intensity was examined at the wavelength of 483 nm by using excitation wavelength of 328 nm.

References:

- 1 S. Tantrawong, P. Styring and J. W. Goodby, Discotic mesomorphism in oxovanadium(IV) complexes possessing four alkyl substituents, *J. Mater. Chem.*, 1993, **3**, 1209–1216.
- 2 V. N. Kozhevnikov, S. J. Cowling, P. B. Karadakov and D. W. Bruce, Mesomorphic 1,2,4-triazine-4-oxides in the synthesis of new heterocyclic liquid crystals, *J. Mater. Chem.*, 2008, **18**, 1703.