Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Coumarin-Benzothiazole-Chlorambucil (Cou-Benz-Cbl) Conjugate: ESIPT Based pH Sensitive Drug Delivery System

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1. Experimental

1.1. Materials and method:

All reagents were purchased from Sigma Aldrich and used without further purification. Acetonitrile and dichloromethane were distilled from CaH_2 before use. ^1H NMR spectra were recorded on a BRUKER-AC 200 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz). ^{13}C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.0 ppm). UV/vis absorption spectra were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer, fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer, FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer and HRMS spectra were recorded on a JEOL-AccuTOF JMS-T100L mass spectrometer. Photolysis of the ester conjugates were carried out using 125 W medium pressure Hg lamp supplied by SAIC (India). Chromatographic purification was done with 60-120 mesh silica gel (Merck). For reaction monitoring, precoated silica gel 60 F254 TLC sheets (Merck) were used. RP-HPLC was taken using mobile phase acetonitrile, at a flow rate of 1mL / min (detection: UV 254 nm).

2. Characterization of compound 3, C_4 and C_5:

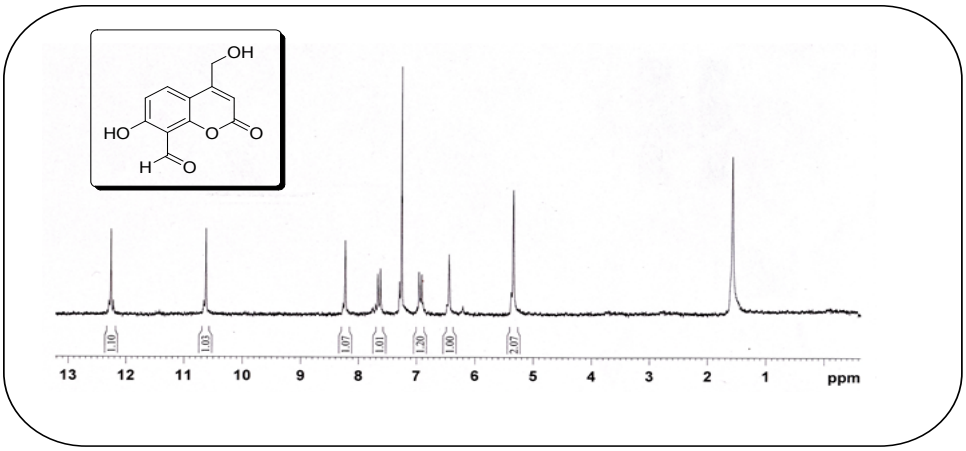


Figure S1: ^{1}H NMR of 8-formyl-7-hydroxyl-4-(hydroxymethyl)coumarin (3).

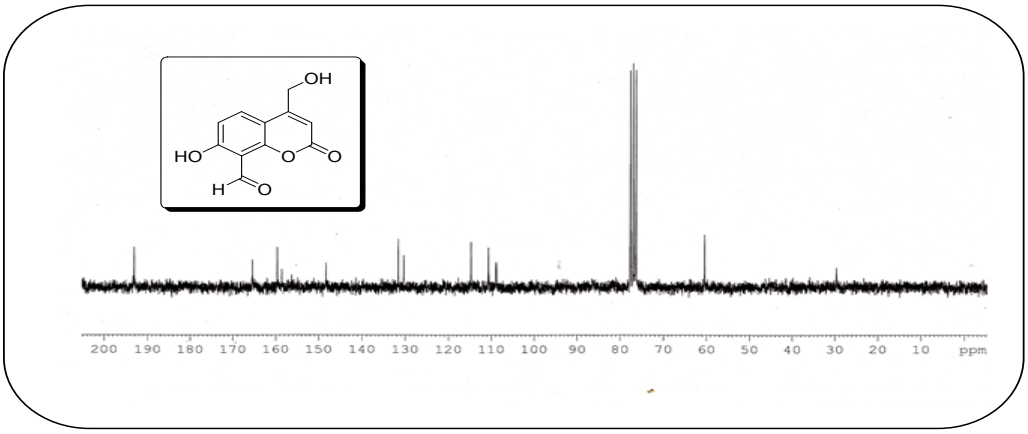


Figure S2: ^{13}C NMR of8-formyl-7-hydroxyl-4-(hydroxymethyl)coumarin(3).

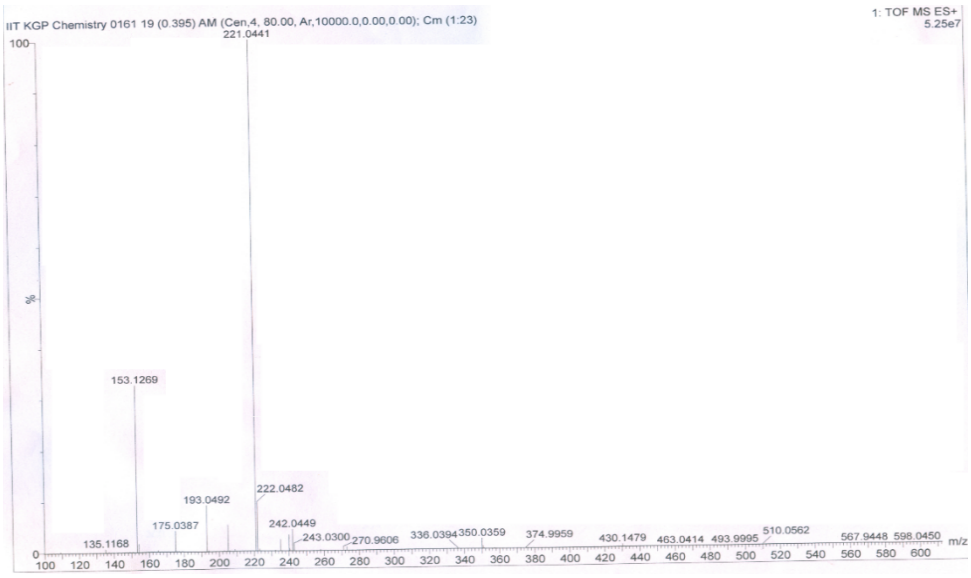


Figure S3: HRMS of 8-formyl-7-hydroxyl-4-(hydroxymethyl)coumarin(3).

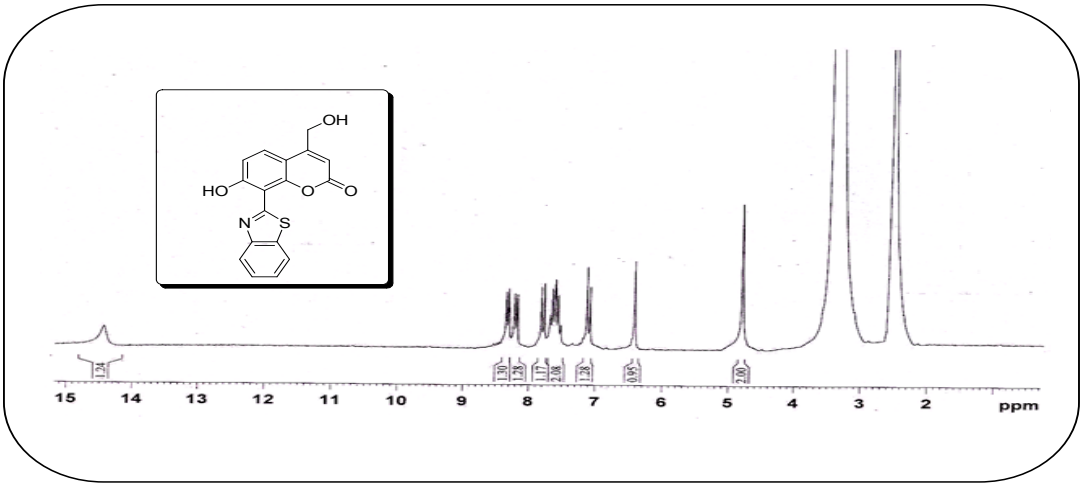


Figure S4: ^{1}H NMR of8-benzothiazoyl-7-hydroxyl-4-(hydroxymethyl)coumarin (Cou-Benz-OH) (C_4).

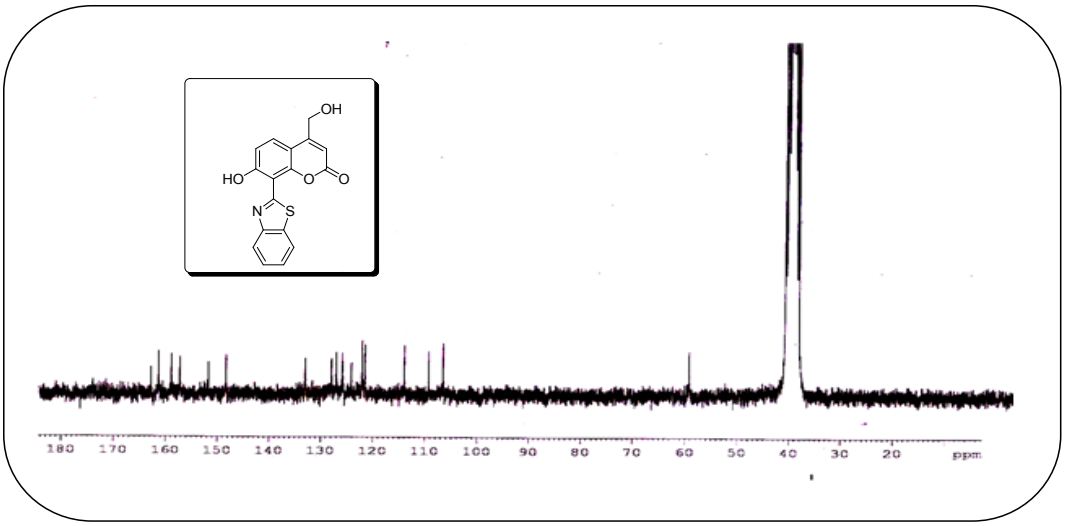


Figure S5: ^{13}C NMR of8-benzothiazoyl-7-hydroxyl-4-(hydroxymethyl)coumarin (Cou-Benz-OH) (C_4).

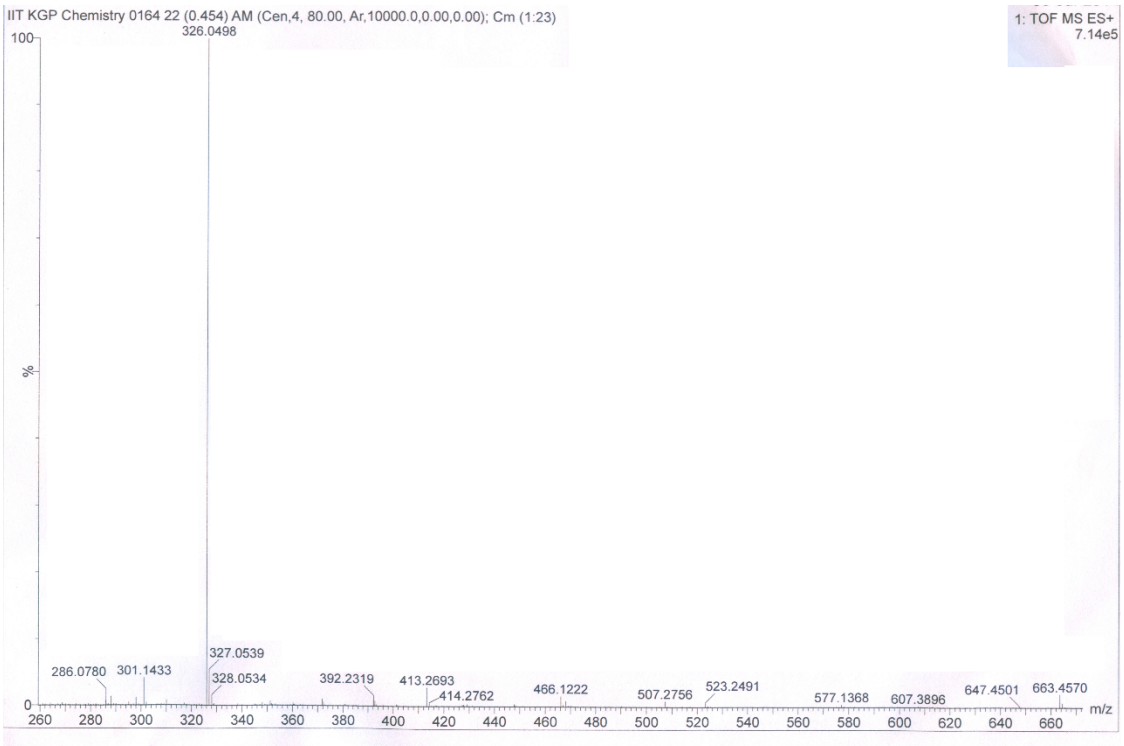


Figure S6: HRMS of 8-benzothiazoyl-7-hydroxyl-4-(hydroxymethyl)coumarin (Cou-Benz-OH) (C_4).

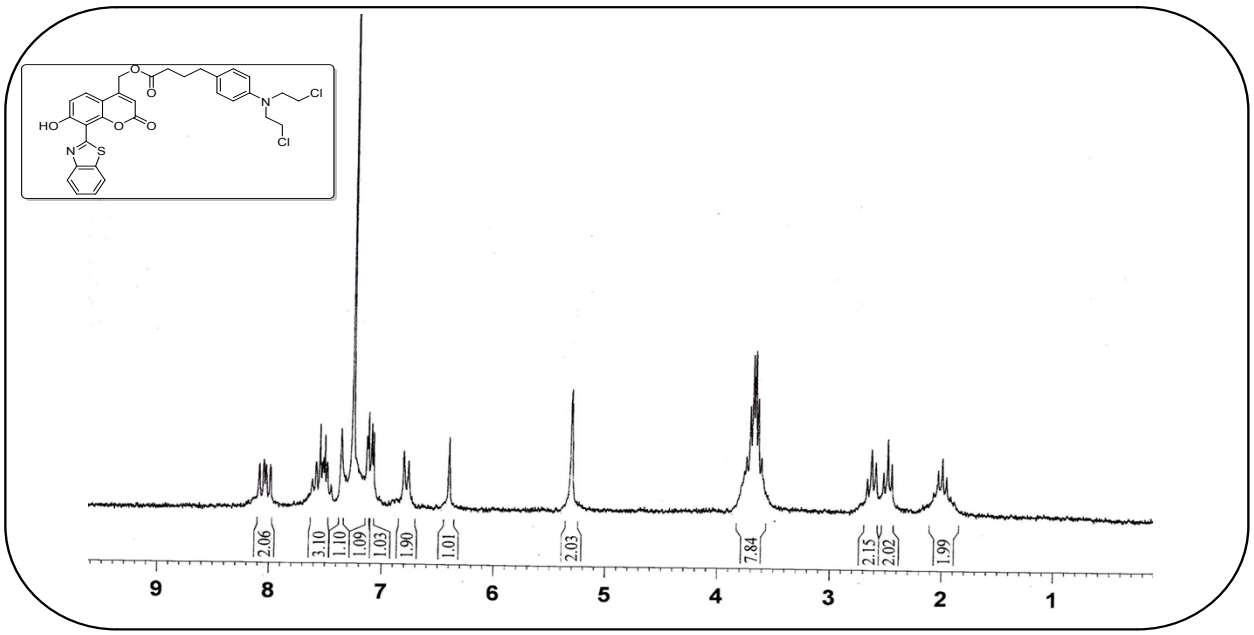
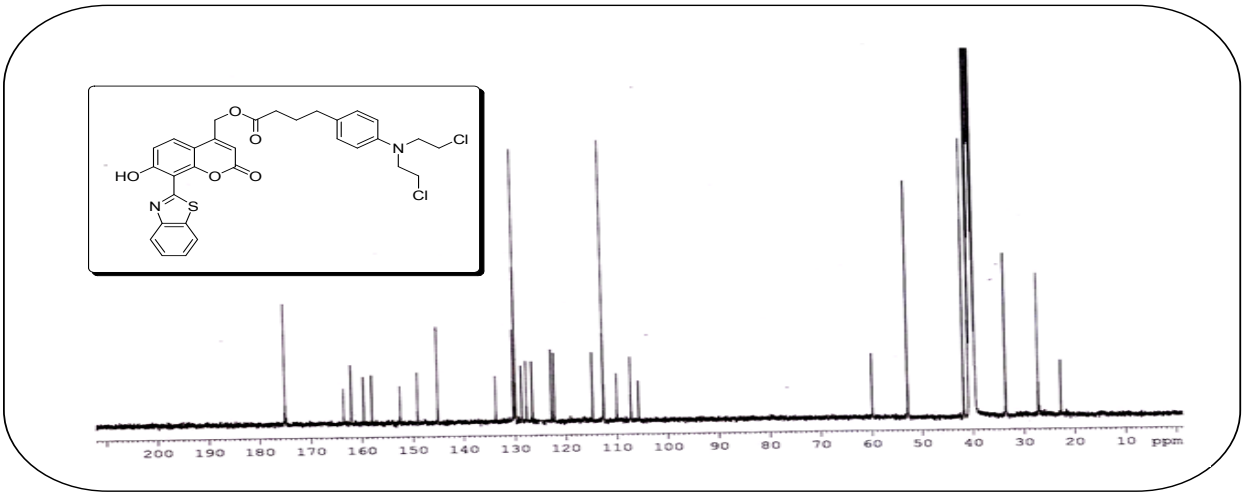


Figure S7: ^{1}H NMR ofCoumarin-Benzothiazoyl-Chlorambucil conjugate (Cou-Benz-Cbl) (C_5)



FigureS8: ^{13} C NMR ofCoumarin-Benzothiazoyl-Chlorambucil conjugate (Cou-Benz-Cbl (C_5).

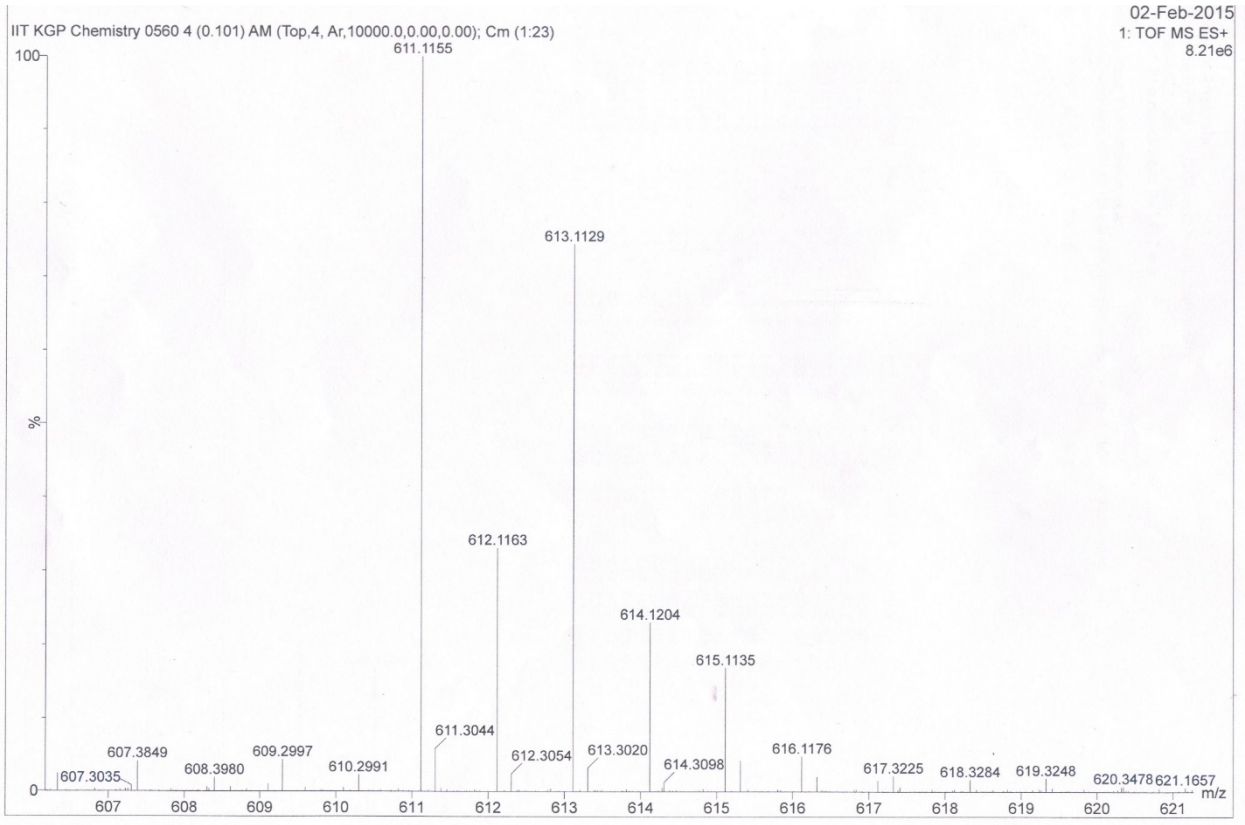


Figure S9: HRMSof Coumarin-Benzothiazoyl-Chlorambucilconjugate (Cou-Benz-Cbl) (C_5).

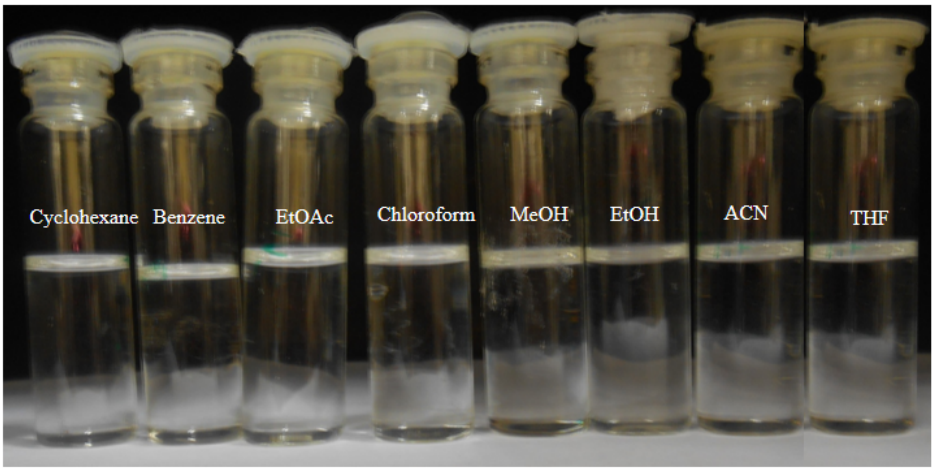


Figure S10: The naked eye colour of the solution of C_5 in different solvents.

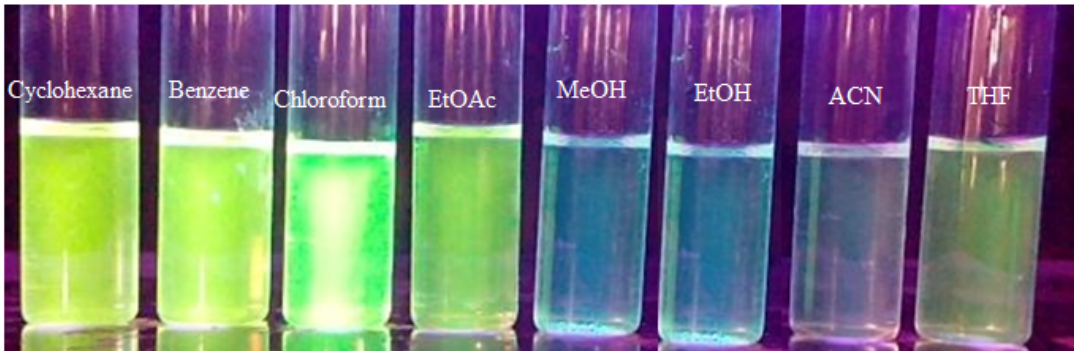


Figure S11: The naked eye colour of the solution of **C_5** in different solvents under fluorescent lamp.

3. Fluorescence quantum yield calculation:

Table S1 : Quantum yield of **C_4, C_5** and 4-methy-7-hydroxycoumarin [1]

Compounds	Quantum yields[a] (Φ_f)
C_4	19.53%
C_5	24.27%
4-methy-7-hydroxycoumarin	0.0617%

[a] measurments were performed in absolute ethanol solvent. Fluorescence quantum yields were measured with quinine sulfate (Φ_f= 0.546% in ethanol) as the reference.

Determination of Φ_f

$$(\Phi_f)_C = (\Phi_f)_r * (Grad_C) * \eta^2_C / (Grad_r) * \eta^2_r$$

c stands for Compound under measurement
r for reference

4. Lifetime calculation:

Table S2: Fluorescence lifetime of $\mathbf{C_5}$ (λ_{max} = 516 nm)

Solvent	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	$<\tau>^a$
Benzene	1.62 (0.16)	3.52 (0.84)	3.21
Methanol	1.17 (0.14)	3.35 (0.86)	3.04
THF	1.28 (0.81)	2.05 (0.19)	1.28

Table S3: Fluorescence lifetime of $\mathbf{C_5}$ (λ_{max} = 406 nm)

Solvent	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	$<\tau>^a$
Methanol	1.03 (0.86)	7.59 (0.14)	1.94
THF	0.81 (0.87)	1.78 (0.13)	0.94

Table S4: Fluorescence lifetime of $\mathbf{C_4}$ (λ_{max} = 516 nm)

Solvent	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	$<\tau>^a$
Benzene	1.5 (0.04)	3.07 (0.96)	3.21
Methanol	0.87 (0.46)	3.12 (0.54)	2.08
THF	1.00 (1.20)	0	1.20

Table S5: Fluorescence lifetime of $\mathbf{C_4}$ (λ_{max} = 406 nm)

Solvent	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	$<\tau>^a$
Methanol	1.31 (0.72)	7.24 (0.28)	2.97
THF	0.75 (0.73)	2.75 (0.27)	1.29

τ = lifetime, a = component, $<\tau>^a$ = average lifetime
Error in experimental data of ±5%

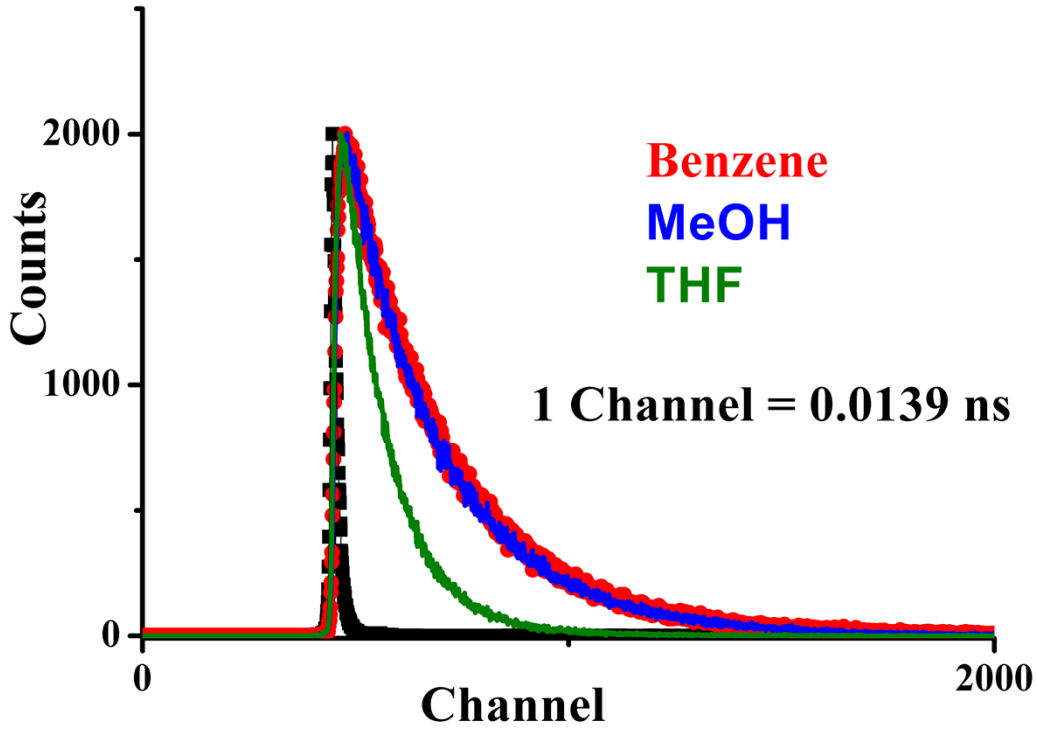


Figure S12: Time-resolved decay curves of C_5 (emission λ_{max} = 516 nm).

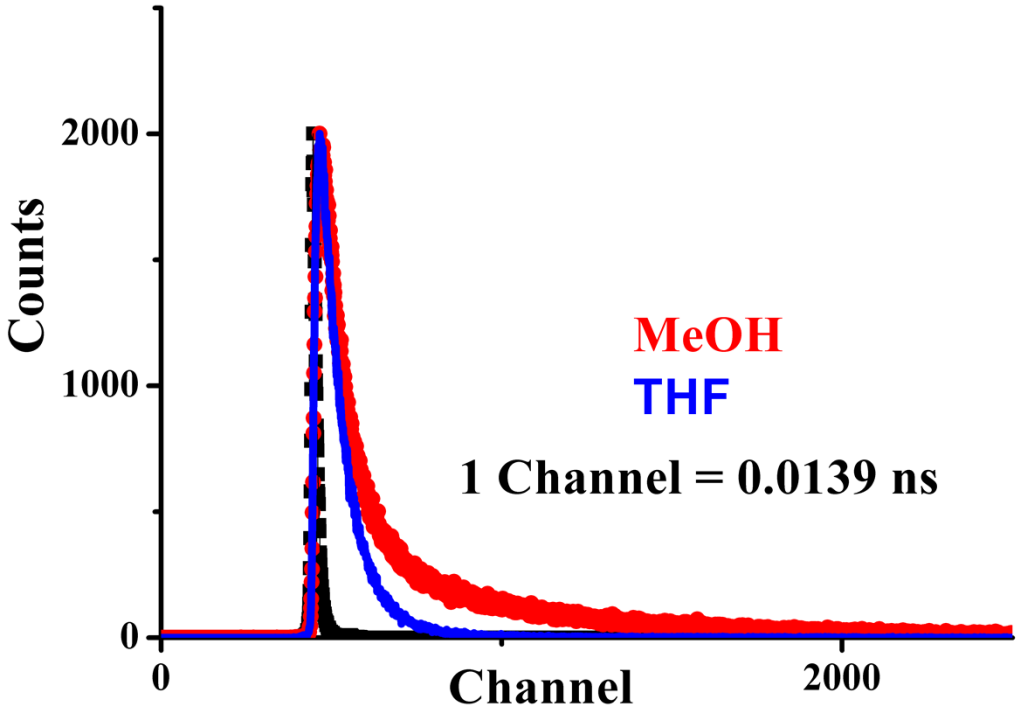


Figure S13: Time-resolved decay curves of C_5 (emission λ_{max} = 406 nm).

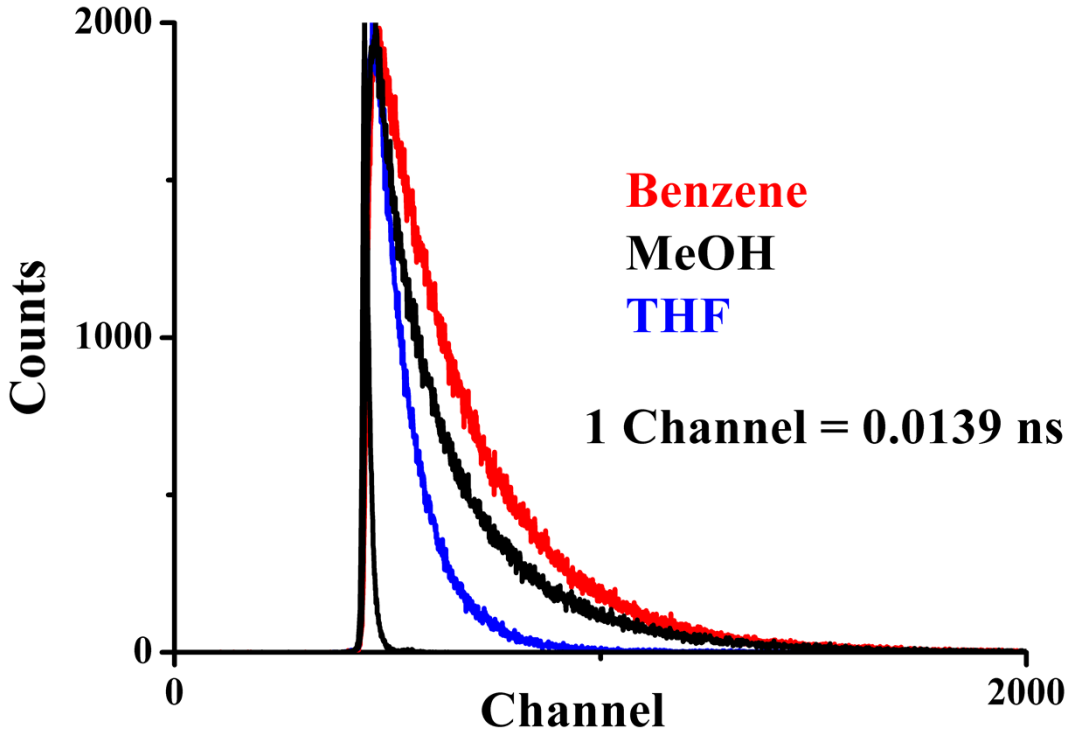


Figure S14: Time-resolved decay curves of **C_4** (emission λ_{max} = 516 nm).

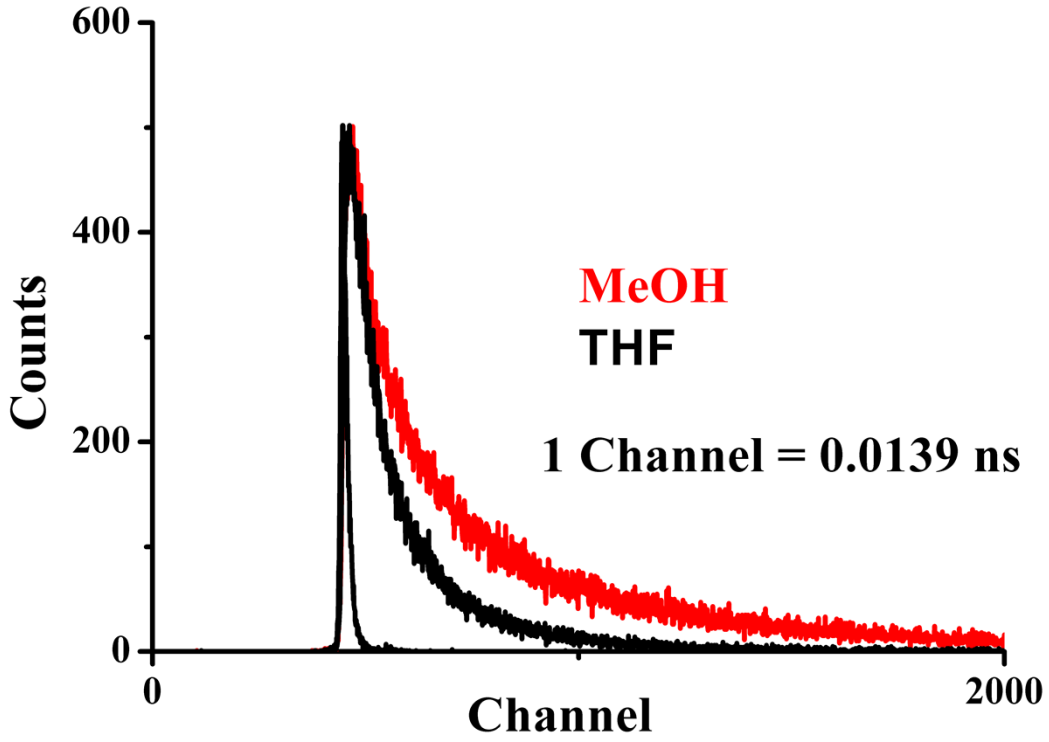


Figure S15: Time-resolved decay curves of **C_4** (emission λ_{max} = 406 nm).

5. Photochemical Quantum yield calculation:

Table S6: Rate constant and Photochemical Quantum Yield calculation of $\mathbf{C_5}$

Compound name	Rate constant k_p [a]	Photochemical Quantum yield ϕ_p [b]
C_5	**1.15 X 10 $^{-3}$. min $^{-1}$**	**0.006**

Determination of ϕ_p

$$(\phi_p)_c = (\phi_p)_{act} * (k_p)_c * (F_{act}) / (k_p)_{act} * (F_c)$$

[a] Rate constant under photolytic condition; [b] Photochemical quantum yield (error limit ± 5%); $_C$ stands for compund ($\mathbf{C_5}$); 'act' stands for actinometer; F is the fraction of light absorbed; Potassium ferrioxalate was used as an actinometer; k_p is the photolysis rate constant and ϕ_p is the photocemical quantum yield

References:

1. L. Xie, Y. Chen, W. Wu, H. Guo, J. Zhao and X. Yu, *Dyes and Pigments*, 2012, **92**, 1361-1369.