

Supporting Information

Cellular deoxyribonucleic-acid probe of two-photon-excited fluorescent quinolinium-substituted carbazole

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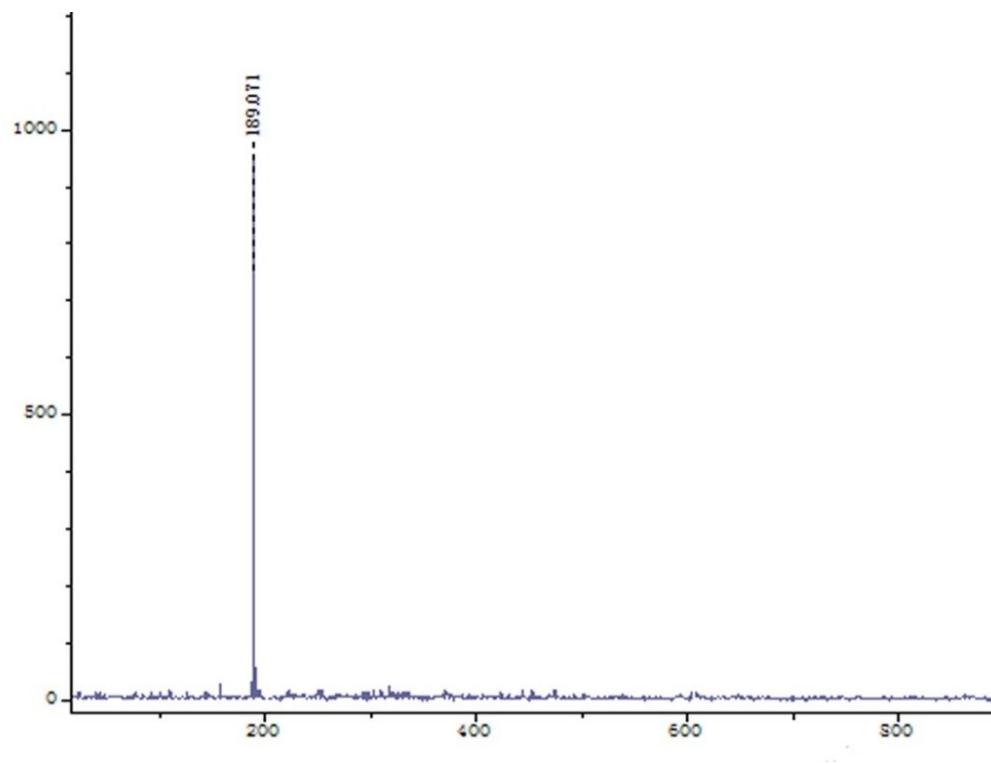


Fig. S1 MALDI-TOF-MS spectra of QL-1

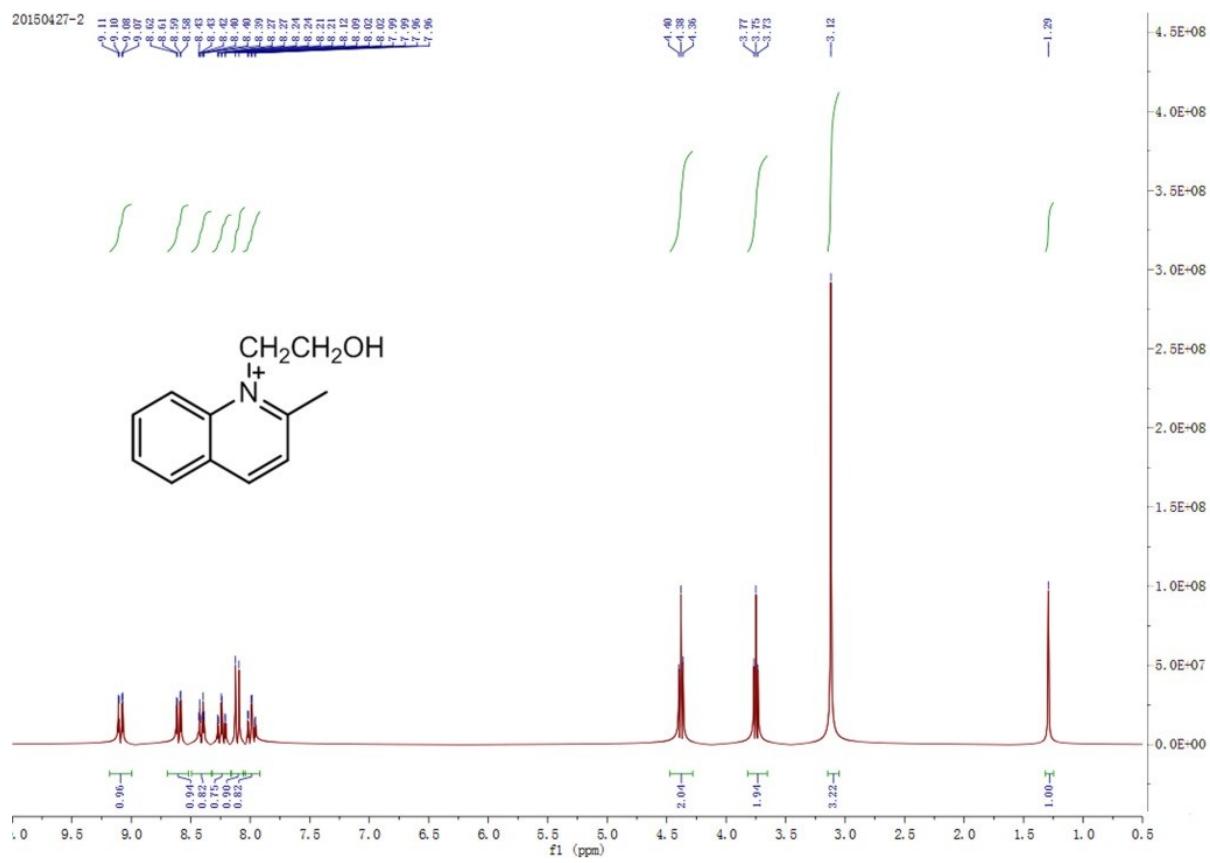


Fig. S2 ^1H -NMR of QL-1 (400 MHz, DMSO-d₆)

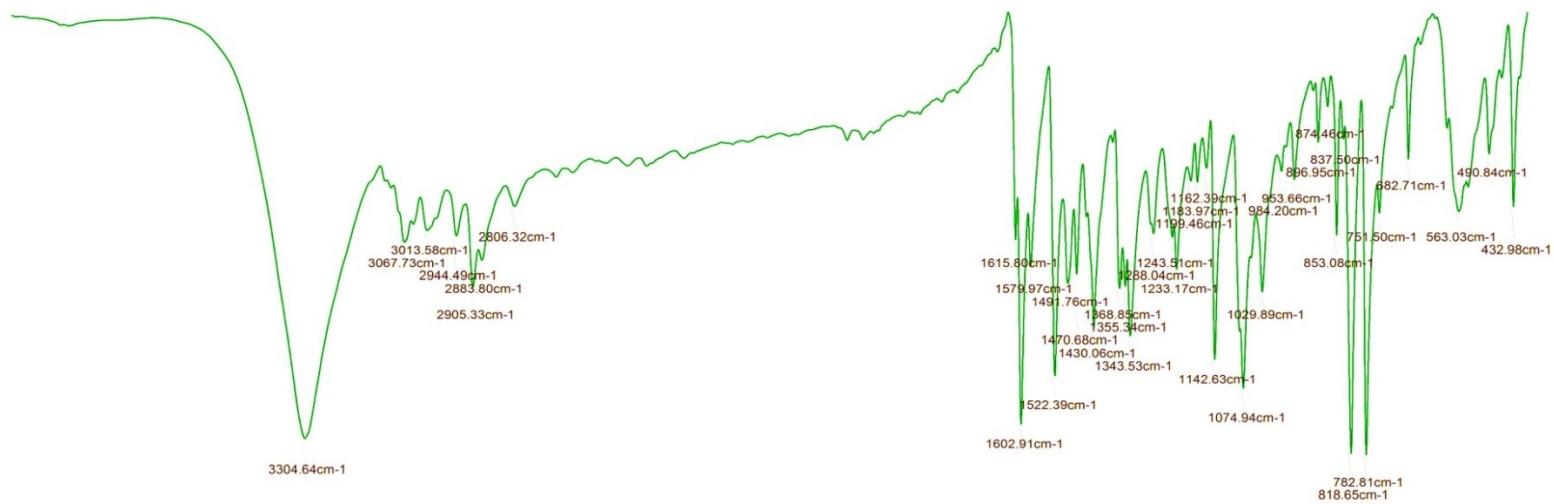


Fig. S3 FT-IR spectra of QL-1 (KBr)

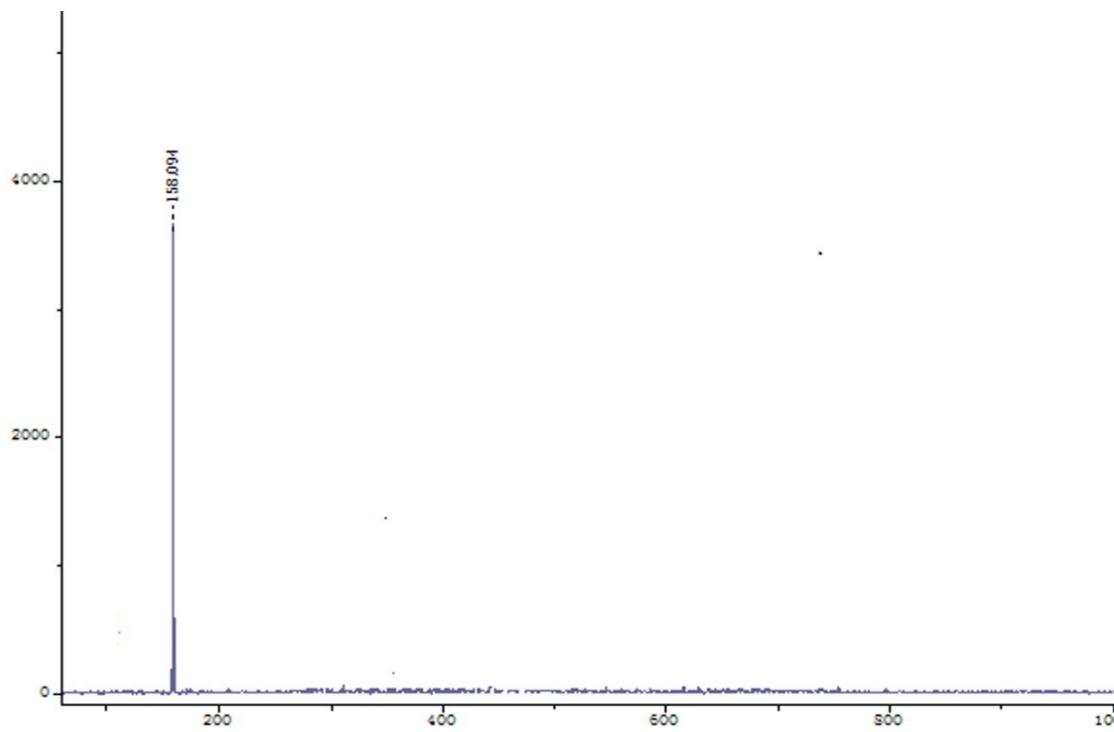


Fig. S4 MALDI-TOF-MS spectra of QL-2

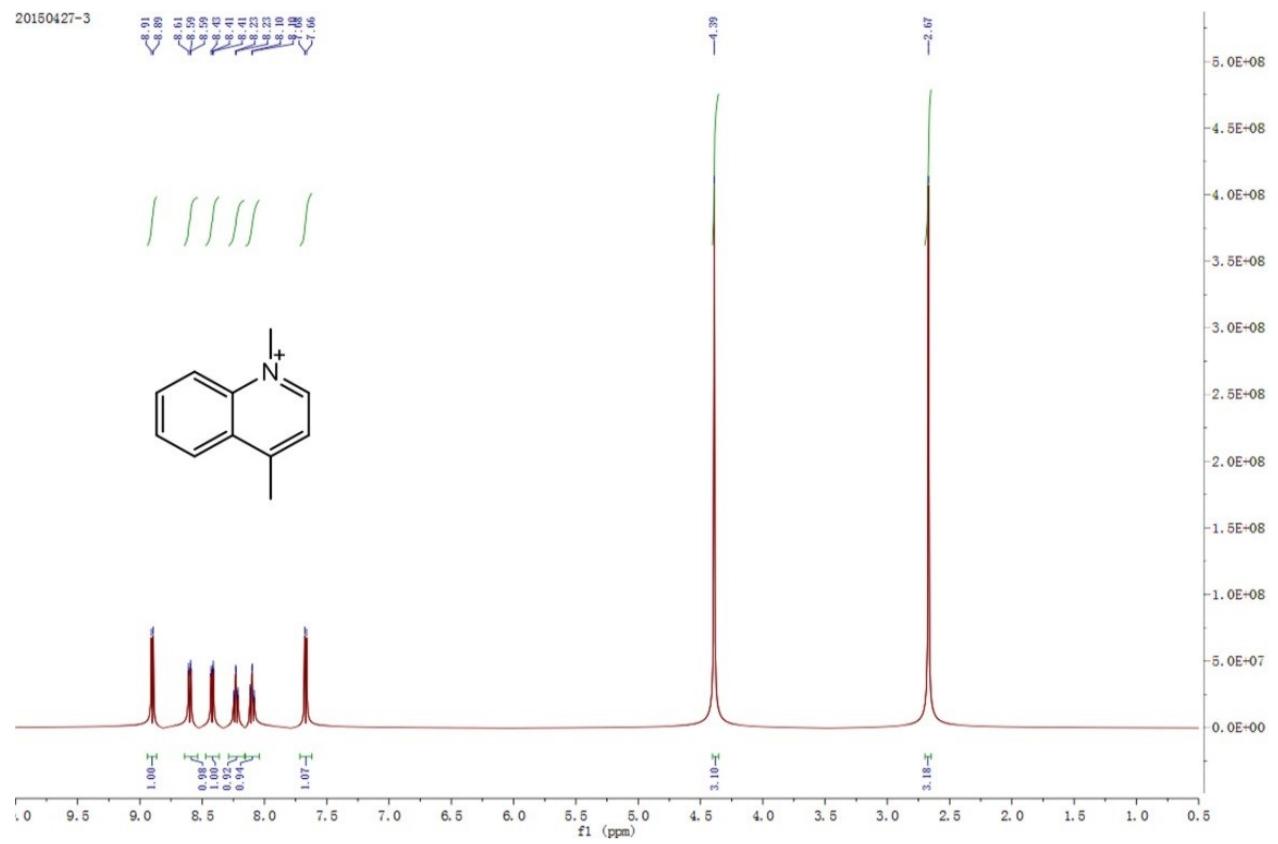


Fig. S5 ^1H -NMR of QL-2 (400 MHz, DMSO-d_6)

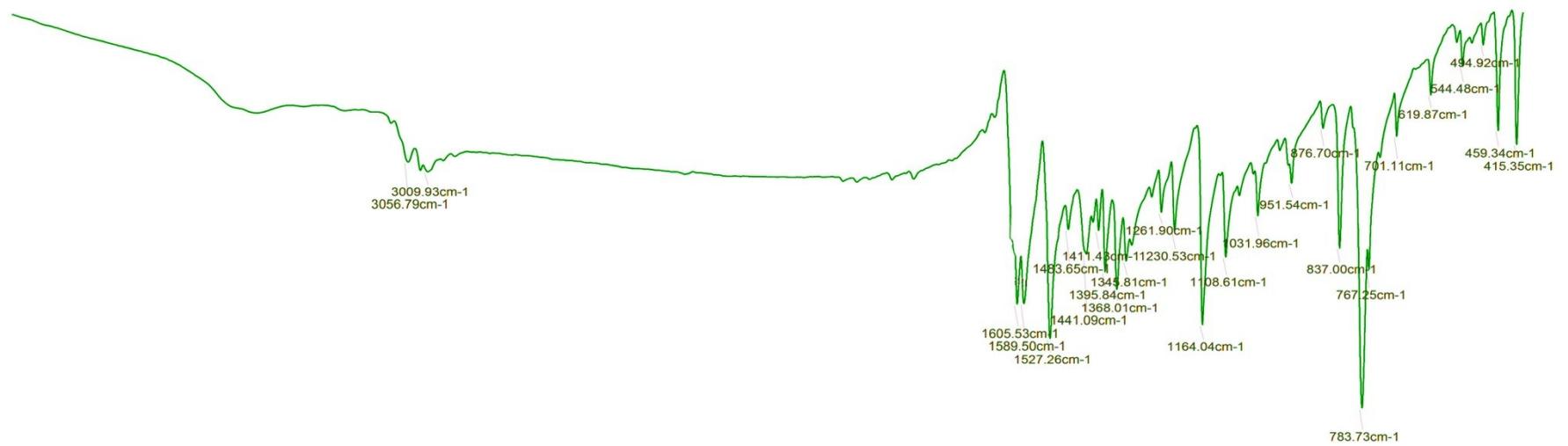


Fig. S6 FT-IR spectra of QL-2 (KBr)

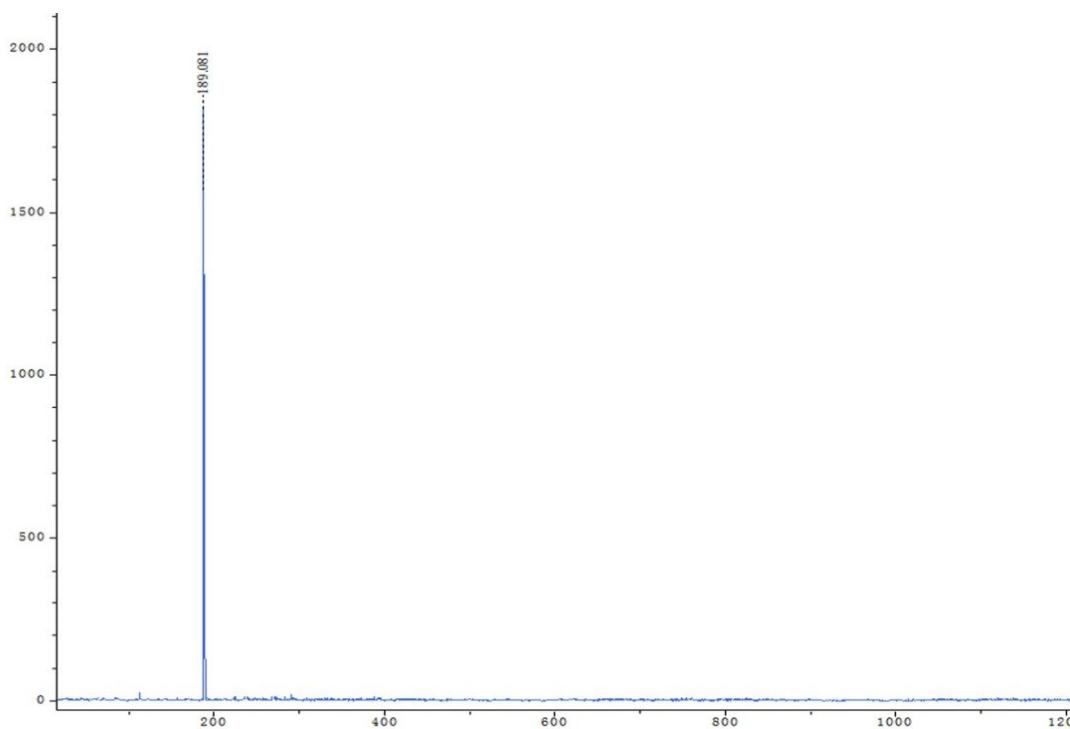


Fig. S7 MALDI-TOF-MS spectra of QL-3

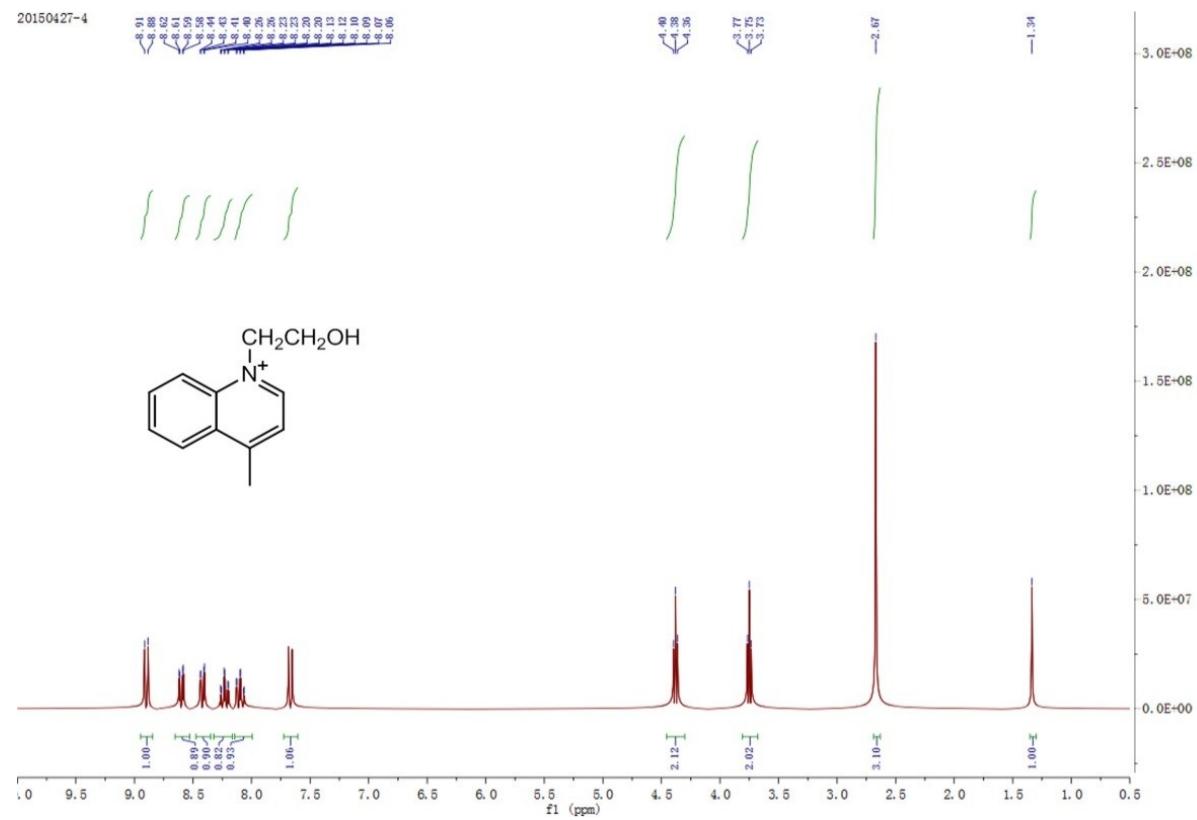


Fig. S8 ^1H -NMR of QL-3 (400 MHz, DMSO-d6)

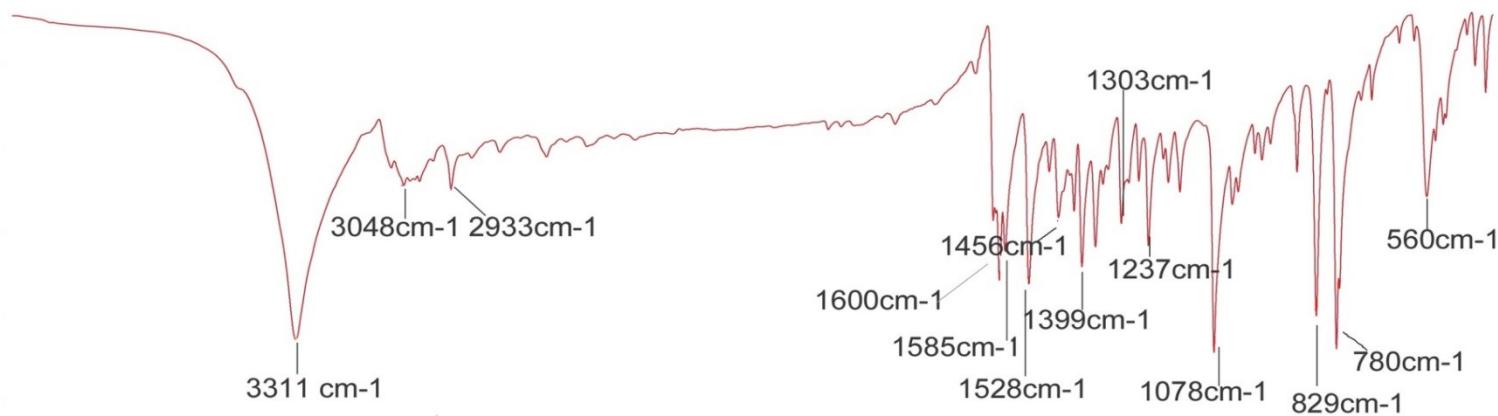


Fig. S9 FT-IR spectra of QL-3 (KBr)

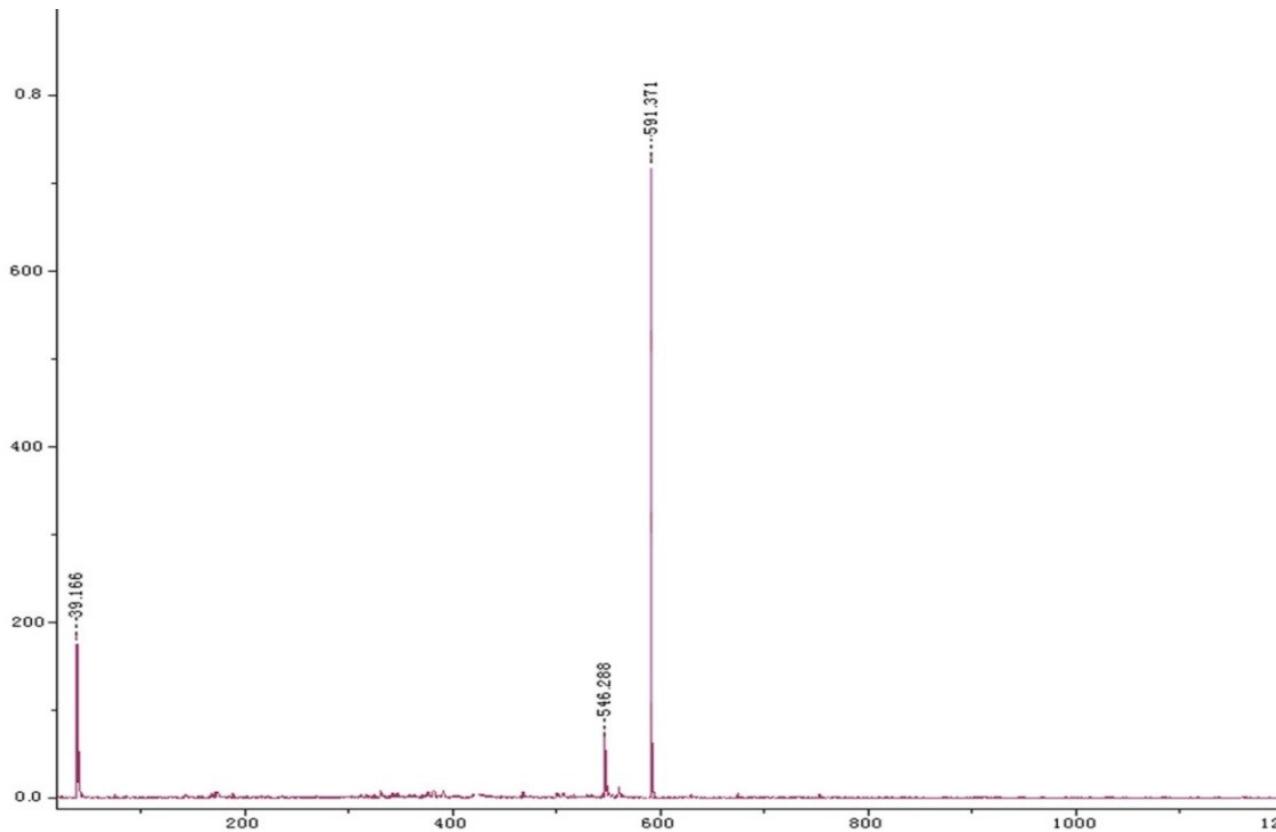


Fig. S10 MALDI-TOF-MS spectra of DH2

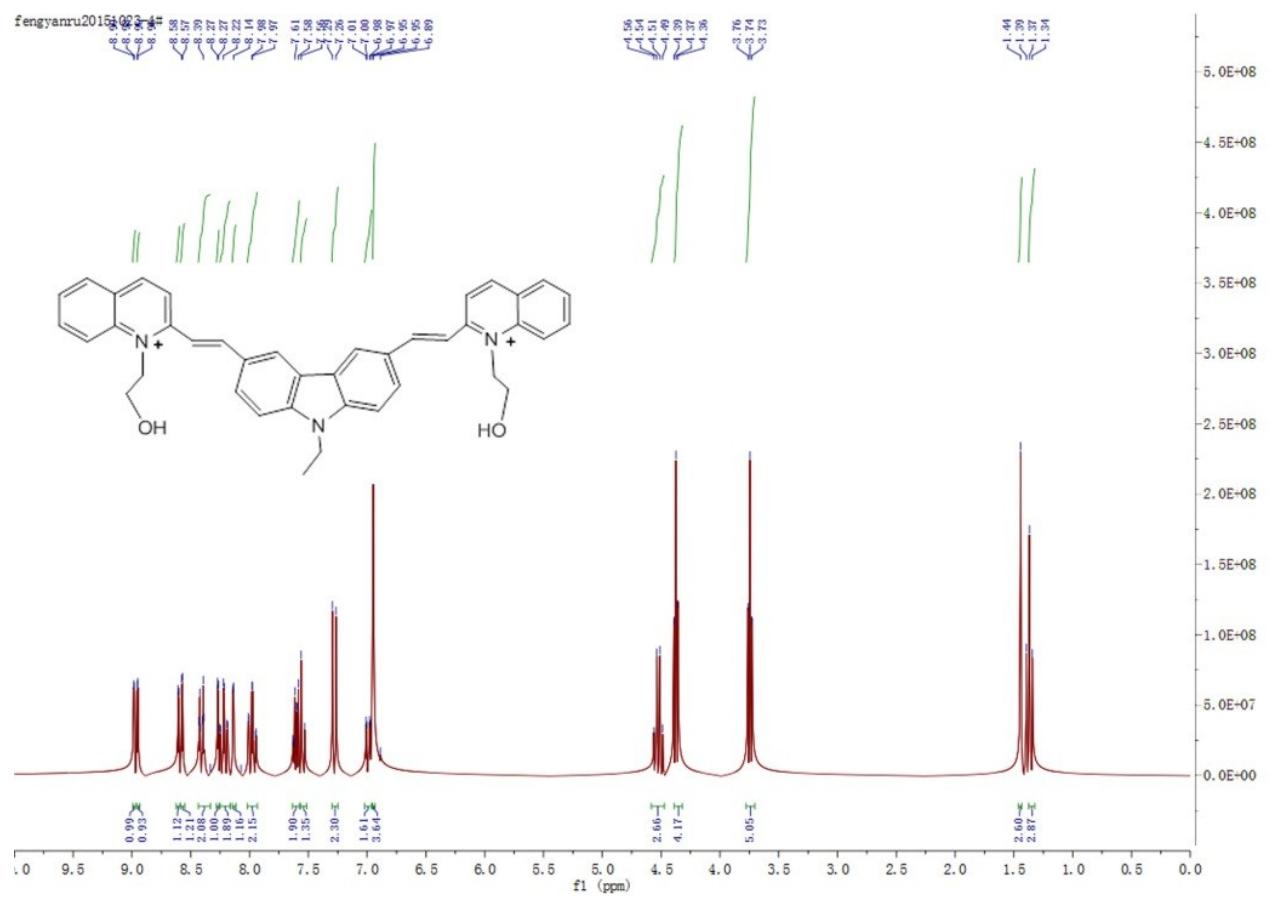


Fig. S11 $^1\text{H-NMR}$ of DH2 (400 MHz, DMSO-d₆)

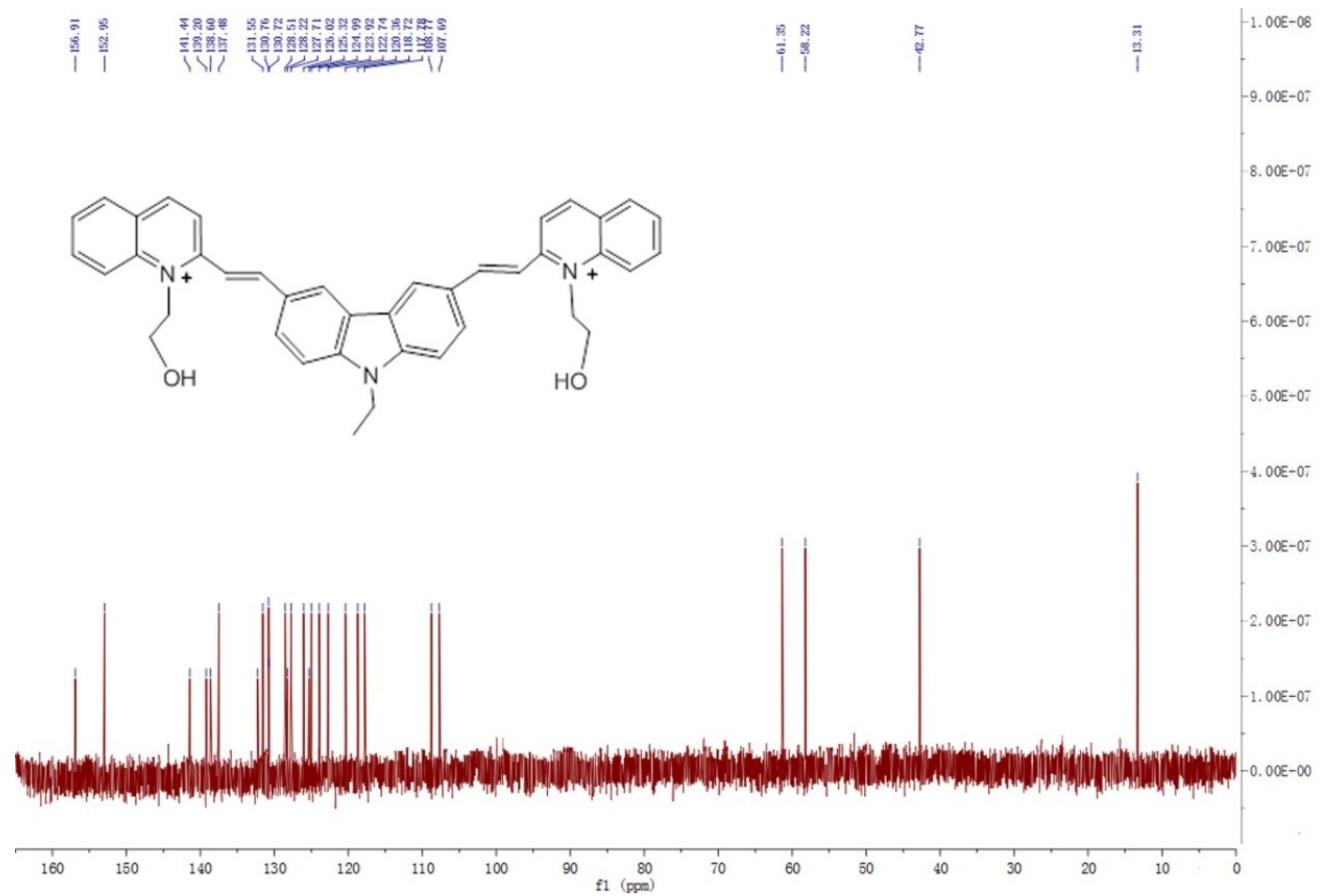


Fig. S12 ^{13}C -NMR of DH2 (125 MHz, DMSO-d6)

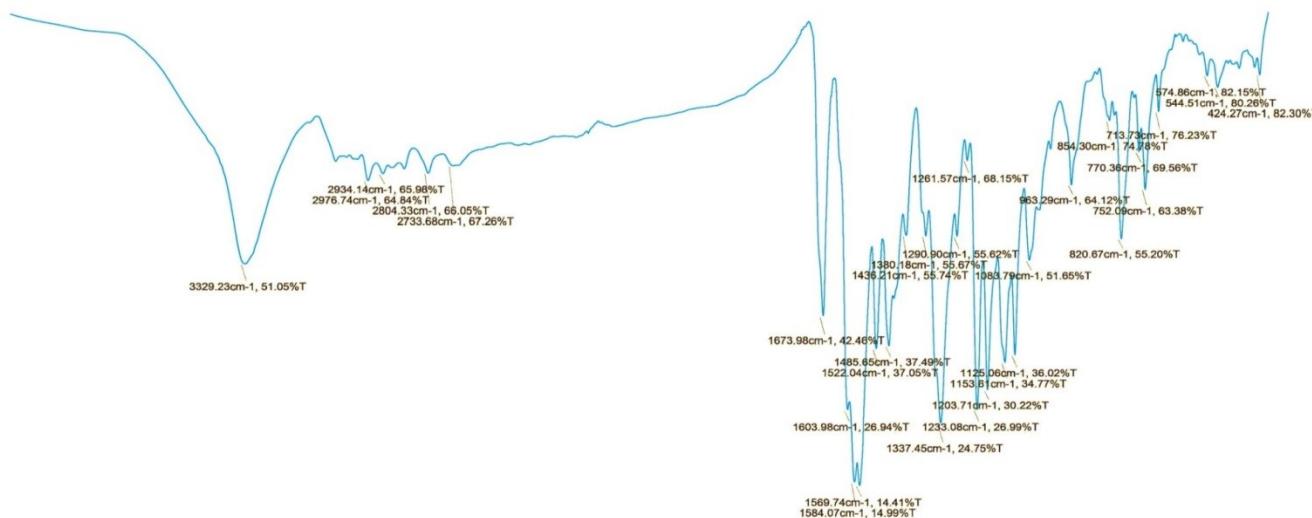


Fig. S13 FT-IR spectra of DH2 (KBr)

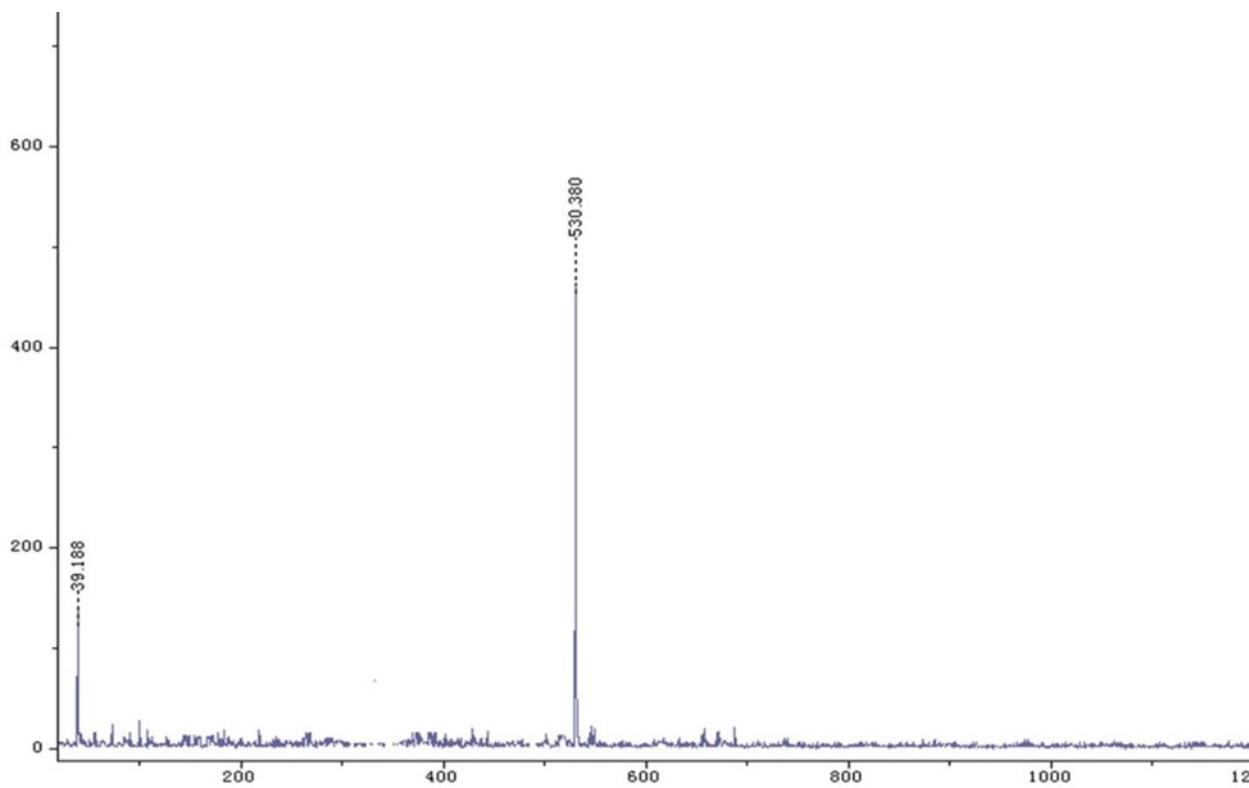


Fig. S14 MALDI-TOF-MS spectra of DM4

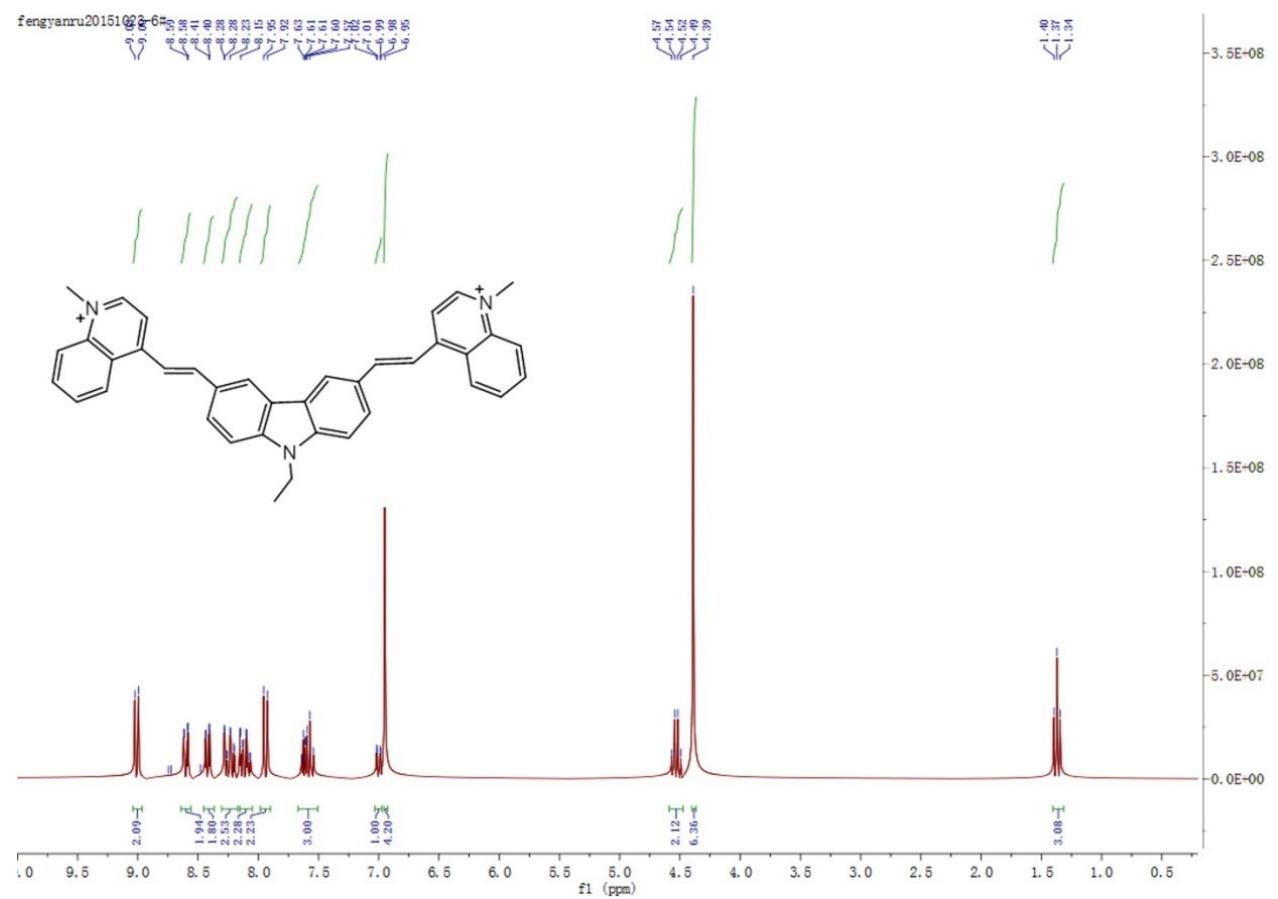


Fig. S15 ^1H -NMR of DM4 (400 MHz, DMSO-d6)

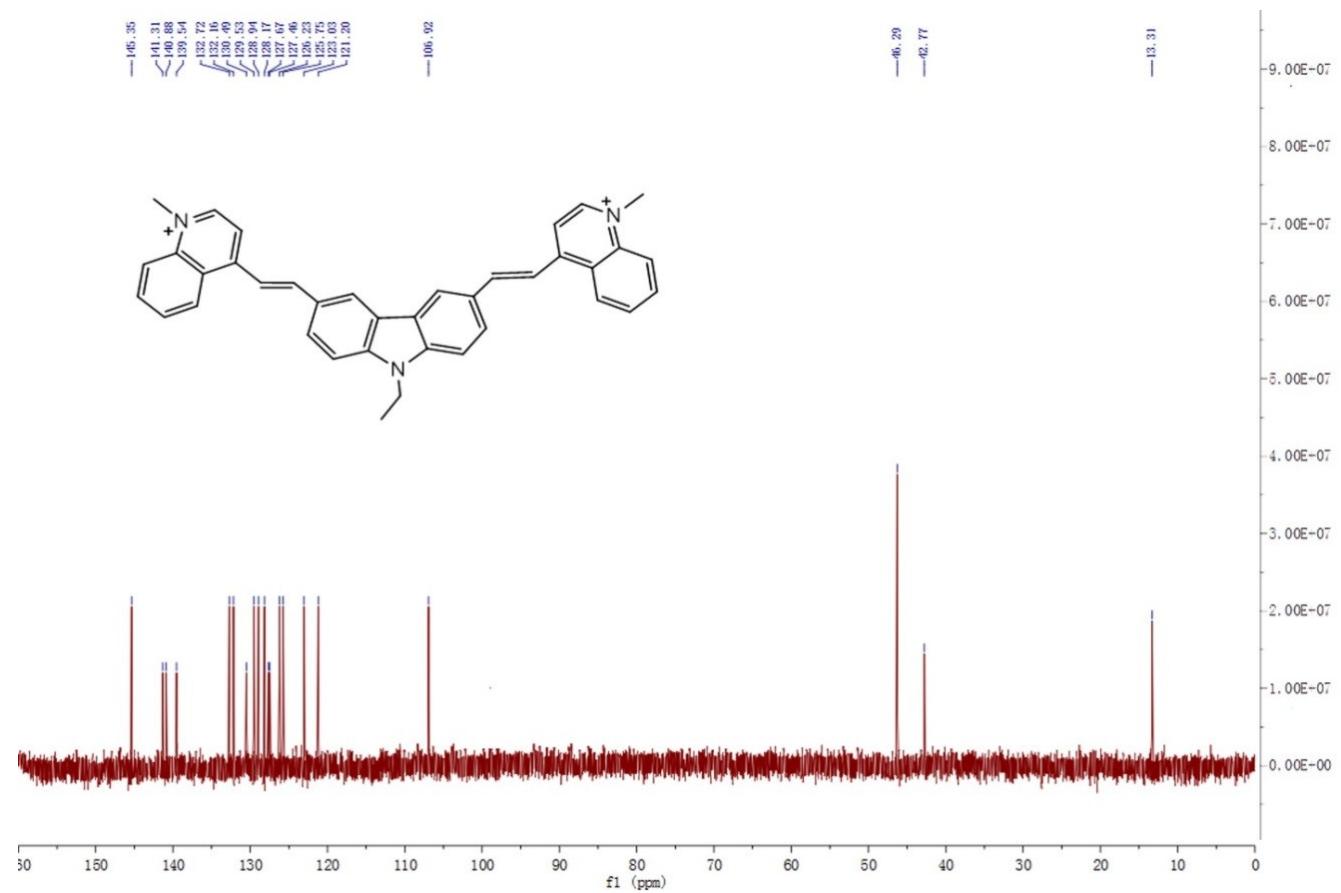


Fig. S16 ^{13}C -NMR of DM4 (125 MHz, DMSO-d₆)

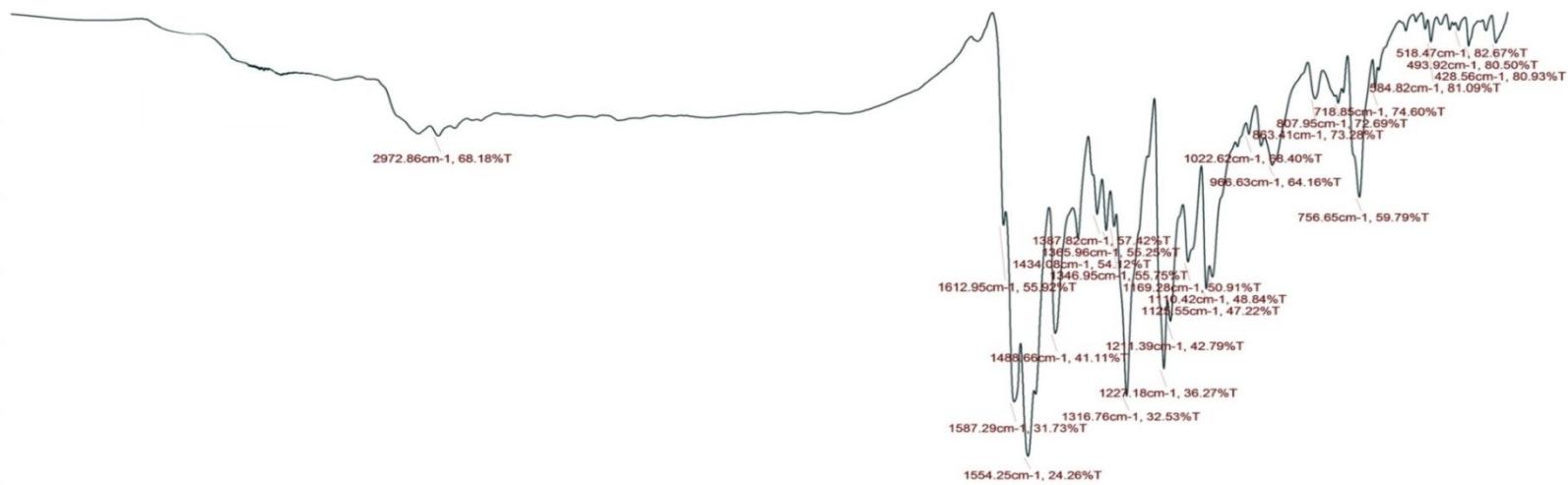


Fig. S17 FT-IR spectra of DM4 (KBr)

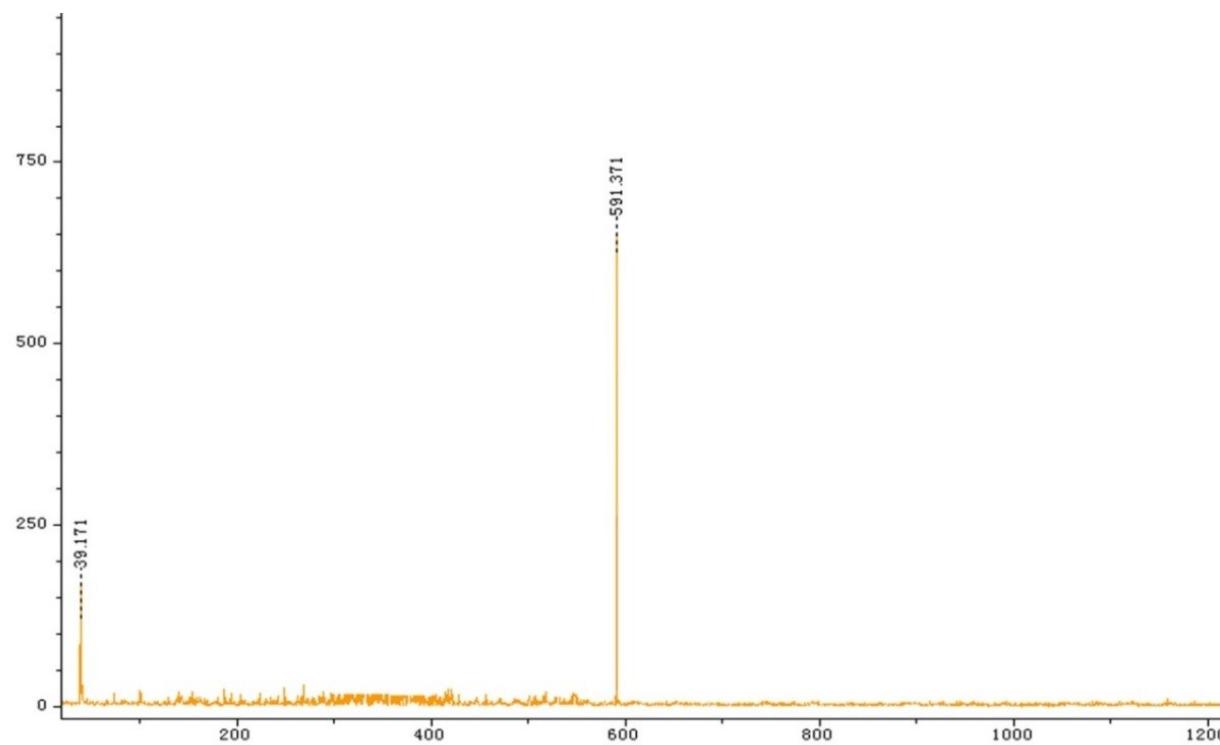


Fig. S18 MALDI-TOF-MS spectra of DH4

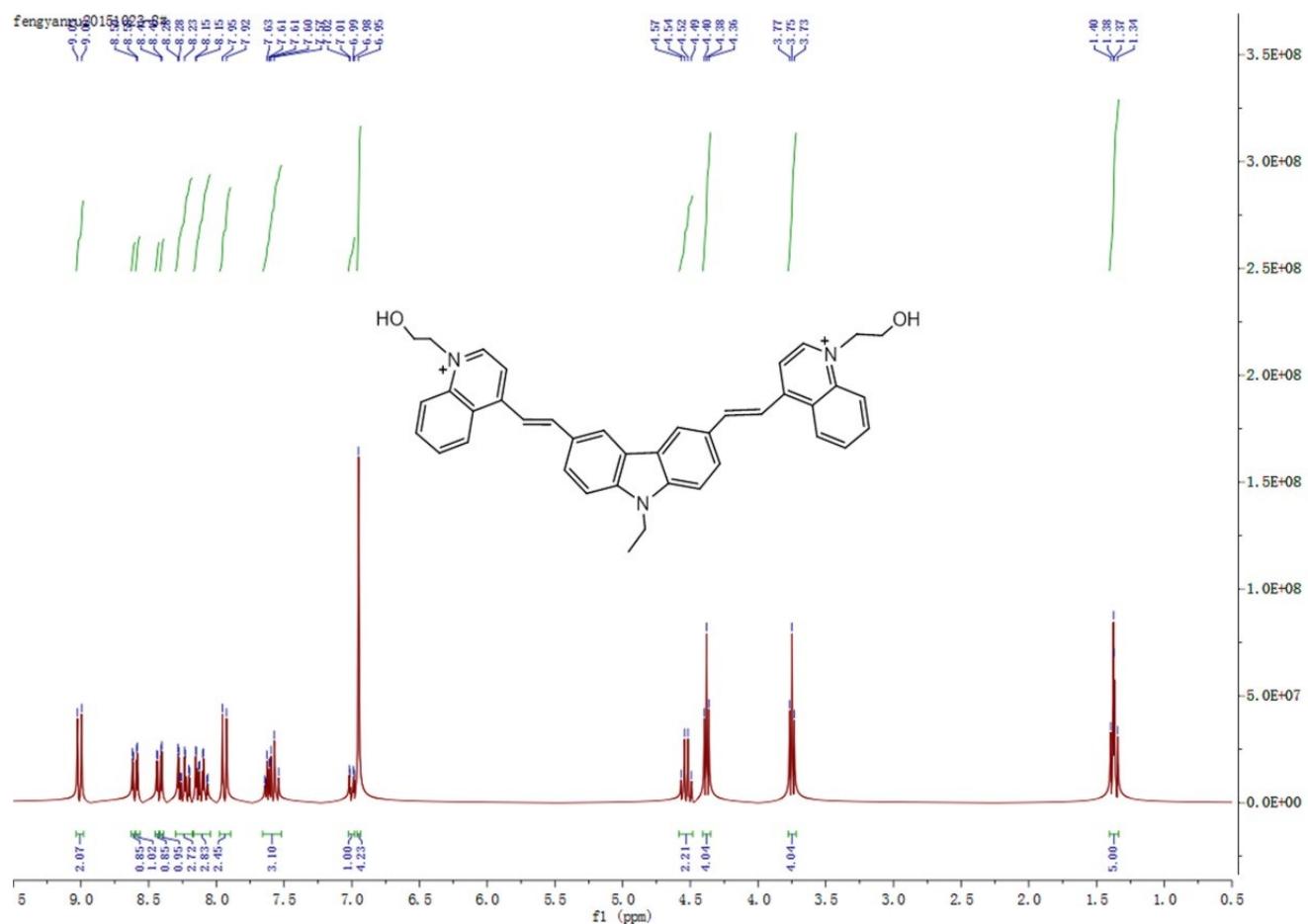


Fig. S19 ^1H -NMR of DH4 (400 MHz, DMSO- d_6)

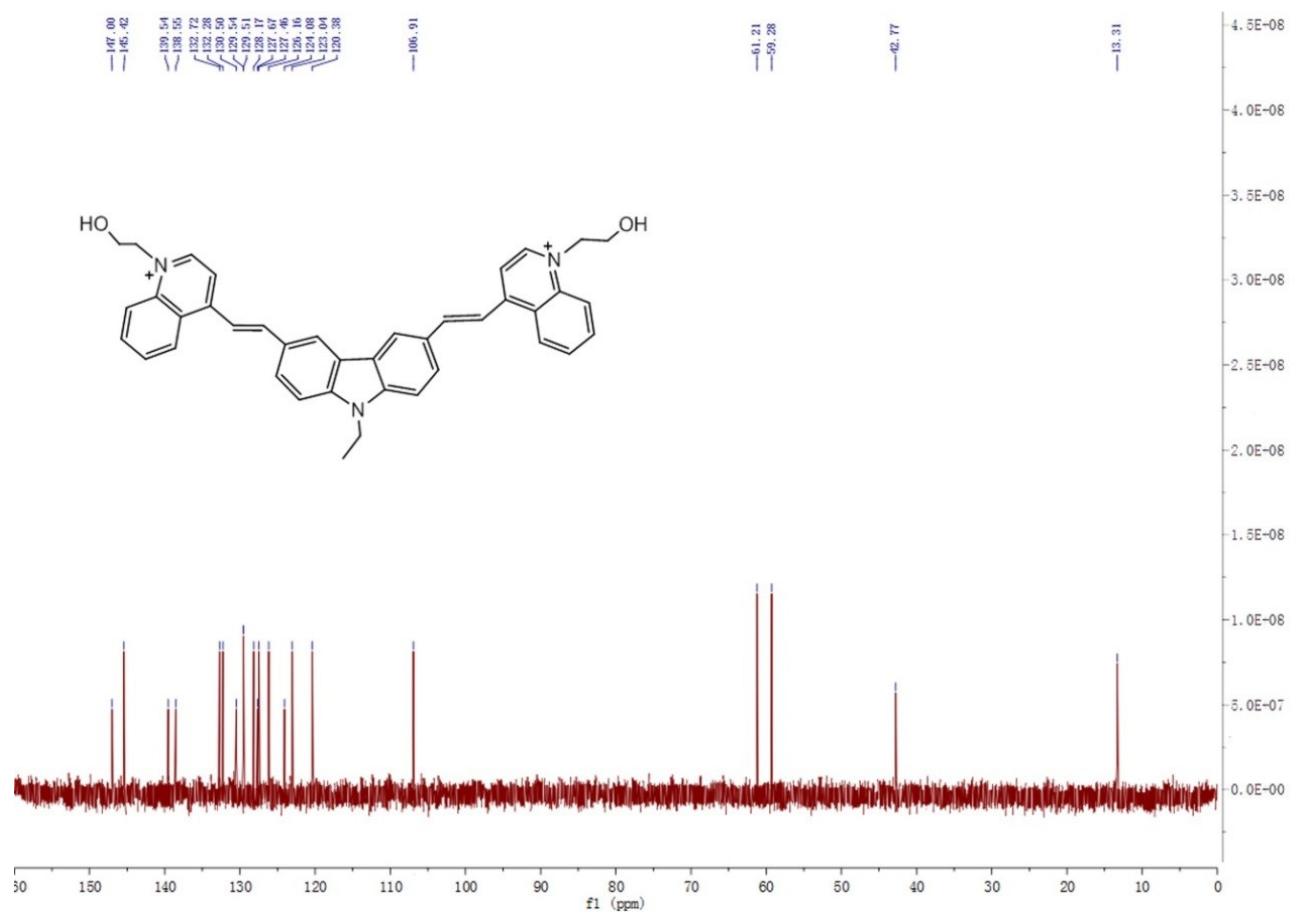


Fig. S20 ^{13}C -NMR of DH4 (125 MHz, DMSO-d6)

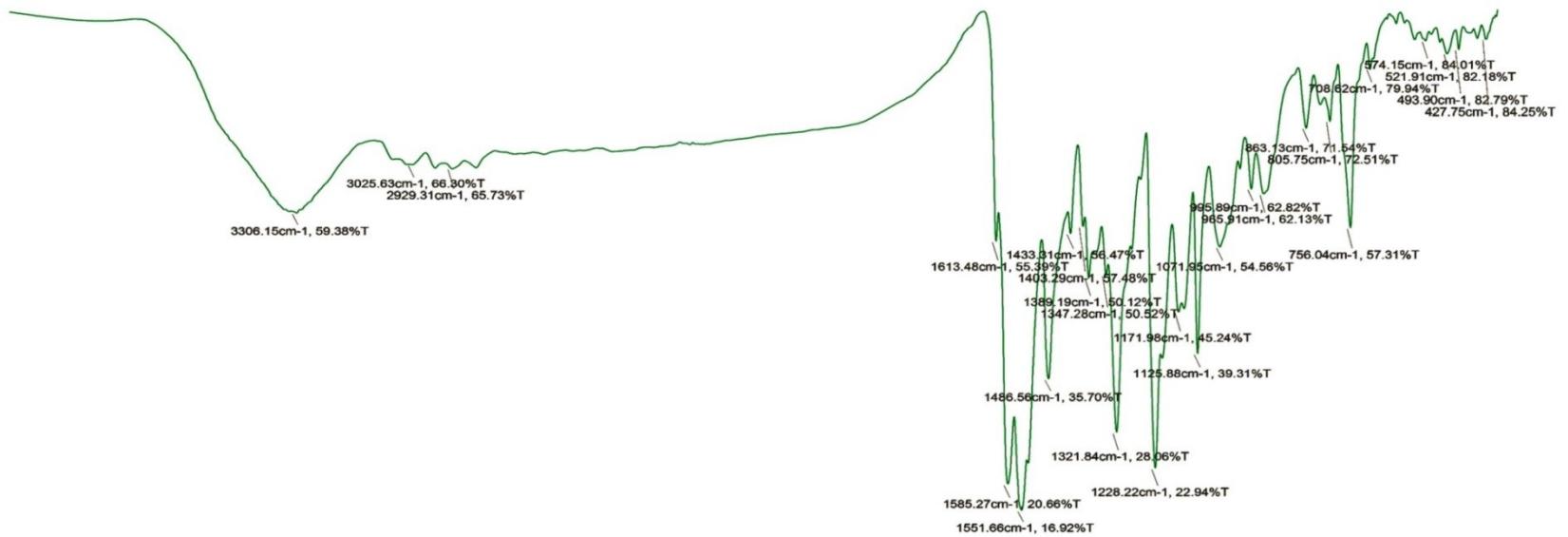


Fig. S21 FT-IR spectra of DH4 (KBr)

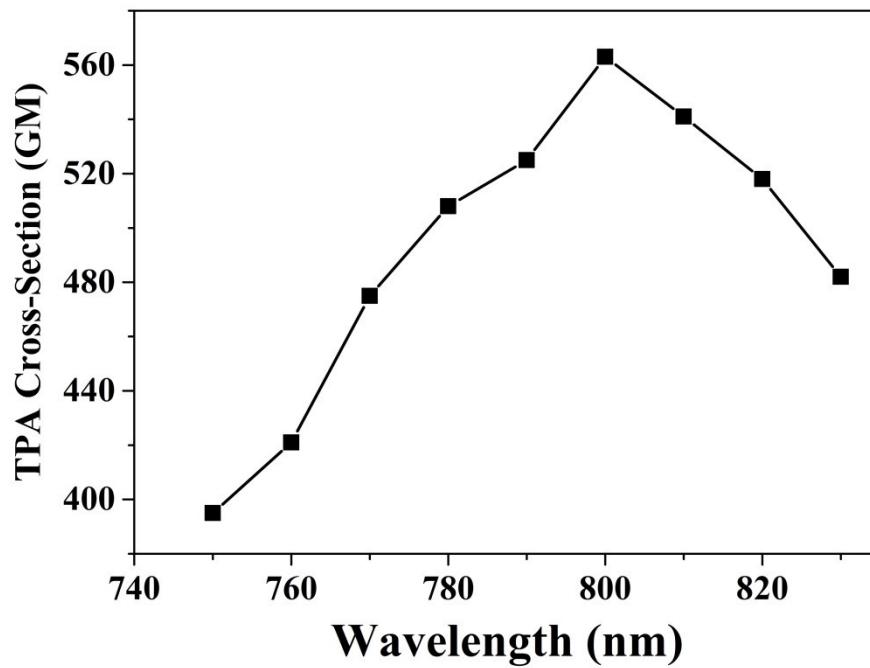


Fig. S22 TPA cross-sections of DM4 under different incident wavelength.

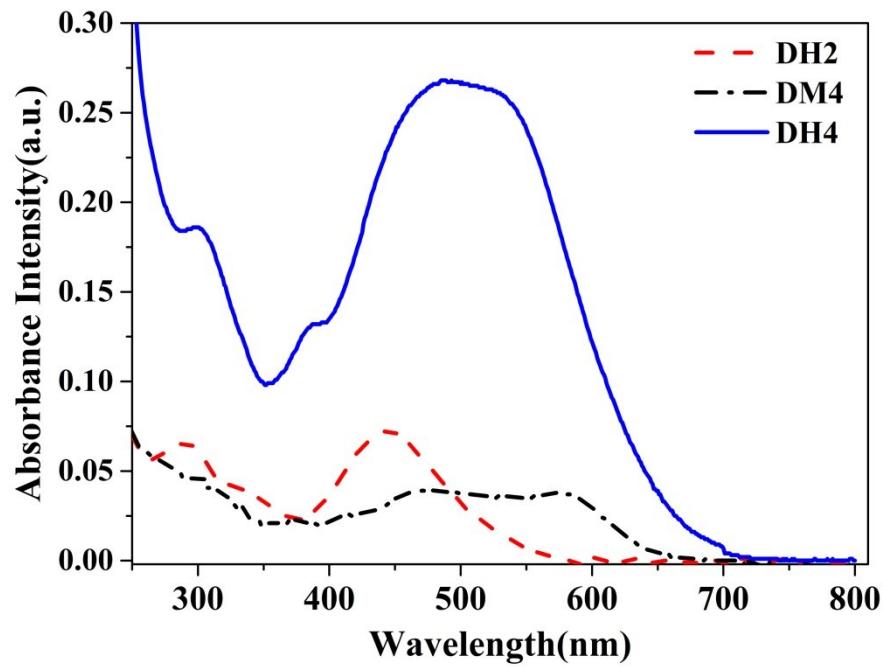


Fig. S23 Normalized absorption spectra of DH2, DM4, and DH4 in Tris-HCl-NaCl.

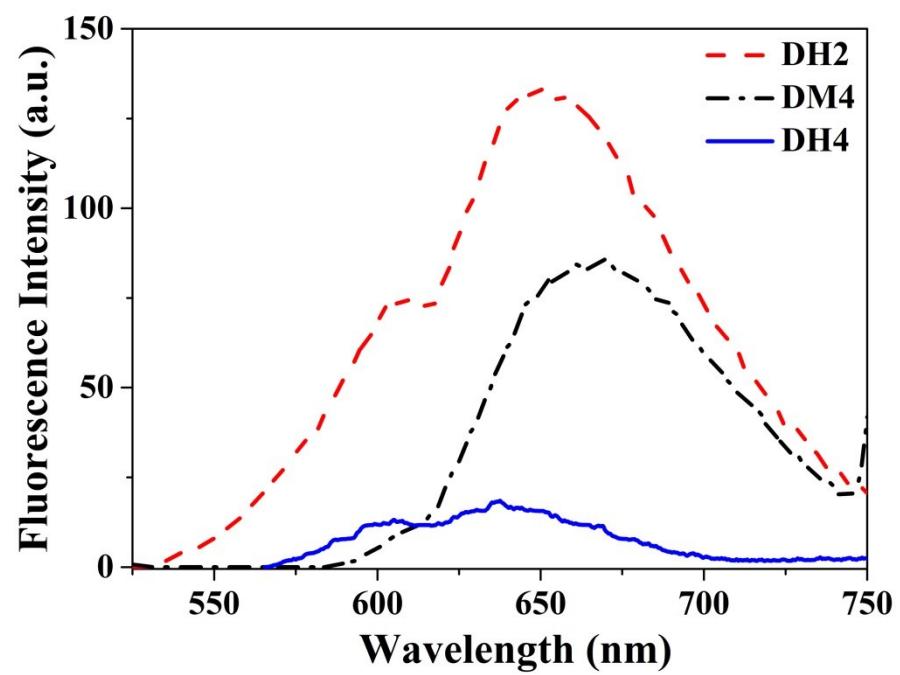


Fig. S24 Normalized fluorescence spectra of DH2, DM4, and DH4 in Tris-HCl-NaCl.

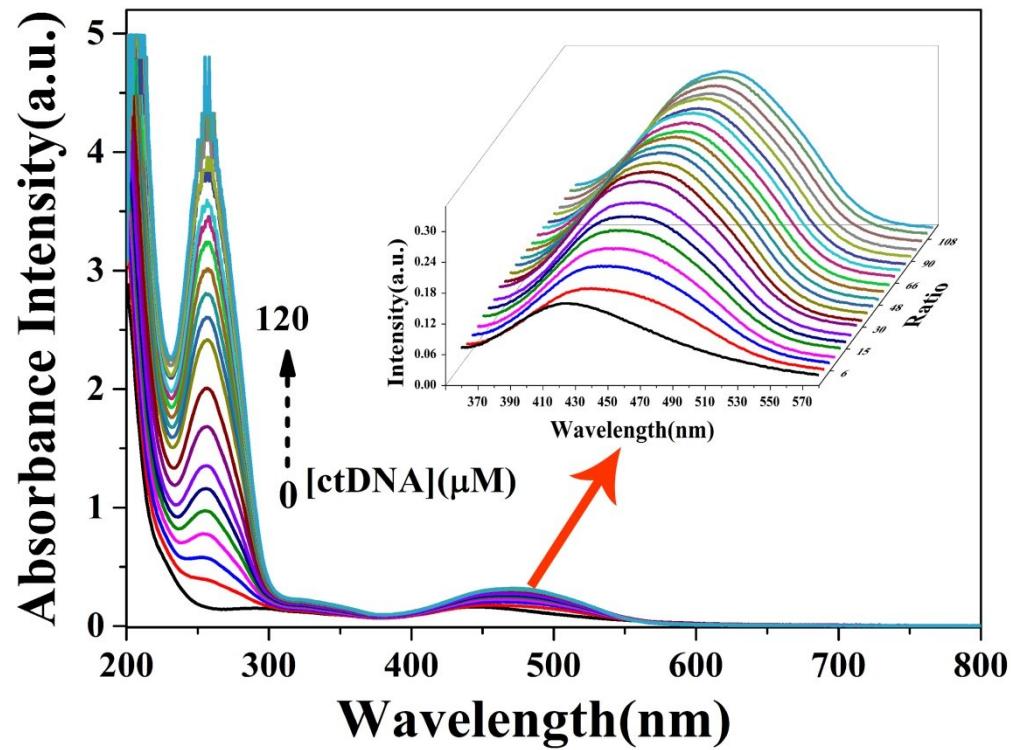


Fig. S25 Normalized absorption spectra of DH2 according [ctDNA] increased

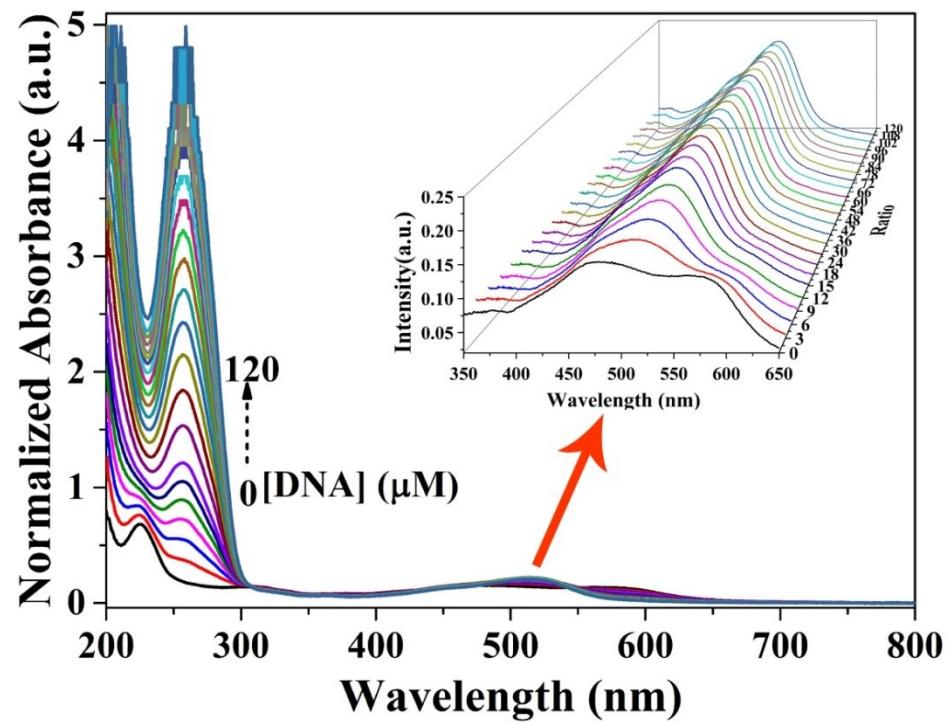


Fig. S26 Normalized absorption spectra of DM4 according [ctDNA] increased

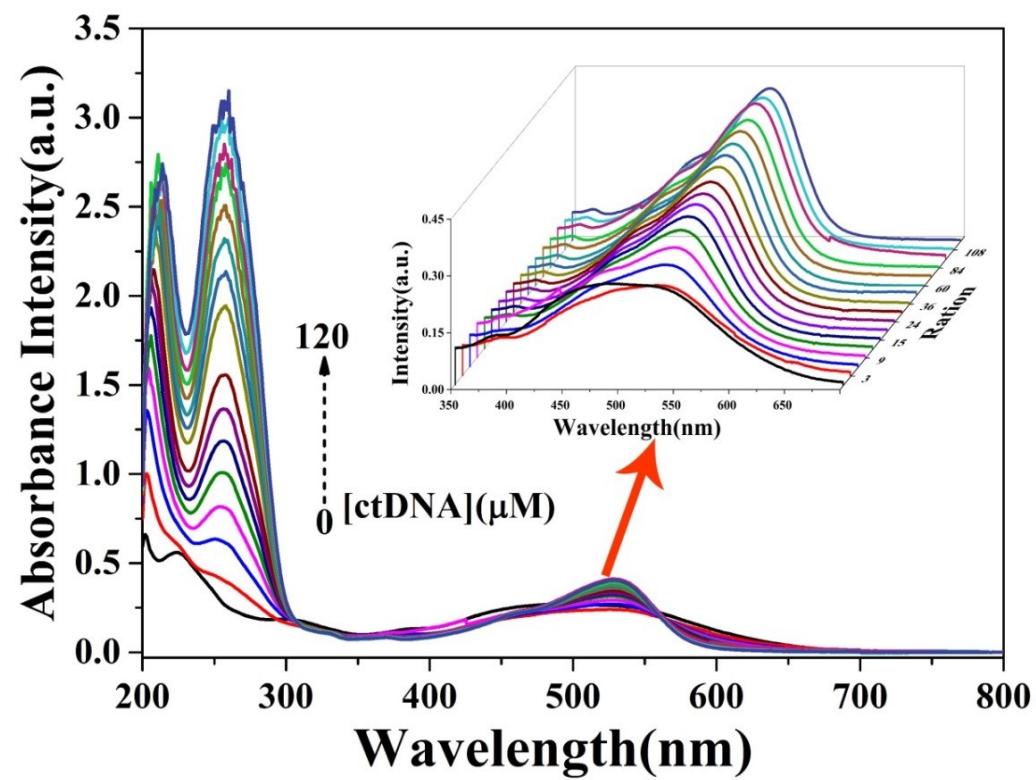


Fig. S27 Normalized absorption spectra of DH4 according [ctDNA] increased

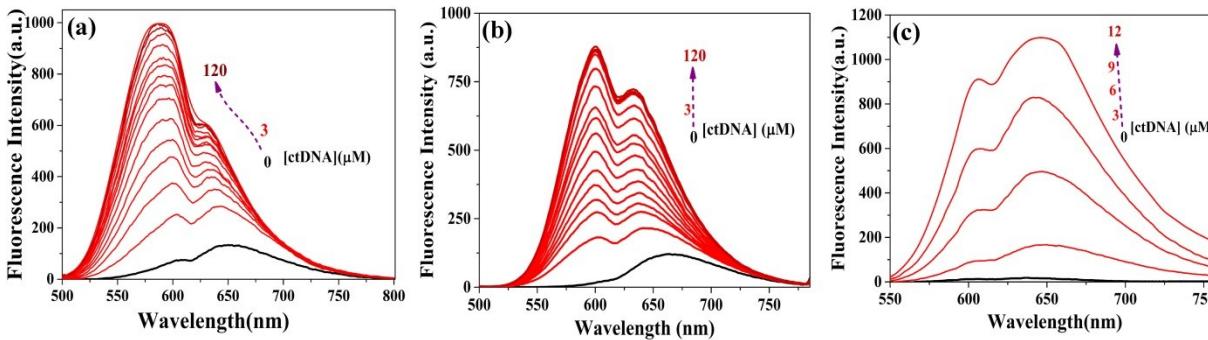


Fig. S28 One-photon excited titration fluorescence spectra of DH2 (a), DM4 (b) and DH4 (c) under 400 nm excited in Tris-HCl buffer solution (a, b: [ctDNA] = 0, 3, 6, ...24, 36, ...120 μM, c: 0, 3, 6, 9, 12).

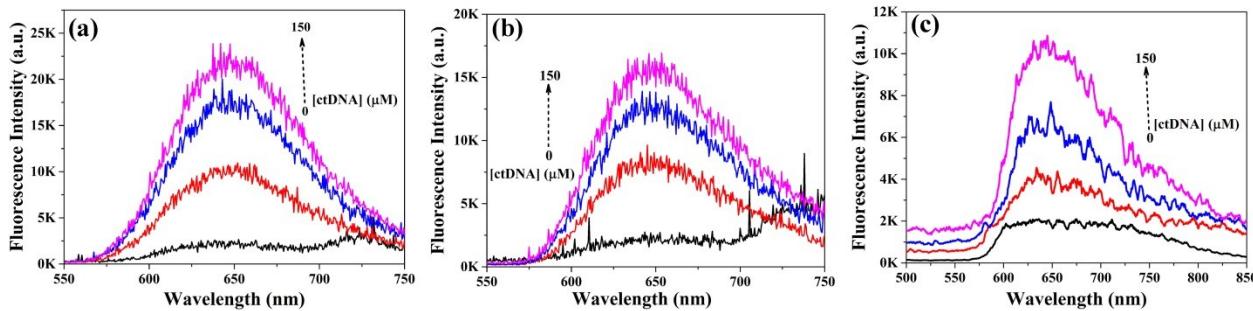


Fig. S29 Two-photon excited titration fluorescence spectra of DH2 (a), DM4 (b) and DH4 (c) under 800 nm excited in Tris-HCl buffer solution ([ctDNA] = 0, 50, 120, 150 μM).

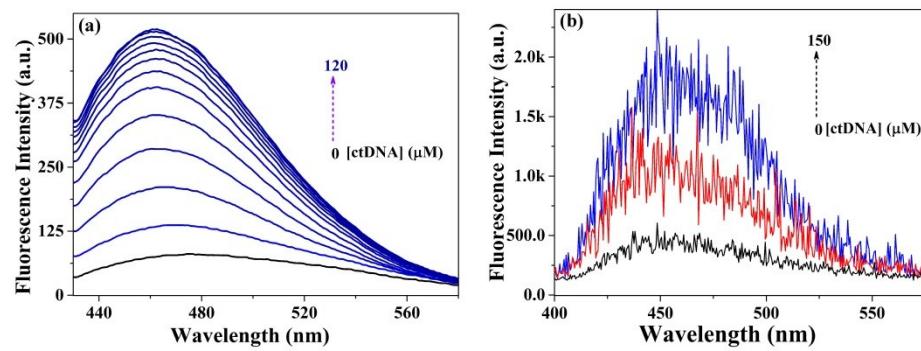


Fig. S30 One-photon (a) and two-photon (b) excited titration fluorescence spectra of DAPI in Tris-HCl buffer solution (a: $[ctDNA] = 0, 3, 6, \dots 24, 36, \dots 120 \mu\text{M}$, $\lambda_{\text{ex}} = 375\text{nm}$, b: $[ctDNA] = 0, 120, 150 \mu\text{M}$, $\lambda_{\text{ex}} = 740\text{nm}$).

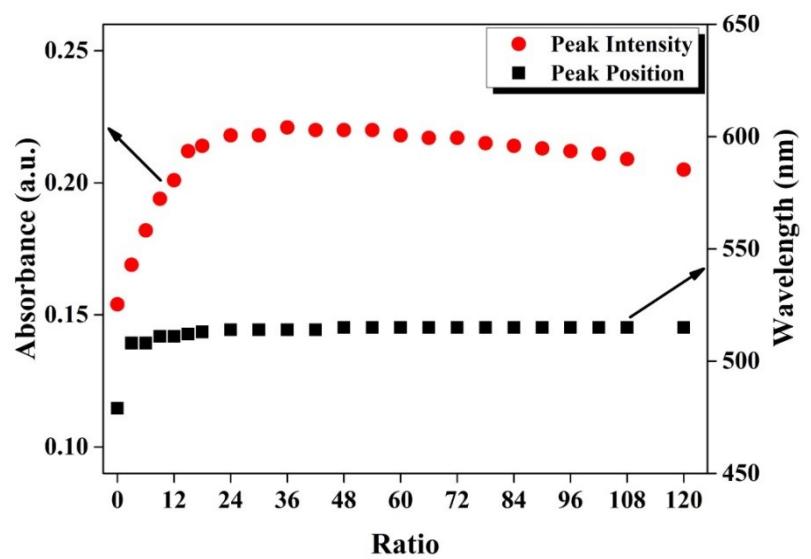


Fig. S31 Peak intensity and position changes of the normalized absorption spectra of DM4 according [ctDNA] increased

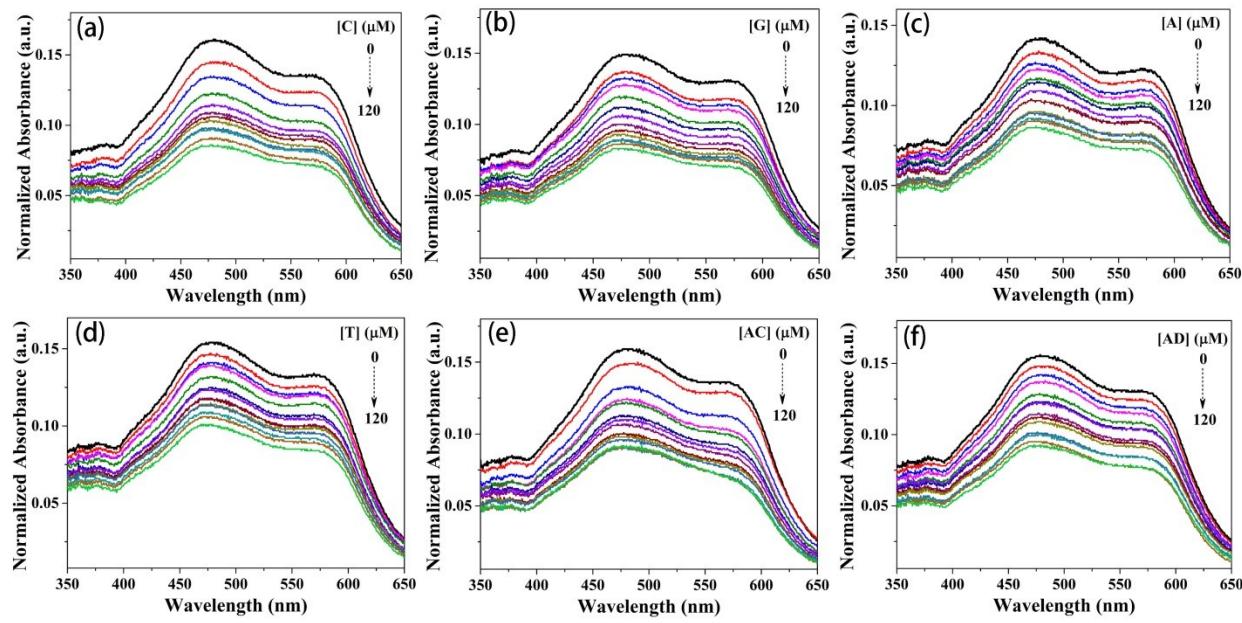


Fig. S32 Electronic absorption spectra of DM4 with base and nucleotide titration in Tris-HCl-NaCl buffer solution ($[S] = 0, 3, 6, \dots 24, 36, \dots 120 \mu\text{M}$), S=
(Fig. a): cytosine (C), (Fig. b): guanine (G), (Fig. c): adenine (A), (Fig.d): thymine (T), (Fig. e): 5-Aza-2'-deoxycytidine(AD), (Fig.f): adenosine cyclic 3', 5'-phosphate(AC).

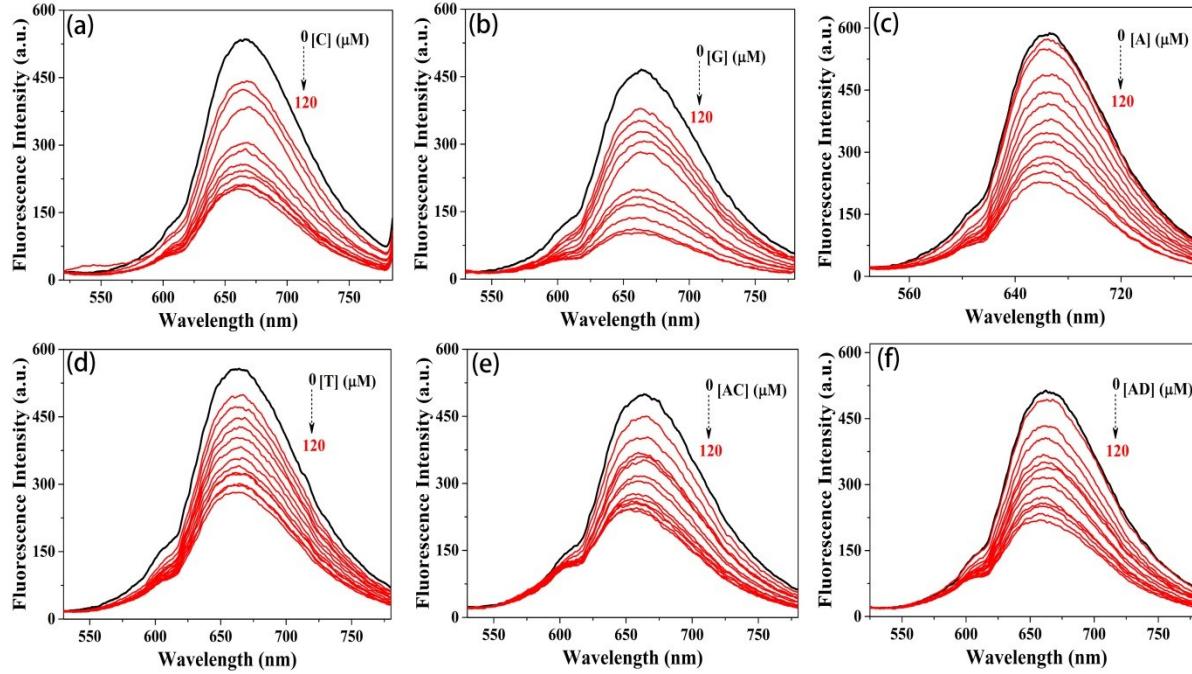


Fig. S33 Normalized fluorescence spectra of DM4 with base and nucleotide titration in Tris-HCl-NaCl buffer solution ($[S] = 0, 3, 6, \dots 24, 36, \dots 120\mu\text{M}$), S= (Fig. a): cytosine (C), (Fig. b): guanine (G), (Fig. c): adenine (A), (Fig. d): thymine (T), (Fig. e): 5-Aza-2'-deoxycytidine(AD), (Fig.f): adenosine cyclic 3', 5'-phosphate(AC).

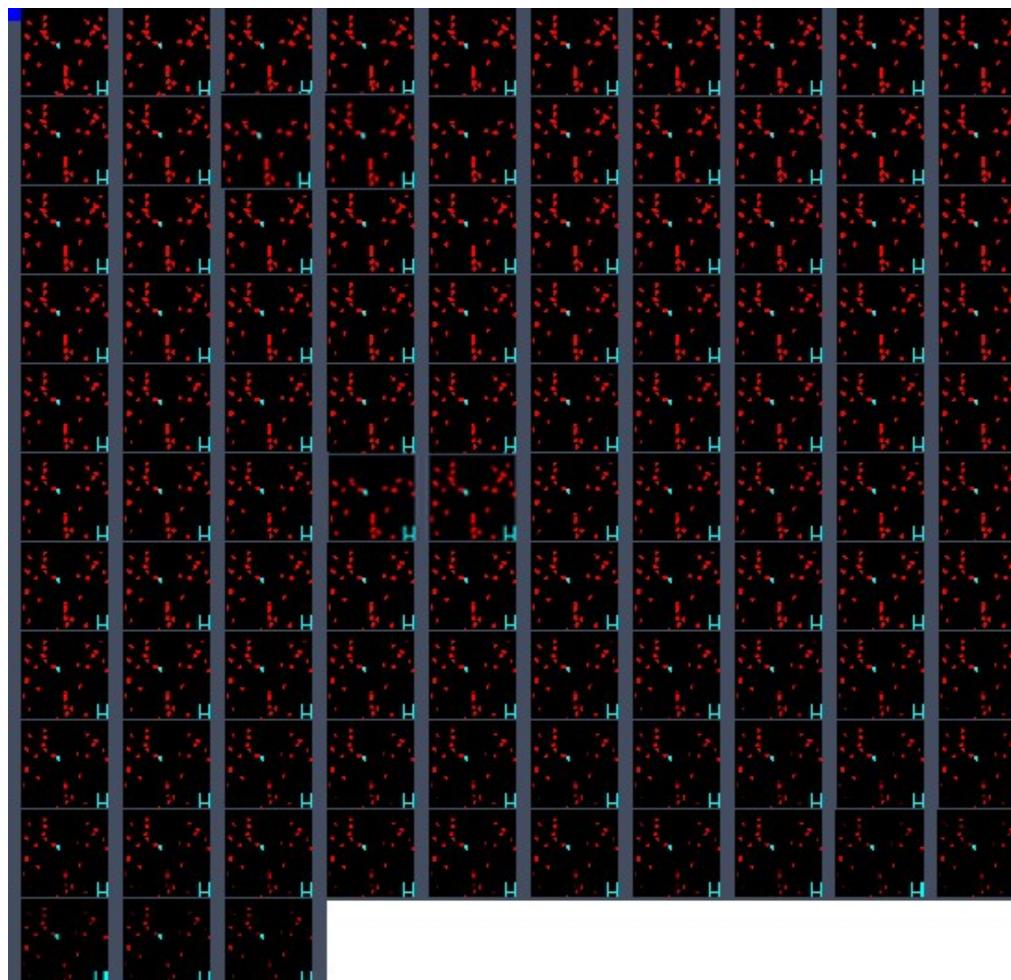
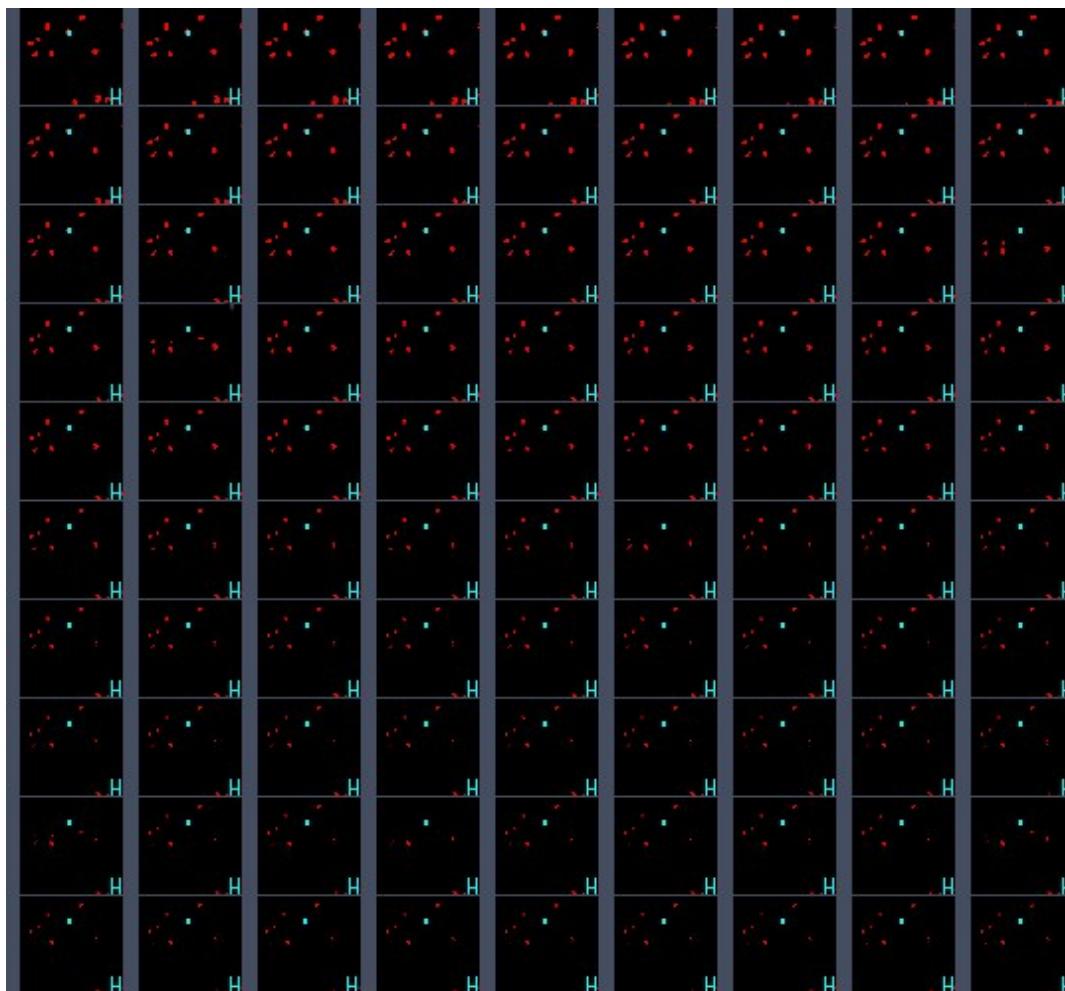


Fig. S34 Time-dependent two-photon confocal fluorescence images of 3T3 cell nucleus stained with DH2 (0.3 μ M) for 15 min, $\lambda_{\text{ex}} = 800\text{nm}$, $\lambda_{\text{em}} = 600\text{-}650\text{ nm}$.
Scale bar was 20 μm . Photograph interval 60 seconds.



**Fig. S35 Time-dependent two-photon confocal fluorescence images of 3T3 cell nucleus stained with DM4 (0.3 μ M) for 15 min, $\lambda_{\text{ex}} = 800\text{nm}$, $\lambda_{\text{em}} = 600\text{-}650\text{ nm}$.
Scale bar was 20 μm . Photograph interval 60 seconds.**

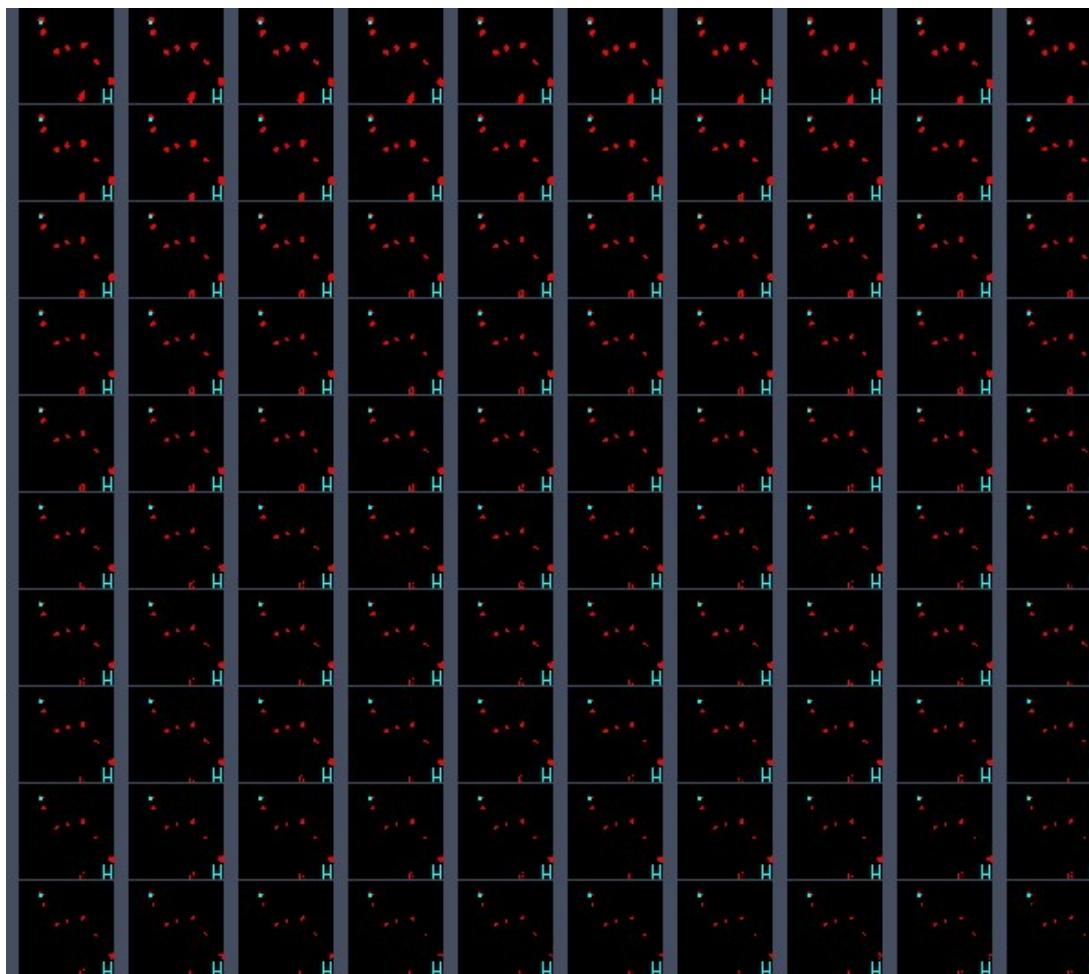


Fig. S36 Time-dependent two-photon confocal fluorescence images of 3T3 cell nucleus stained with DH4 (0.3 μ M) for 15 min, $\lambda_{\text{ex}} = 800\text{nm}$, $\lambda_{\text{em}} = 600\text{-}650\text{ nm}$.
Scale bar was 20 μm . Photograph interval 60 seconds.

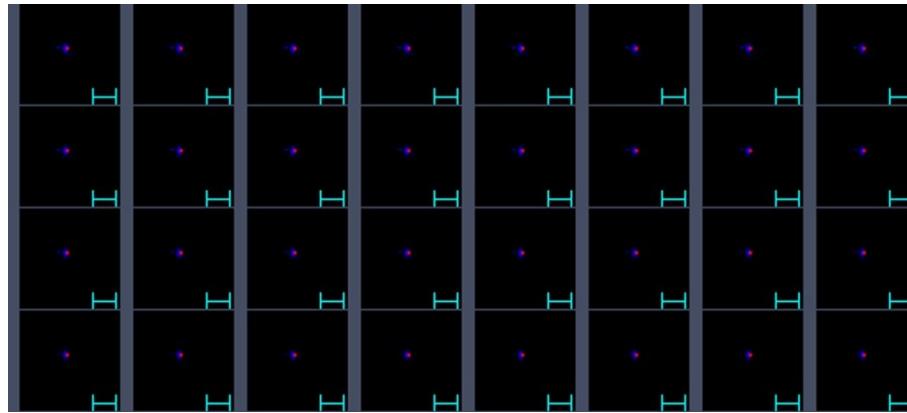


Fig. S37 Time-dependent two-photon confocal fluorescence images of 3T3 cell nucleus stained with DAPI (0.3 μ M) for 15 min, $\lambda_{\text{ex}} = 740\text{nm}$, $\lambda_{\text{em}} = 410\text{-}490\text{ nm}$. Scale bar was 20 μm . Photograph interval 60 seconds.

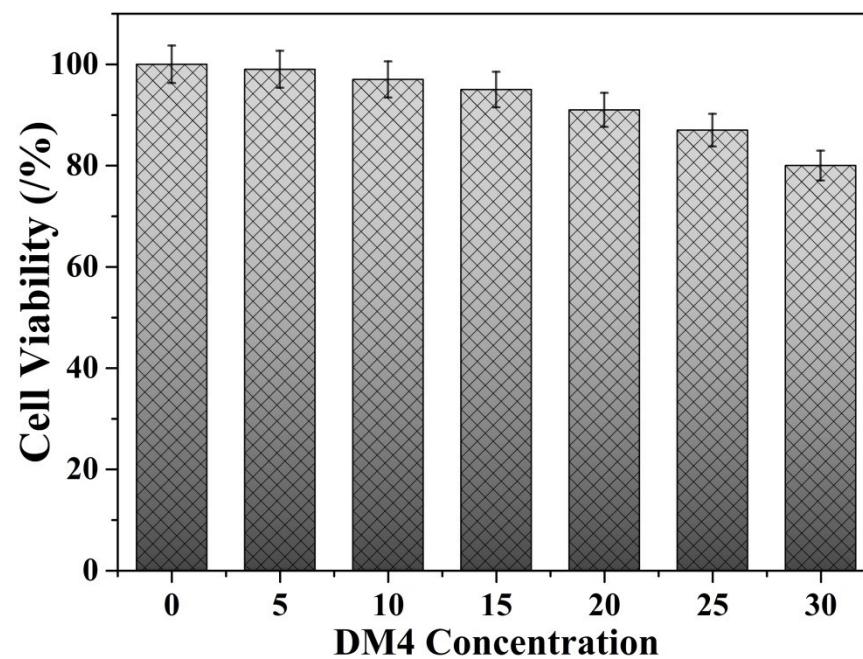
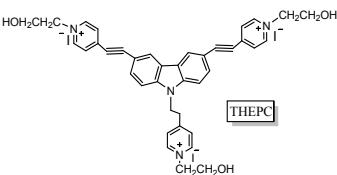
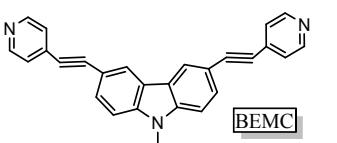
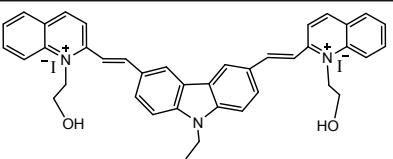
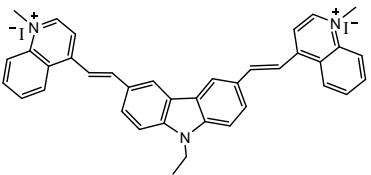
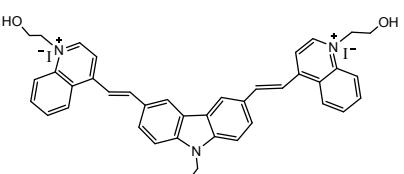


Fig. S38 SMMC-7721 cells Viability stained with DM4 (incubated for 24h).

Table S1 Main data of two-photon fluorescence probe TP properties of carbazole derivatives reported in recent years

[No.]	Compound Structure	Code name	λ_{em} /nm	TP $\lambda_{\text{ex/}}$ nm	Fluorescence Quantum Yield(ϕ)	TPA Cross- Section/ GM(δ)	TPA action $\times \phi$	Solvent
[1]		(III)	570	800	0.023	578	13.29	Glycol
[2]		CAEI	564	800	13.8%	--	29.2	MeCN
[3]		V-carbazole	573	830	0.29%	1241	3.60	Phosphate buffer solution
[4]		Cbz-2Py Cbz-3Py Cbz-2Ox5Py	575 581 560	800 760 --	0.33 0.16 <0.01	190 540 --	64 84 --	Glycol

Continued Table S1

[5]		THEPC	592	800	0.96%	1030	9.89	DMF
[6]		BEMC	650	800	--	220 (δ_{ND}) 34.18(δ_D)	--	DMF
		DH2	647	800	0.51	563	287.13	DMF
This article		DM4	650	800	0.45	595	267.75	DMF
		DH4	654	800	0.35	675	236.25	DMF

-- Not measured.

Reference

- [1] Y.C. Zheng, M.L. Zheng, S. Chen, Z.S. Zhao, X.M. Duan, *Journal of Materials Chemistry B*, 2(2014) 2301-2310.
- [2] M. Fang, W. Zhang, Y. Sun, R. Zhang, Y. Liu, F. Guo, et al., *Biosensors and Bioelectronics*, 55(2013) 423-429.
- [3] X.J. Feng, P.L. Wu, F. Bolze, H.W.C. Leung, K.F. Li, N.K. Mak, et al., *Organic Letters*, 12(2010) 2194-2197.
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- [6] S. Chen, Y.C. Zheng, M.L. Zheng, X.Z. Dong, F. Jin, Z.S. Zhao, et al., *Journal of Materials Chemistry C*, 5(2017) 470-475.