

Electronic Supplementary Information for:

New anti-counterfeiting materials based on hemicyanine dyes:

HSO₃⁻/SO₃²⁻ encryption and UV light decryption

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Experimental

Synthesis of compound 2

4,4'-(2-(4-bromophenyl)-2-phenylethene-1,1-diyl)bis(methoxybenzene) (1.0 mmol, 0.47g), (5-formylthiophen-2-yl)boronic acid (5.0 mmol, 0.65g), K₂CO₃ (10 g), toluene (50 ml), methanol (50 ml). The above drugs were added to three flasks under argon protection at room temperature for 30 min, then 0.72 g of Pd(dppf)Cl₂ was added and the system was refluxed for 12h. On cooling to room temperature, the system was filtered, dried and purified by ethyl acetate column chromatography, to afford a yellow powder in a yield of 69%. m.p: 163~164°C. ¹H NMR (600 MHz, DMSO-d₆) δ = 9.88 (s, 1H, -CHO-H), 8.00 (d, *J*=4.0, 1H, thiophene-H), 7.68 (d, *J*=4.0, 1H, thiophene-H), 7.59 (d, *J*=8.3, 1H, Ar-H), 7.18 – 7.06 (m, 1H, Ar-H), 7.02 (d, *J*=8.3, 2H, Ar-H), 6.98 (d, *J*=7.0, 2H, Ar-H), 6.91 (d, *J*=8.7, 2H, Ar-H), 6.86 (d, *J*=8.7, 2H, Ar-H), 6.72 (d, *J*=8.7, 2H, Ar-H), 6.68 (d, *J*=8.7, 2H, Ar-H), 3.67 (s, 6H, -OCH₃-H). ¹³C NMR (151 MHz, DMSO-d₆) δ = 184.02, 158.05, 157.92, 152.44, 145.40, 143.55, 141.76, 140.84, 139.34, 137.93, 135.52, 135.47, 132.18, 132.13, 131.78, 130.90, 130.14, 128.05, 126.51, 125.69, 125.14, 113.46, 113.25, 54.99. MS (HR-ESI): calcd for is C₃₃H₂₆O₃S [M⁺]: 525.6280; found: 525.1488. IR (KBr pellet, cm⁻¹): 3030 (w), 2930 (w), 2830 (w), 1670 (vs), 1600 (s), 1500 (vs), 1440 (vs), 1300 (m), 1240 (vs), 1180 (s), 1110 (m), 1030 (m), 838 (s), 817 (s), 760 (m), 701 (m), 583(w) (Figs. S1–S4).

Synthesis of the TPA-S-Cy3

A mixture of 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl) propane-1-sulfonate (0.36 g, 1.00 mmol) and compound **1** (0.46 g, 1.00 mmol) in ethanol (20.00 mL) was refluxed for 8 h. On cooling to room temperature, recrystallization afforded a solid. The compound **TPA-S-Cy3** was obtained as a black-purple solid in 78.9% yield. m.p: 291~292°C. ¹H NMR (600 MHz, DMSO-d₆) δ 8.64 (d, *J* = 15.7 Hz, 1H), 8.32 (d, *J* = 3.4 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.73 (t, *J* = 5.9 Hz, 3H), 7.60 – 7.56 (m, 1H), 7.38 (q, *J* = 7.5 Hz, 5H), 7.13 (ddd, *J* = 19.3, 15.8, 8.1 Hz, 7H), 6.99 (dd, *J* = 8.5, 2.4 Hz, 2H), 4.77 (d, *J* = 6.5 Hz, 2H), 2.65 (d, *J* = 5.6 Hz, 2H), 2.16 (d, *J* = 4.7 Hz, 2H), 1.77 (s, 6H). ¹³C NMR (151 MHz, DMSO-d₆) δ 180.33, 154.59, 149.27, 144.93, 143.60, 140.20, 138.15, 138.07, 137.79, 133.76, 132.91, 131.03, 130.30, 130.00, 128.34, 127.35, 126.84, 125.45, 125.08, 124.34, 122.96, 119.93, 112.85, 108.07, 53.28, 41.85, 39.52, 25.70, 20.45, 13.73. MS (HR-ESI): calcd for is C₃₇H₃₄N₂O₃S₂ [M+Na]⁺: 641.2011; found: 641.1899. IR (KBr pellet, cm⁻¹): 3050 (w), 2360 (w), 1570 (vs), 1530 (m), 1490 (m), 1420 (vs), 1360 (m), 1330 (s), 1280 (vs), 1220 (s), 1190 (vs), 1150 (s), 1080 (m), 1030 (m), 996 (w), 808 (m), 758 (m), 700 (m), 525 (w) cm⁻¹ (Figs. S5–S8).

Synthesis of the MOTPE-S-Cy3

A mixture of 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl) propane-1-sulfonate (0.36 g, 1.00 mmol) and compound **2** (0.52 g, 1.00 mmol) in ethanol (20.00 mL) was refluxed for 8 h. On cooling to room temperature, recrystallization afforded a solid. The compound **MOTPE-S-Cy3** was obtained as a purple solid in 76% yield. m.p: 256~257°C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.64 (d, *J* = 15.8 Hz, 1H), 8.32 (d, *J* = 4.1 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.80 (d, *J* = 4.1 Hz, 1H), 7.65 – 7.49 (m, 6H), 7.21 – 7.09 (m, 2H), 7.05 (t, *J* = 6.6 Hz, 2H), 7.00 (dd, *J* = 11.3, 4.5 Hz, 2H), 6.93 (dd, *J* = 11.6, 4.8 Hz, 2H), 6.90 – 6.84 (m, 2H), 6.79 – 6.73 (m, 2H), 6.72 – 6.67 (m, 2H), 4.85 – 4.71 (m, 2H), 3.69 (d, *J* = 4.3 Hz, 6H), 2.70 – 2.58 (m, 2H), 2.15 (s, 2H), 1.77 (s, 6H). ¹³C NMR (126 MHz, DMSO-d₆) δ 180.63, 158.09, 157.93, 153.79, 145.95, 145.65, 143.62, 143.52, 141.01, 139.27, 137.93, 135.50, 132.24, 132.16, 131.95, 130.96, 130.28, 129.13, 128.92, 128.11, 126.67, 126.59, 125.61, 123.03, 114.86, 113.51, 113.26, 110.27, 55.01, 54.99, 51.31, 47.73, 27.12, 24.61. MS (HR-ESI): calcd for is C₄₇H₄₃NO₅S₂ [M+Na]⁺: 788.2583; found: 788.2455. IR (KBr pellet, cm⁻¹): 3040 (w), 2920 (w), 1580 (vs), 1500 (s), 1420 (vs), 1300 (m), 1240 (s), 1170 (vs), 1030 (m), 970 (w), 833 (m), 809 (m), 761 (m), 704 (m), 595 (m), 506 (w) cm⁻¹. (Figs. S9–S12).

X-ray Crystallography

A Bruker APEX 2 CCD diffractometer was used to collect crystallographic data for TPA-S-Cy3 and MOTPE-S-Cy3. The data was collected in the ω scan mode using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).^[1] The structures were solved by a charge flipping algorithm and refined by full-matrix least-squares methods on F2.^[2] All esds were estimated using the full covariance matrix. In Table S2, further details are provided. Structural data for TPA-S-Cy3 and MOTPE-S-Cy3 have been deposited in the Cambridge Crystallography Data Centre with CCDC numbers 2309464 and 2309465, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General methods for optical tests

Preparation of the probe stock solution and the analytical test solution: the **TPA-S-Cy3** and **MOTPE-S-Cy3** probes were dissolved in DMF and prepared as a 1 mM stock solution. A series of reactive oxygen species and common ions solutions (10 mM) were prepared with deionized water, including GSH, Cys, C₂O₄²⁻, AcO⁻, BF₄⁻, Br⁻, SO₄²⁻, S₂O₃²⁻, HSO₄⁻, Cl⁻, SCN⁻, HSO₃⁻, HPO₄²⁻, CO₃²⁻, F⁻, H₂PO₄⁻, NO₂⁻, PO₄³⁻, HCO₃⁻, I⁻, •OH, ¹O₂, ONOO⁻, NaClO, H₂O₂. The specific pH (2-12) of the solution required for the experiment was prepared by adjusting the pH of the Tris-HCl buffer. The stock solution (100 μ L) and the substance to be tested were placed in 5 mL tube and diluted to 5 mL with DMF/Tris-HCl (2/3, v/v, pH=7.0) to determine the UV-visible absorbance at room temperature.

Preparation of the anti-counterfeiting ink

Neutral ink was designed and prepared by reviewing the relevant literature.^[3-6] 0.05g of **TPA-S-Cy3/MOTPE-S-Cy3** was dissolved in 5 mL of ethanol and sonicated for 30 min., then 1 mL of propanetriol and 4 mL of ultrapure water were added and sonication was continued for 30 min. The pH of the above solution was adjusted to neutral with 0.5 M NaOH/HCl. After filtration, a medium viscosity, uniformly dispersed full colored ink was afforded. HSO₃⁻/SO₃²⁻ ink: 0.04g NaHSO₃ was dissolved in 5 mL of ultrapure water, 4 mL of absolute ethanol and 1 mL of propyl alcohol were added and sonication was continued for 20 min.

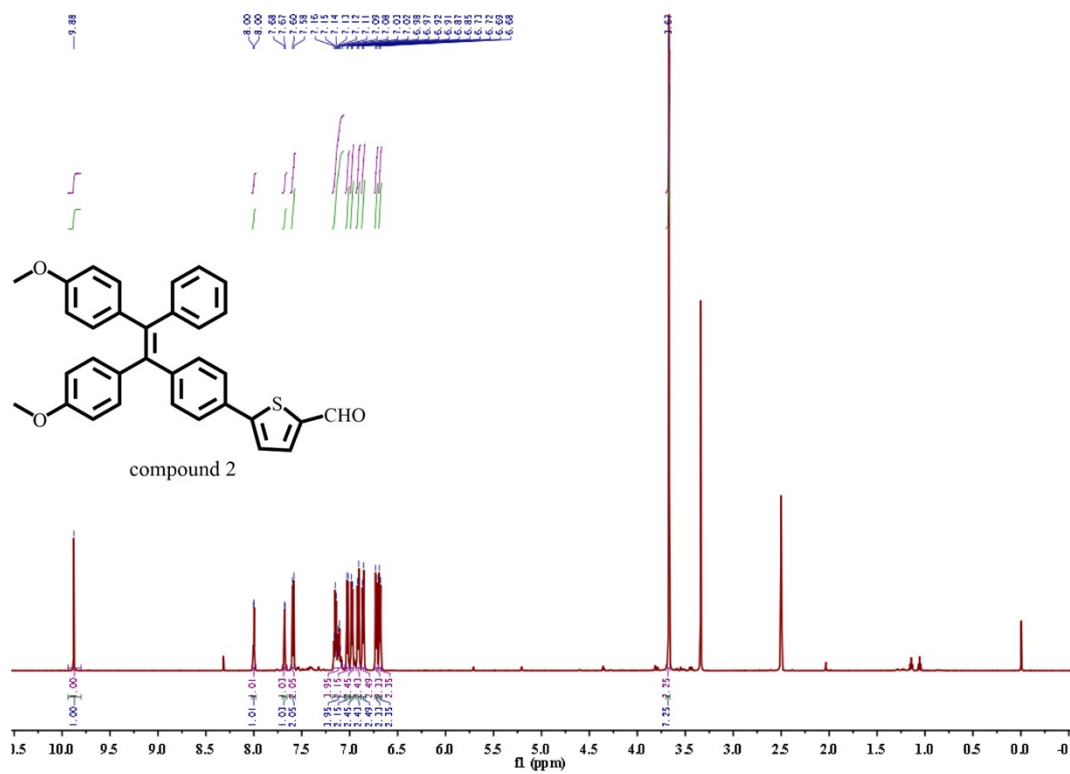


Fig. S1. $^1\text{H NMR}$ spectrum of compound 2.

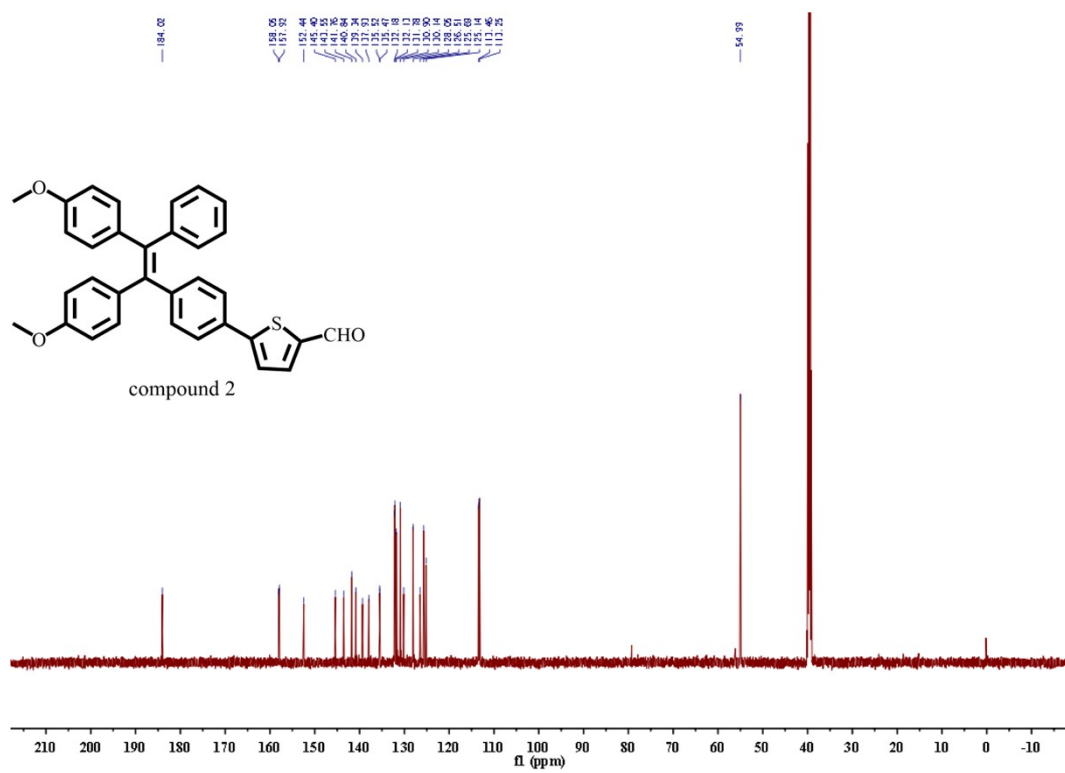


Fig. S2. $^{13}\text{C NMR}$ spectrum of compound 2.

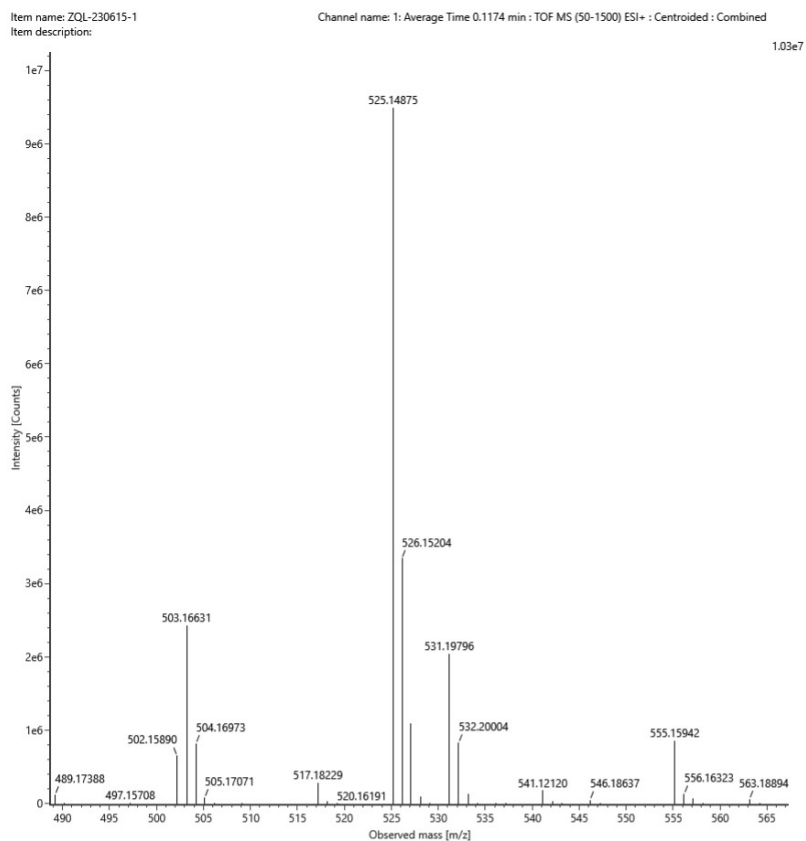


Fig. S3. HR-MS spectrum of compound 2.

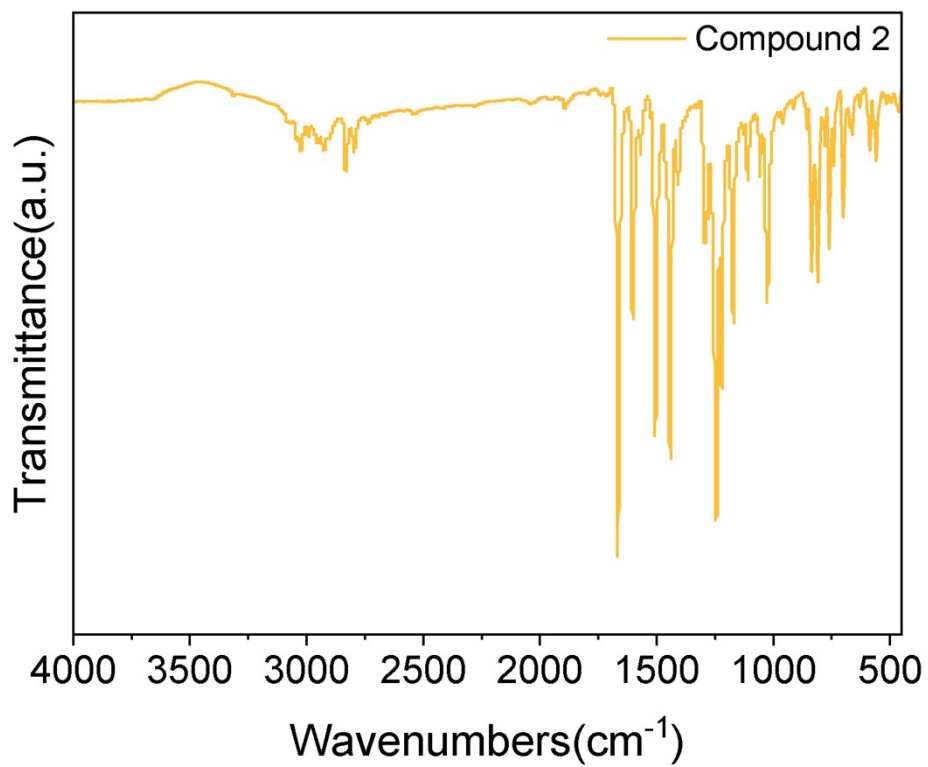


Fig. S4. FT-IR spectrum of compound 2.

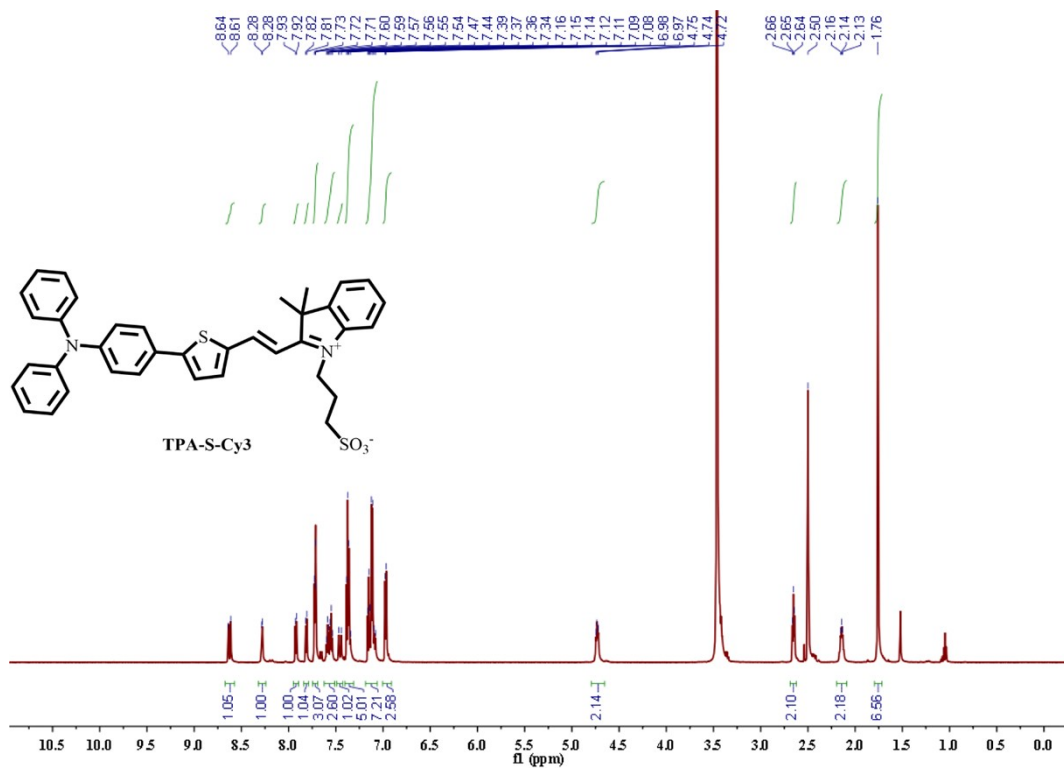


Fig. S5. ¹H NMR spectrum of TPA-S-Cy3.

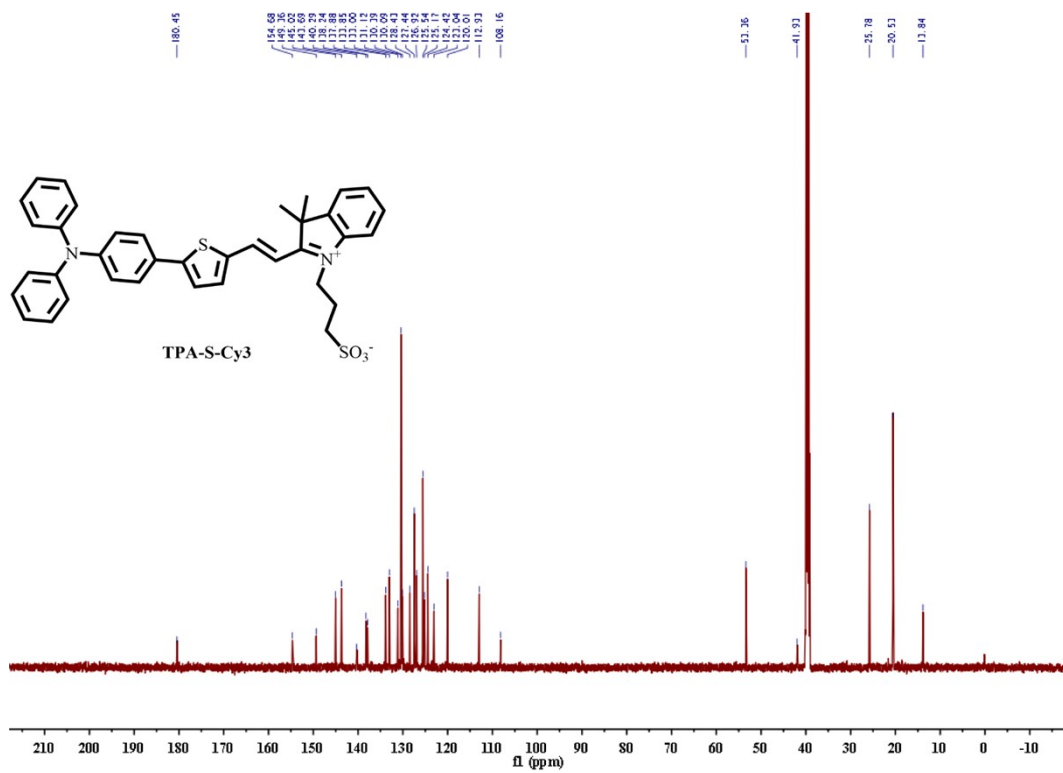


Fig. S6. ¹³C NMR spectrum of TPA-S-Cy3.

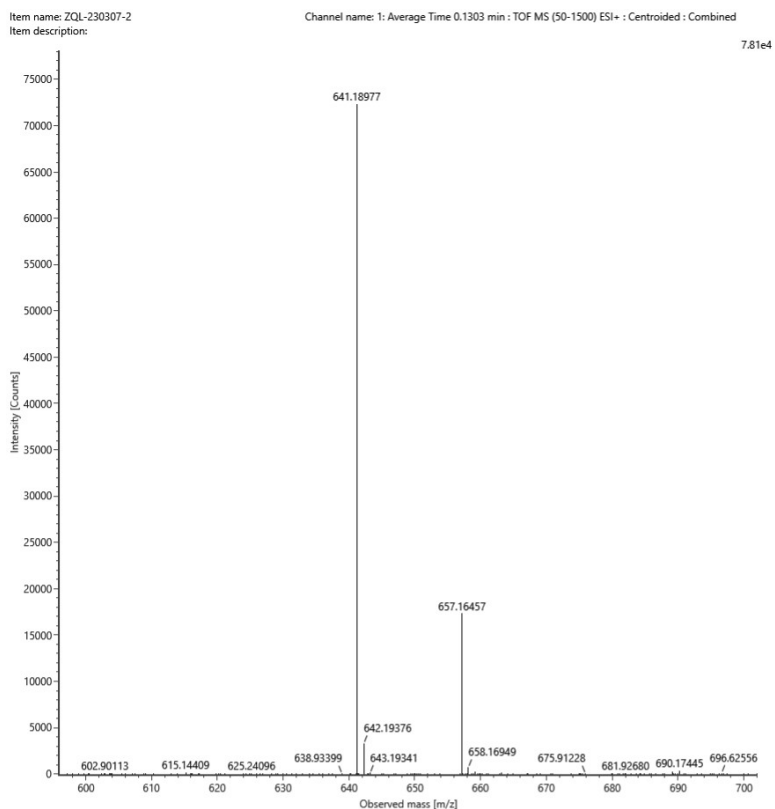


Fig. S7. HR-MS spectrum of TPA-S-Cy3.

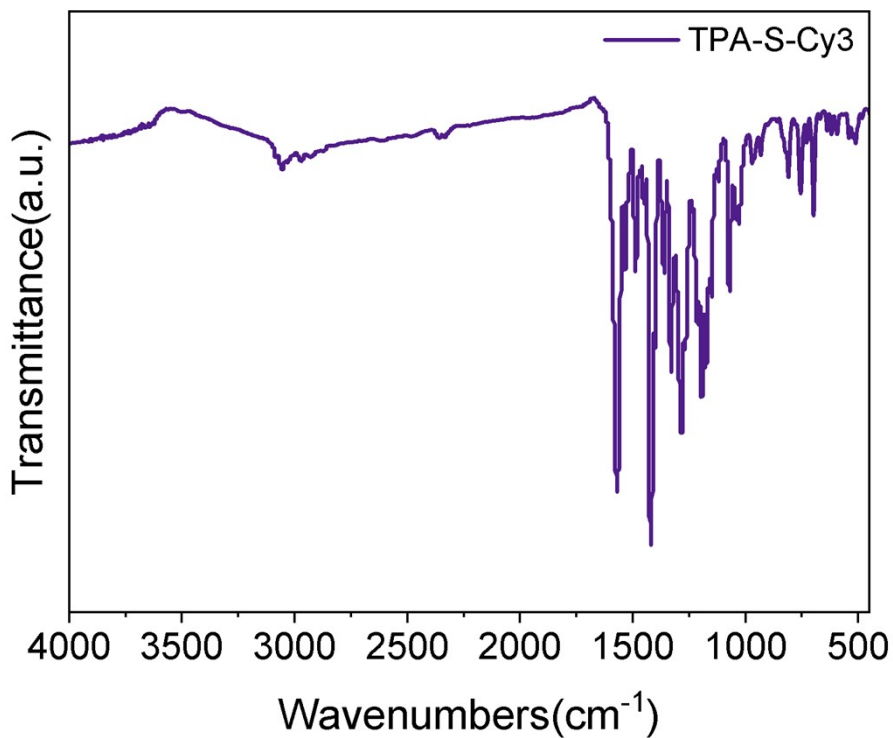


Fig. S8. FT-IR spectrum of TPA-S-Cy3.

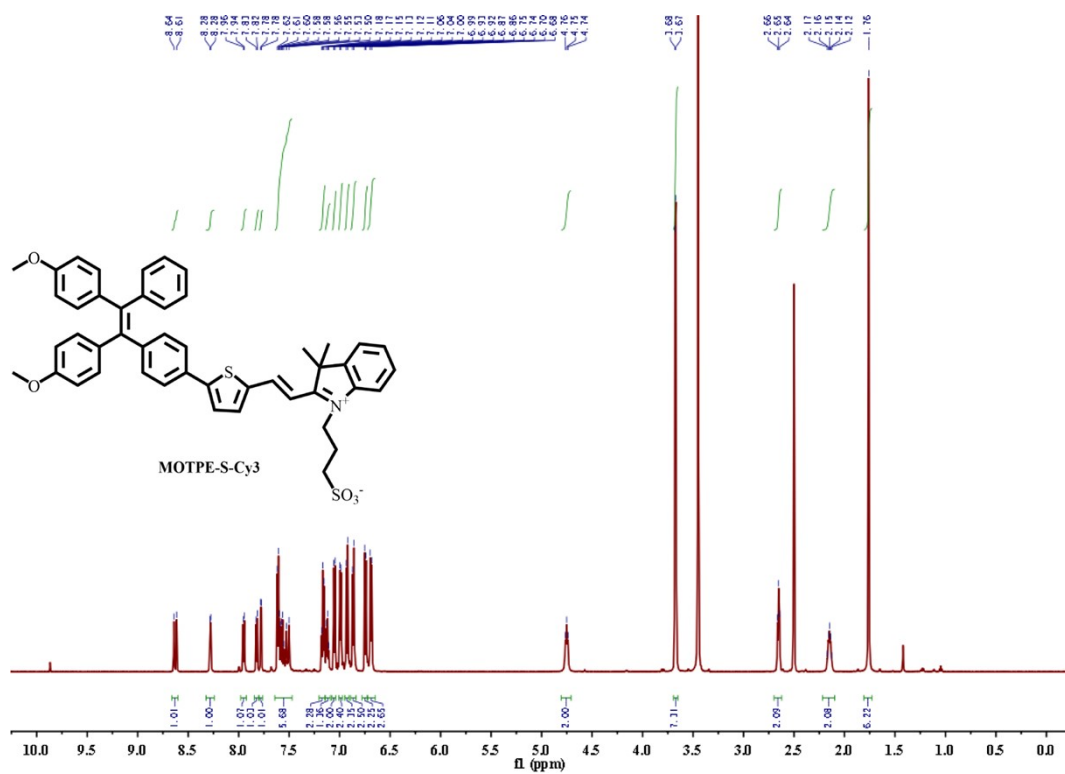


Fig. S9. ^1H NMR spectrum of MOTPE-S-Cy3.

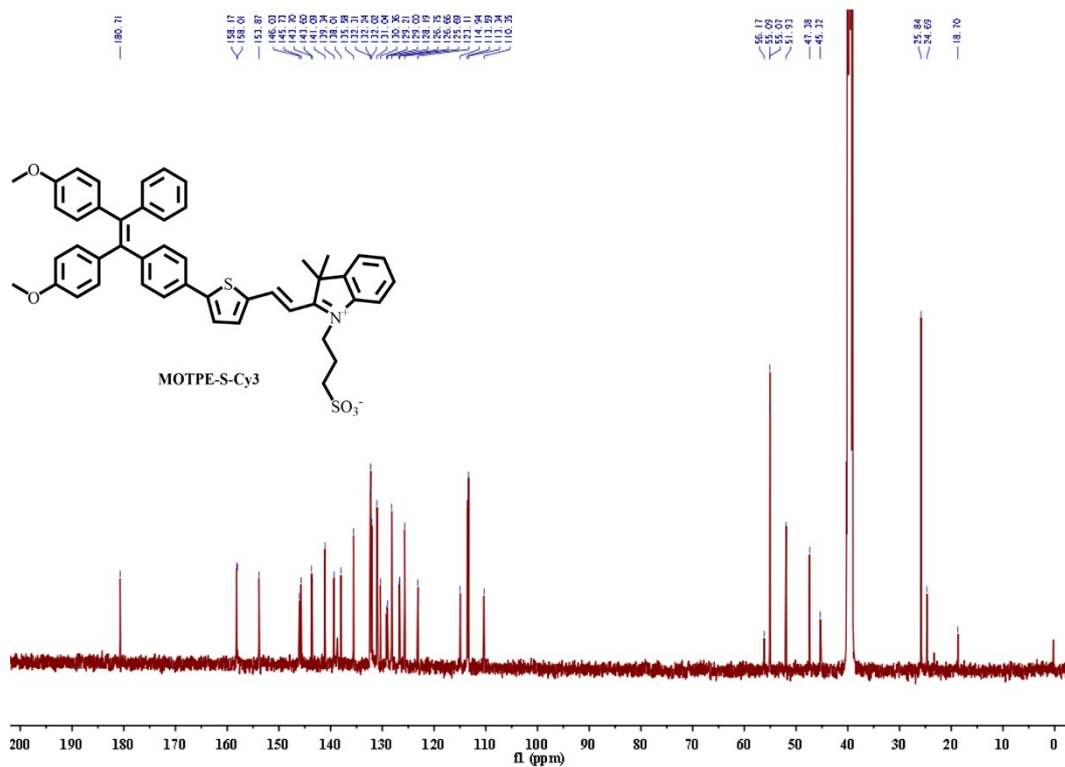


Fig. S10. ^{13}C NMR spectrum of MOTPE-S-Cy3.

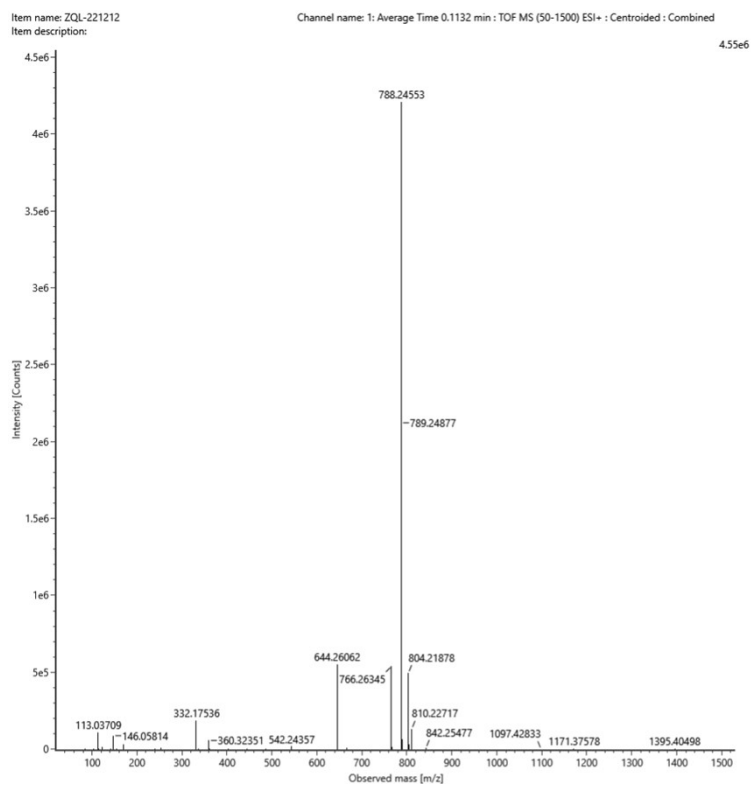


Fig. S11. HR-MS spectrum of MOTPE-S-Cy3.

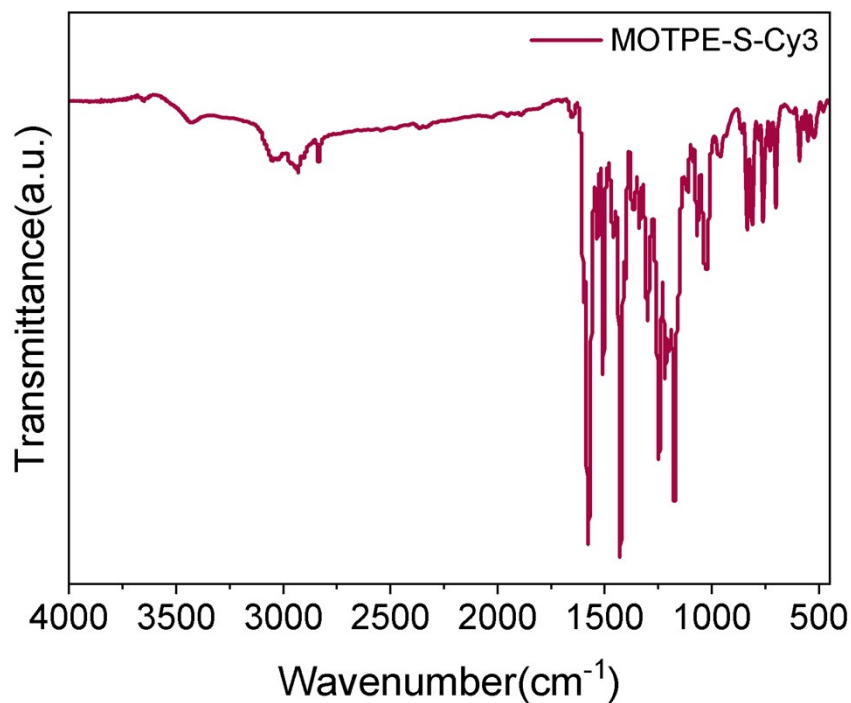
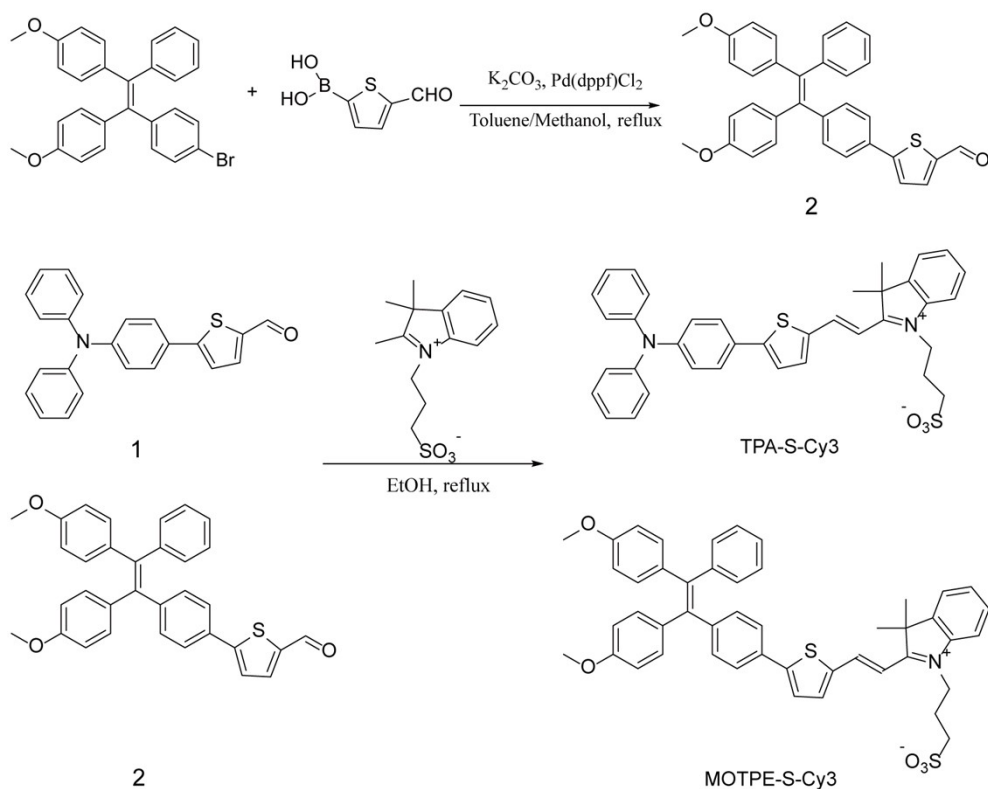


Fig. S12. FT-IR spectrum of MOTPE-S-Cy3.



Scheme 1. Synthetic routes for compound 2, and probes TPA-S-Cy3 and MOTPE-S-Cy3.

Table S2. Crystallographic data for the probes TPA-S-Cy3 and MOTPE-S-Cy3.

Parameter	TPA-S-Cy3	MOTPE-S-Cy3
Empirical formula	$C_{39}H_{41}N_2O_5S_2$	$C_{47}H_{43}NO_5S_2$
Formula weight [$g\ mol^{-1}$]	681.86	765.94
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P-1$
a [Å]	16.4660(16)	9.9474(14)
b [Å]	12.3702(11)	10.2779(12)
c [Å]	18.3226(16)	20.097(3)
α	90.00°	$89.204(3)^\circ$
β	$109.556(3)^\circ$	$78.583(3)^\circ$
γ	90.00°	$85.065(4)^\circ$
Volume [Å ³]	3516.8(6)	2006.6(5)
Z	4	2
Density, calcd [gm^{-3}]	1.288	1.268
Temperature [K]	273(2)	293(2)
Unique reflns	4565	4168

Obsd reflns	8817	5653
Parameters	440	555
R_{int}	0.0970	0.0498
$R[>2\sigma(I)]^a$	0.0813	0.0996
$W[\text{all data}]R^b$	0.1531	0.2116
GOF on F^2	1.043	1.093

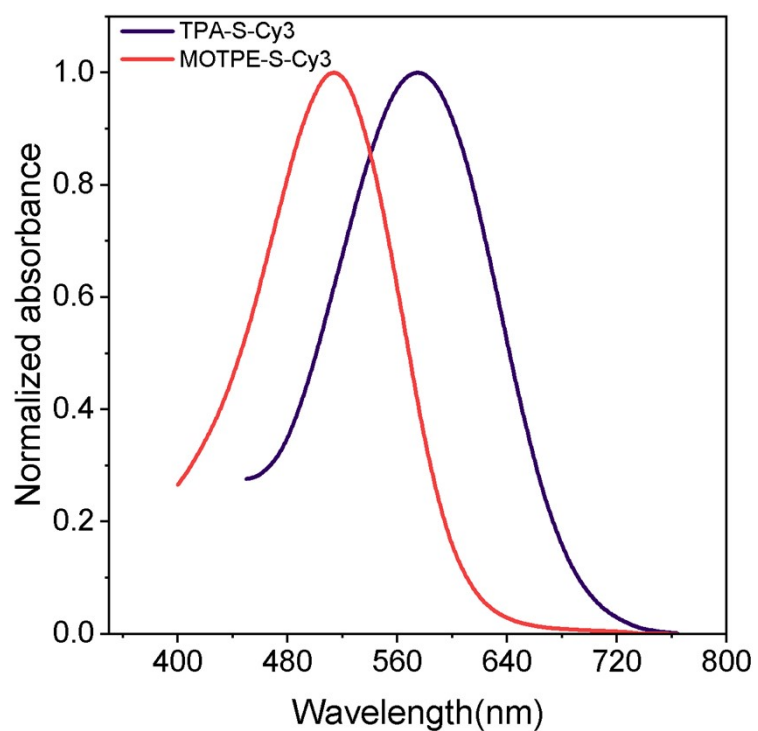


Fig. S13. Normalized UV absorbance spectra of the probes TPA-S-Cy3 and MOTPE-S-Cy3.

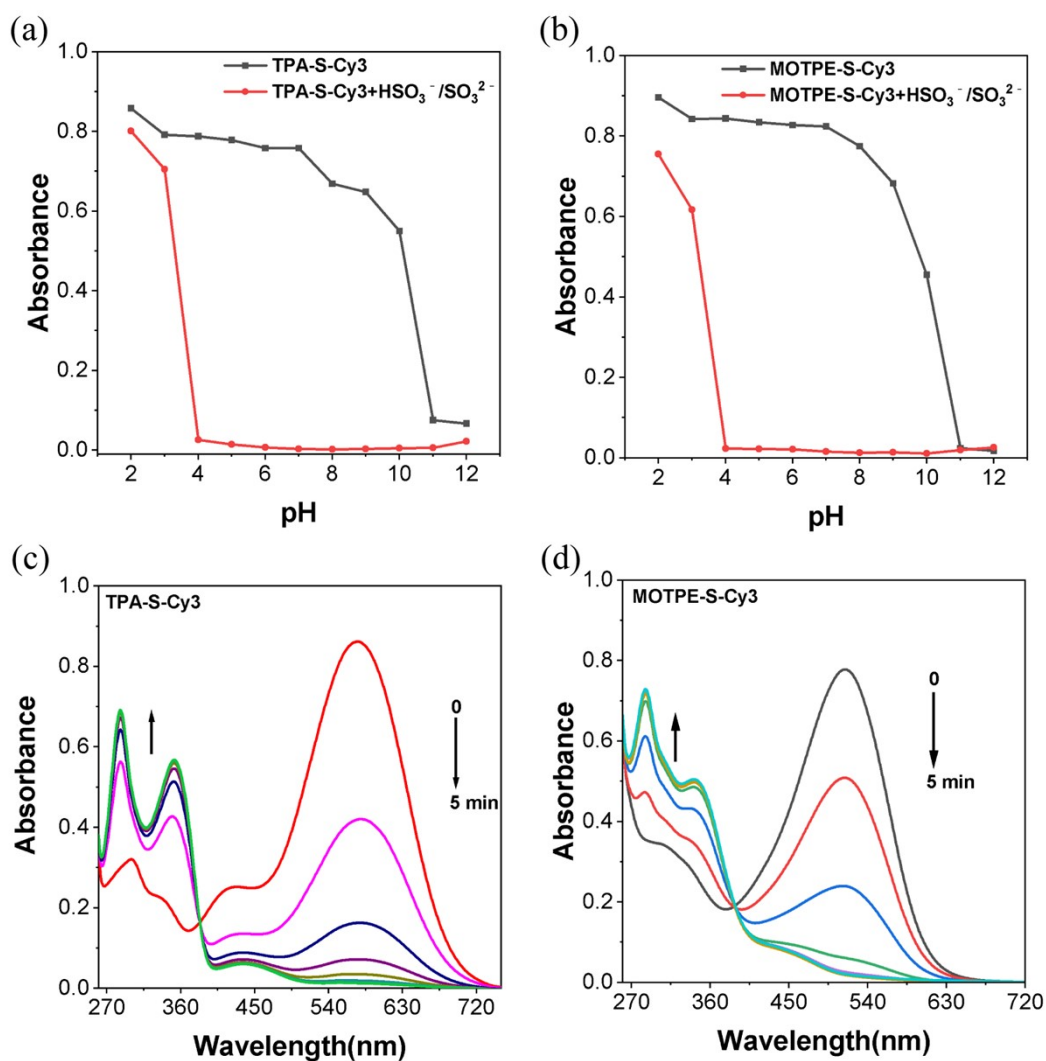


Fig. S14. Stability of the probes (a) TPA-S-Cy3 and (b) MOTPE-S-Cy3 at different pH values; UV spectra versus reaction time of the probes (c) TPA-S-Cy3 and (d) MOTPE-S-Cy3 with HSO₃⁻ (40 μM).

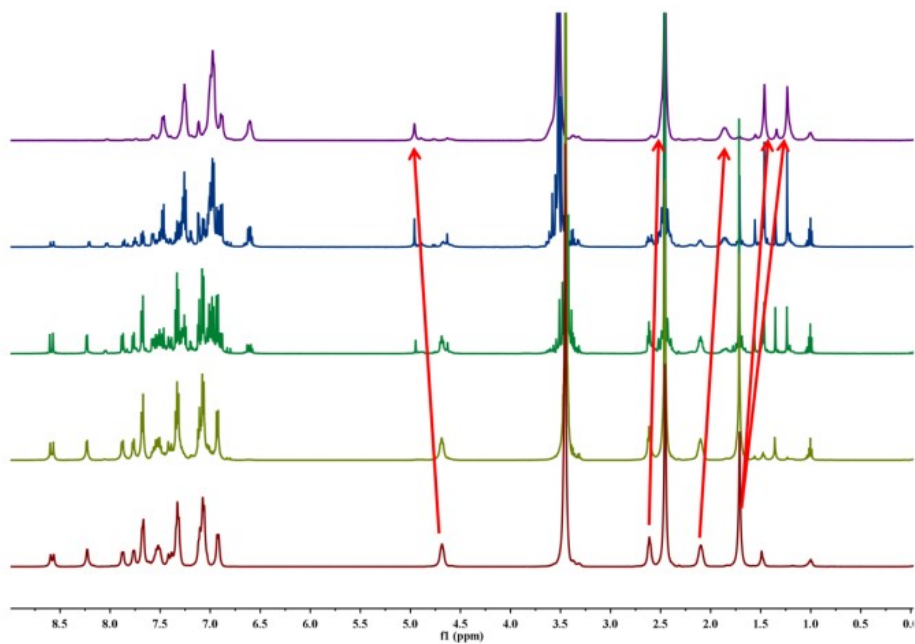


Fig. S15. ¹H NMR spectra of the TPA-S-Cy3 probe upon interaction with different concentrations of HSO₃⁻.

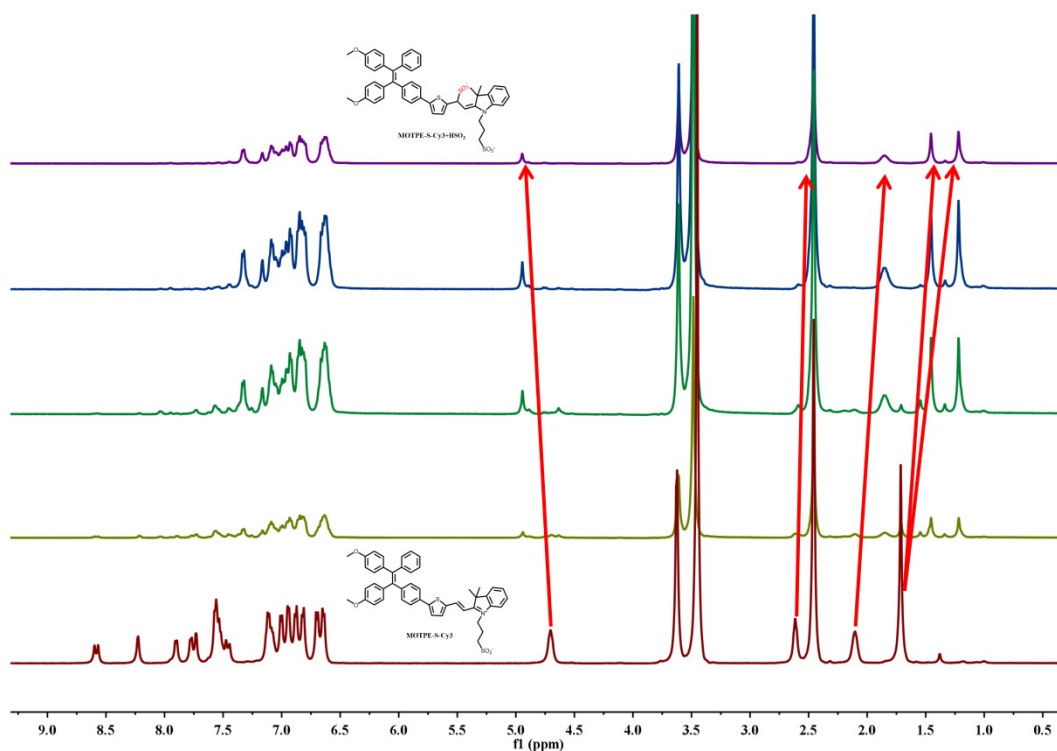


Fig. S16 ¹H NMR spectra of the MOTPE-S-Cy3 probe upon interaction with different concentrations of HSO₃⁻.

Fig. S17. High-resolution mass spectrum (HR-MS) of the reaction product on interaction of the probe **TPA-S-Cy3** with HSO_3^- .

Fig. S18. High-resolution mass spectrum (HR-MS) of the reaction product on interaction of the probe **MOTPE-S-Cy3** with HSO_3^- .

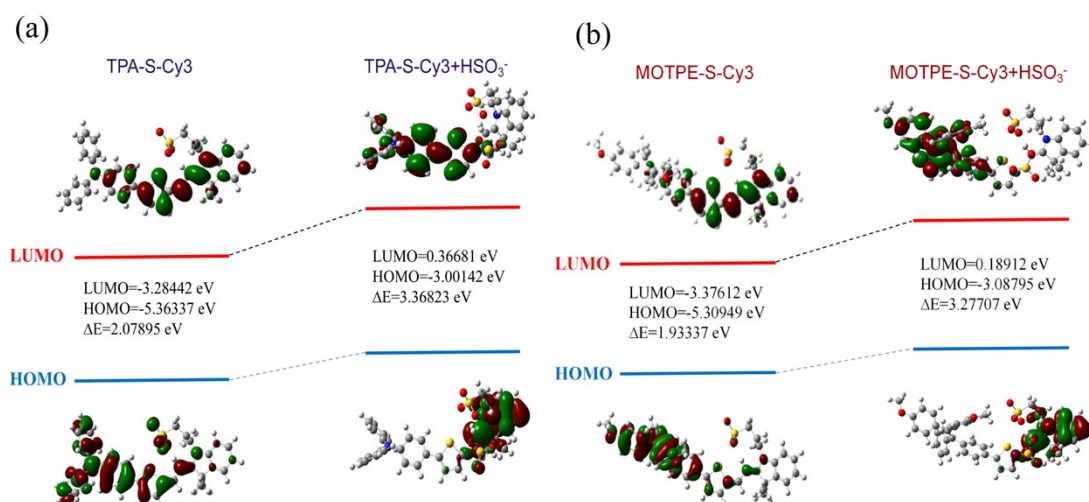


Fig. S19. a) The frontier molecular orbitals of TPA-S-Cy3 and TPA-S-Cy3+ HSO_3^- ; b) The frontier molecular orbitals of MOTPE-S-Cy3 and MOTPE-S-Cy3+ HSO_3^- .

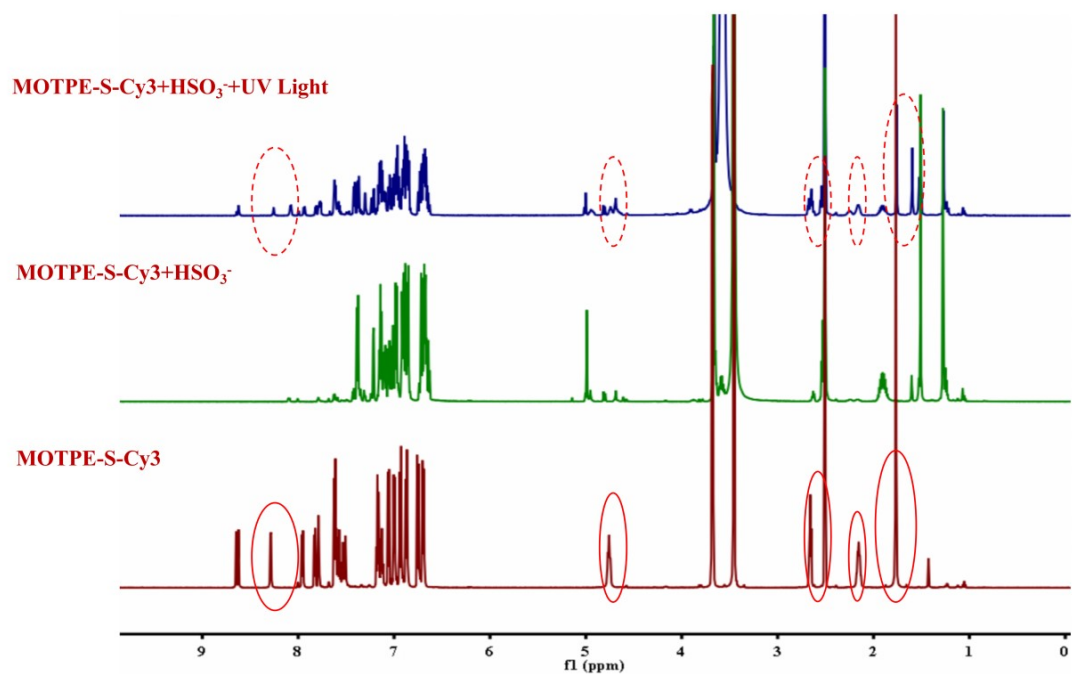


Fig. S20. ^1H NMR spectra of HSO_3^- were reproducibly identified by the UV-induced MOTPE-S-Cy3 probe.

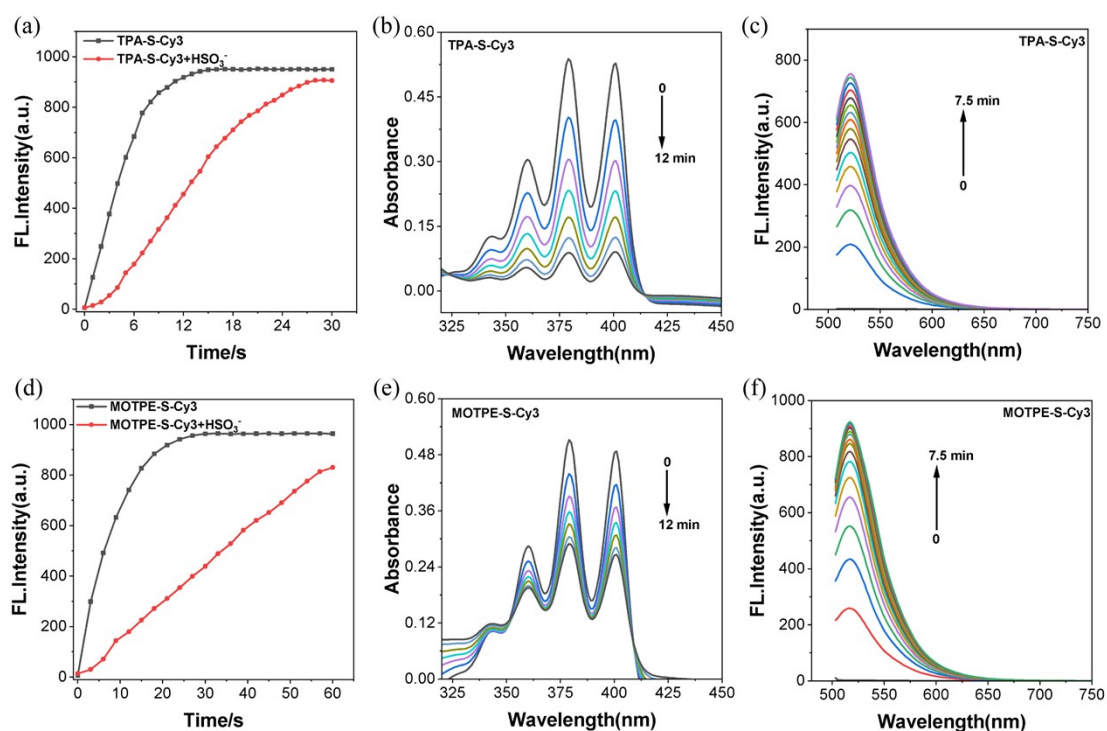


Fig. S21. a) The fluorescence intensity of TPA-S-Cy3 and TPA-S-Cy3+ HSO_3^- probes with DCFH indicator varies with time under white light ($40 \text{ mW}\cdot\text{cm}^{-2}$) irradiation ($\lambda_{\text{em}}=525 \text{ nm}$); b) UV absorption spectra of the TPA-S-Cy3 probe and

ABDA indicator under white light irradiation; c) Fluorescence spectra of the **TPA-S-Cy3** probe and HPF indicator under white light irradiation; d) The fluorescence intensity of **MOTPE-S-Cy3** and **MOTPE-S-Cy3+HSO₃⁻** probes with DCFH indicator varies with time under white light irradiation; e) UV absorption spectra of the **MOTPE-S-Cy3** probe and ABDA indicator under white light irradiation; f) Fluorescence spectra of the **MOTPE-S-Cy3** probe and HPF indicator under white light irradiation.

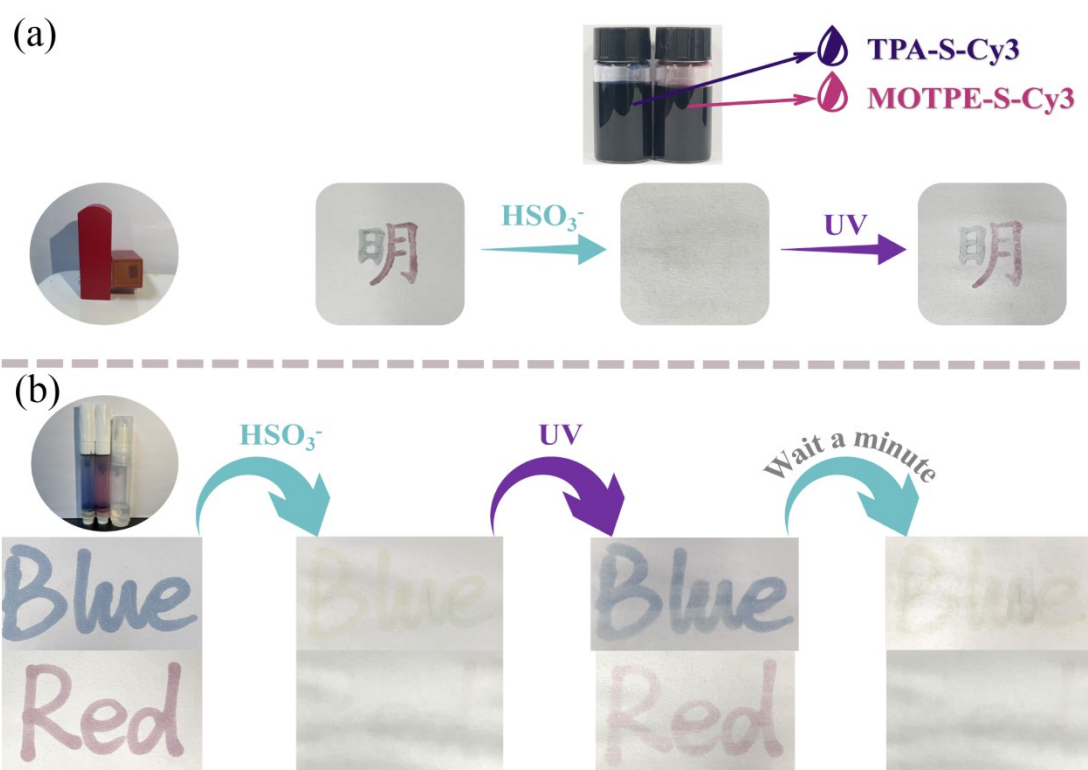


Fig. S22. Use of the probes **TPA-S-Cy3** and **MOTPE-S-Cy3** for text encryption and decryption process under $\text{HSO}_3^-/\text{SO}_3^{2-}$ action: (a) inkpad and (b) ink.

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