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

Supporting Information

Biotinylated and fluorophore-incorporated polymeric mixed micelles for tumor cell-specific turn-on fluorescence imaging of Al^{3+}

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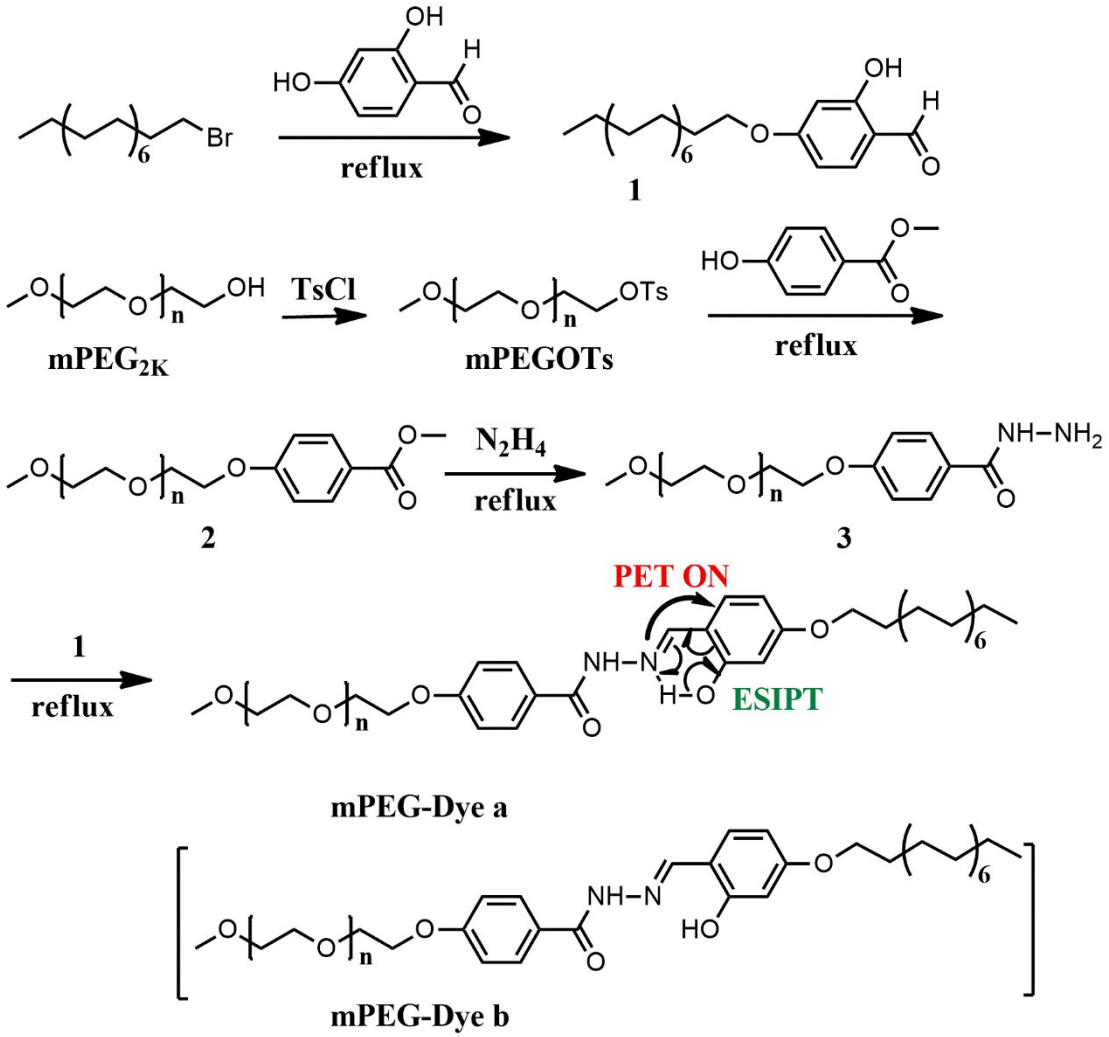

Figure S1. Synthesis of mPEG-Dye.

The structural characterization of compound 1

^{1}H NMR ($CDCl_3$, 400 MHz):δ11.486 (s, H_a), 9.706 (s, H_b), 7.43 (d, H_c), 6.545 (d, H_d), 6.416 (s, H_e), 4.003 (t, 2 H_f), 1.793 (t, 2 H_g), 1.585(d, 2 H_h), 1.447-1.259 (m, 24H_i), 0.88 (d, 3 H_i).

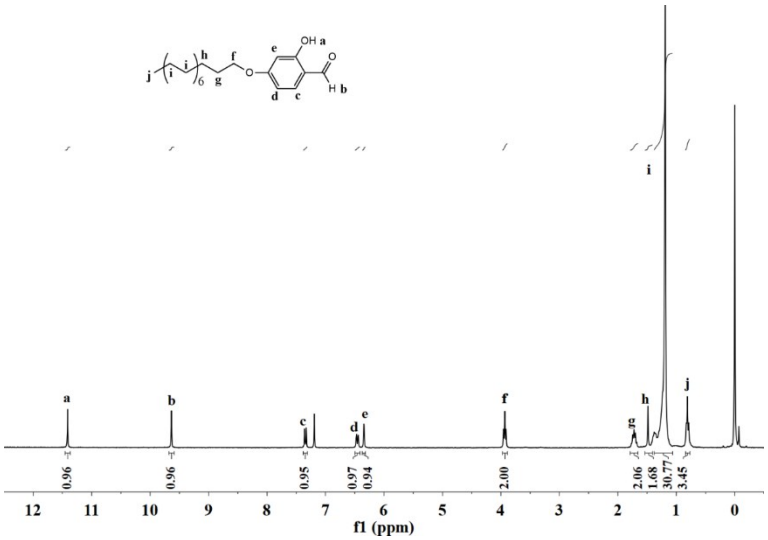

Figure S2. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

The structural characterization of compound 2

^{1}H NMR (DMSO-d_6, 400 MHz):δ7.90 (d, 2H_a), 7.054 (d, 2H_b), 4.157 (t, 2H_c), 3.792 (s, 3H_d), 3.738(t, 2H_e), 3.486 -3.421 (m, 176 H_f), 3.247 (s, 3 H_g).

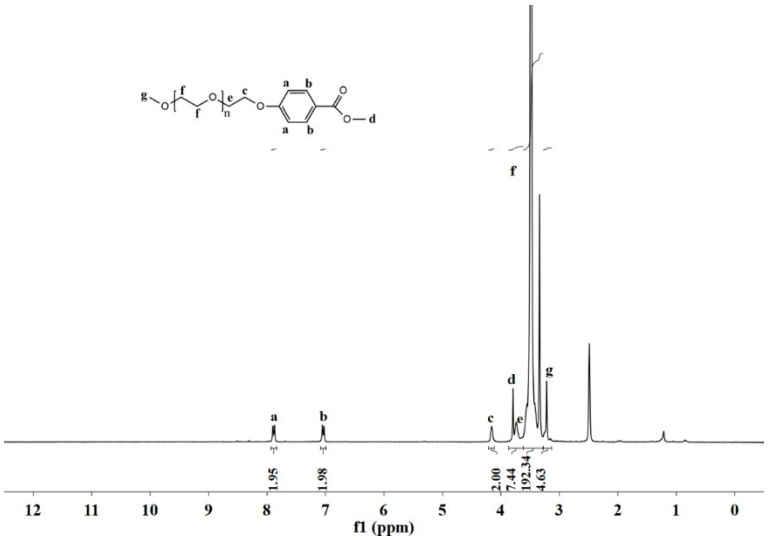

Figure S3. ^{1}H NMR spectrum of compound **2** in deuterated DMSO.

^{1}H NMR ($CDCl_3$, 400 MHz):δ7.907 (d, $2H_a$), 6.866 (d, $2H_b$), 4.117 (t, $2H_c$), 3.81 (s, $3H_d$), 3.746 (t, $2H_e$), 3.646 -3.487 (m, 176 H_f), 3.313 (s, 3 H_g).

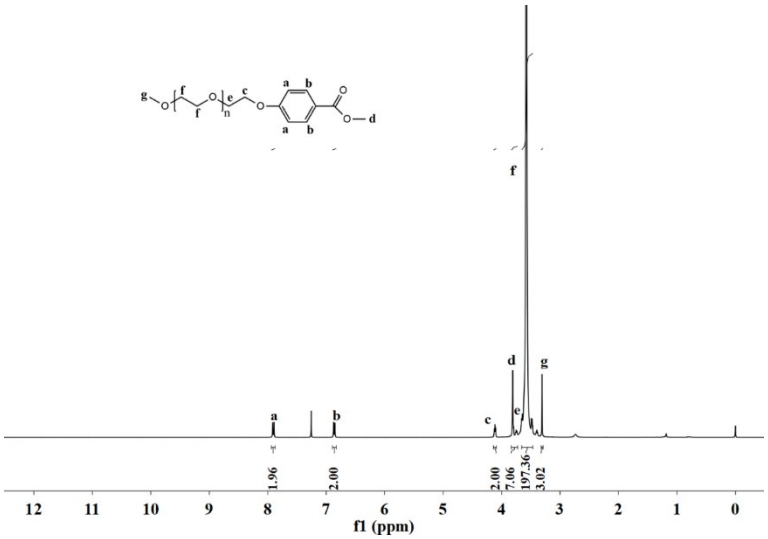

Figure S4. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

The structural characterization of compound 3

^{1}H NMR (DMSO-d_6, 400 MHz):δ9.622 (t, H_a), 7.799 (d, $2H_b$), 6.997 (d, $2H_c$), 4.157 (d, $2H_d$), 4.134 (t, $2H_e$), 3.742(t, $2H_f$), 3.505 -3.43 (m, 176 H_g), 3.235 (s, 3 H_h), 1.234 (s, H_2O).

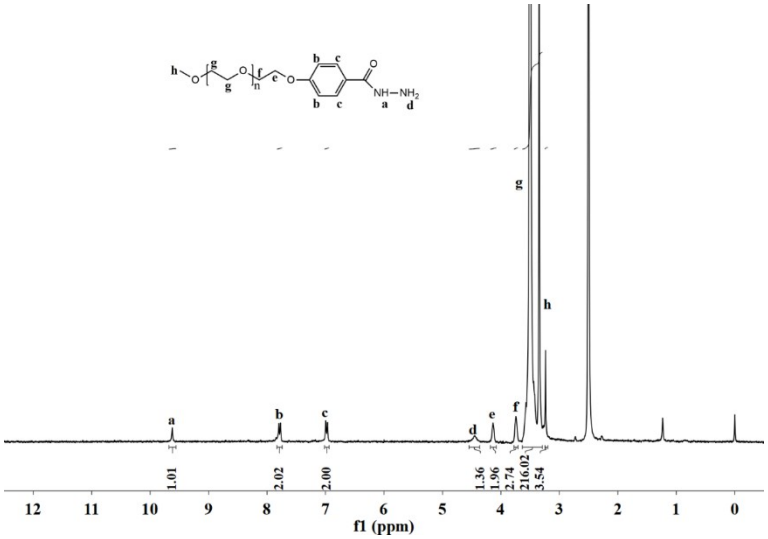

Figure S5. ^{1}H NMR spectrum of compound **3** in deuterated DMSO.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.762 (d, $2H_b$), 6.942 (d, $2H_c$), 4.163 (d, $2H_e$), 3.846 (t, $2H_f$), 3.689 -3.523 (m, 176 H_g), 3.355 (s, 3 H_h), 1.228 (s, H_2O).

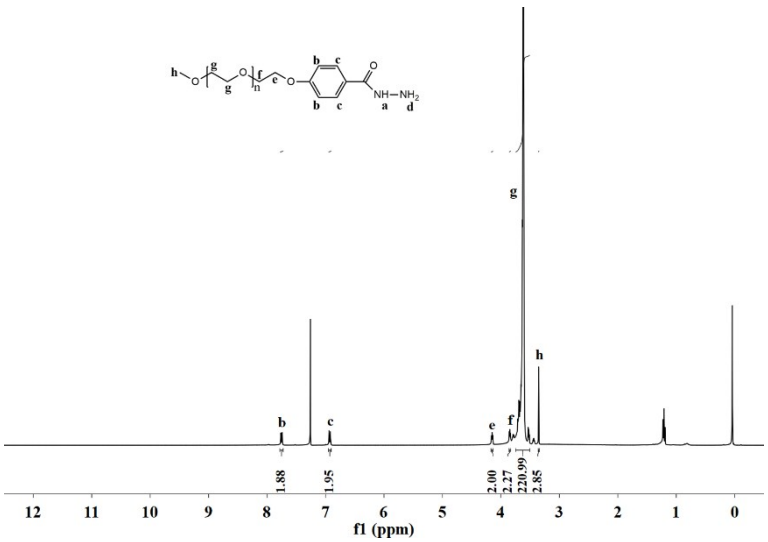

Figure S6. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

The structural characterization of the polymer mPEG-Dye

Isomer a: ^{1}H NMR (DMSO-d_6,400 MHz): δ11.888 (s, H_1), 8.514 (s, H_2), 7.916 (d, $2H_3$), 7.398(d, H_4), 7.099(d, $2H_5$), 6.517(m, H_6, H_7),4.18(t, $2H_8$),3.973(t, $2H_9$), 3.771 (t,$2H_{10}$), 3.582-3.501 (m, $176H_{11}$), 3.232 (s, $3H_{12}$), 1.693 (m,$2H_{13}$), 1.40 -1.232 (m, $26H_{14}$), 0.845 (t, $3H_{15}$)

Isomer b: ^{1}H NMR (DMSO-d_6,400 MHz): δ11.689 (s, H_1), 8.319 (s, H_2), 7.892(d, $2H_3$), 7.369(d, H_4), 7.070(d, $2H_5$), 6.468(m, H_6, H_7), 4.18(t, $2H_8$),3.973(t, $2H_9$), 3.771 (t,$2H_{10}$), 3.582-3.501 (m, $176H_{11}$), 3.232 (s, $3H_{12}$), 1.693 (m,$2H_{13}$), 1.40 -1.232 (m, $26H_{14}$), 0.845 (t, $3H_{15}$)

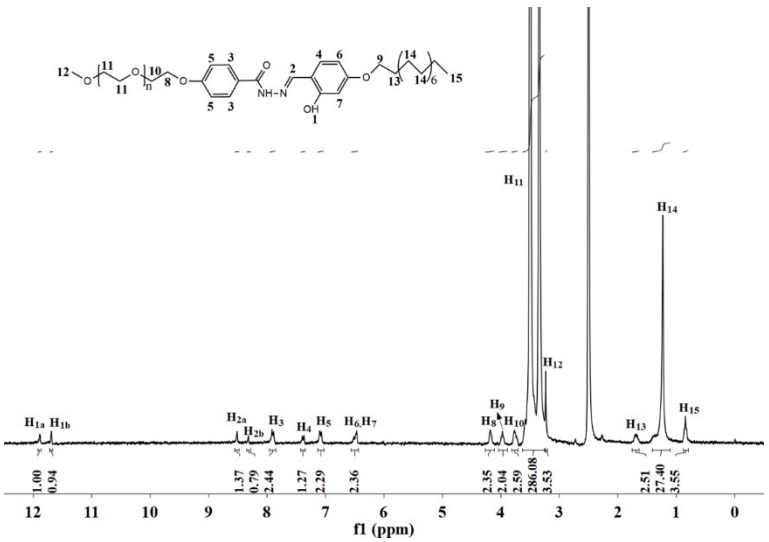

Figure S7. ^{1}H NMR spectrum of polymer mPEG-Dye in deuterated DMSO.

^{1}H NMR ($CDCl_3$,400 MHz): δ8.409 (s, H_2), 7.821(d, $2H_3$), 7.303(d, H_4), 6.945(d, $2H_5$), 6.513(m, H_6, H_7), 4.178(t, $2H_8$),3.937(t, $2H_9$), 3.861 (t,$2H_{10}$), 3.702-3.537 (m, $176H_{11}$), 3.366 (s, $3H_{12}$), 1.738 (m,$2H_{13}$), 1.429 -1.241 (m, $26H_{14}$), 0.862 (t, $3H_{15}$)

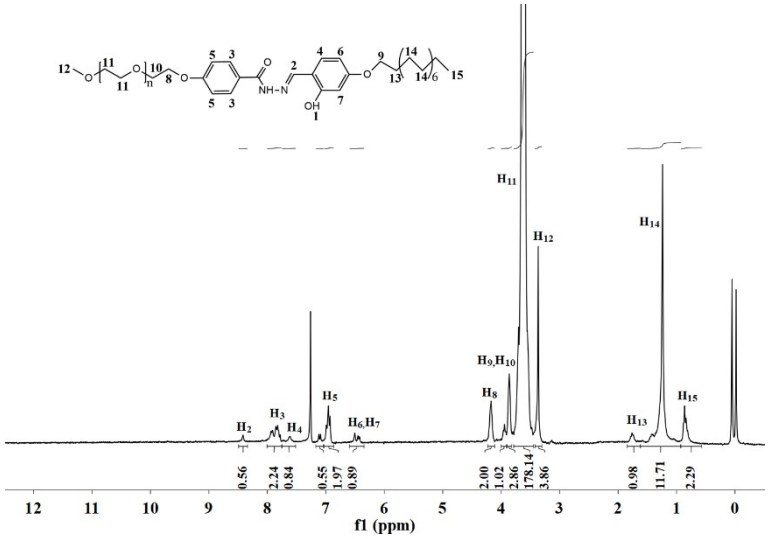

Figure S8. ^{1}H NMR spectrum of polymer mPEG-Dye in $CDCl_3$.

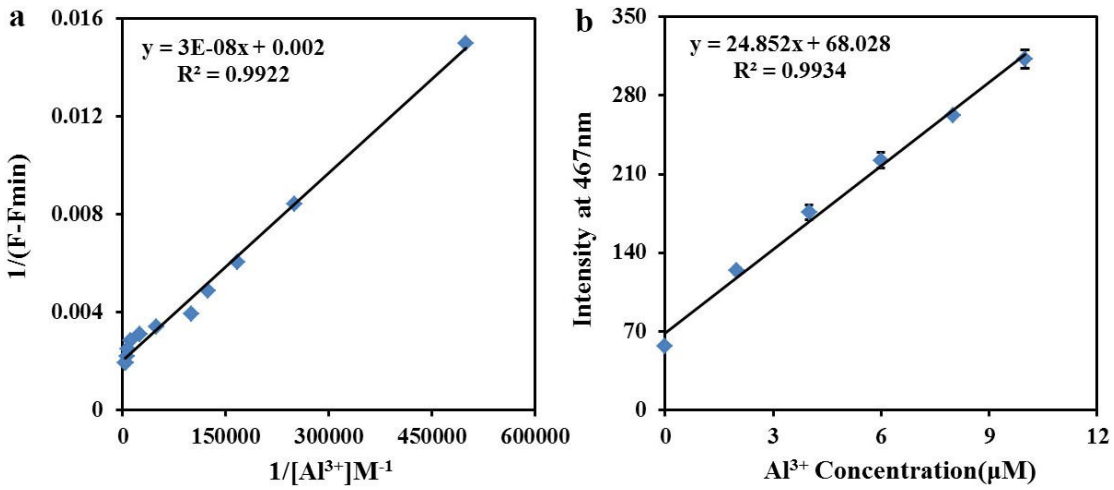

Figure S9. (a) Benesi-Hildebrand analysis of the emission changes for the complexation between mPEG-Dye and Al^{3+}. (b) Linear fluorescence enhancement of mPEG-Dye (20 μM) response to Al^{3+} concentration (0-10 μM).

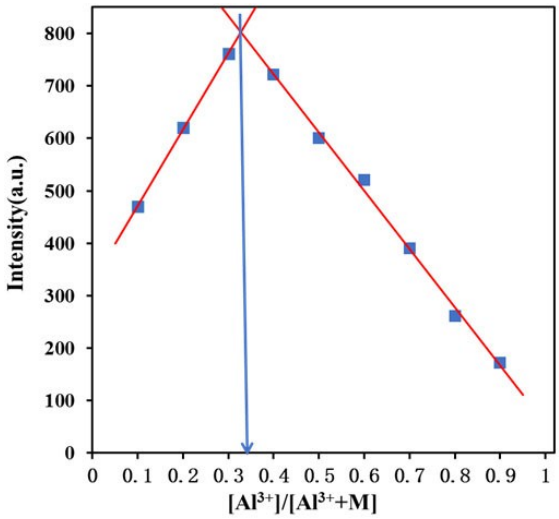

Figure S10. Job's plots for determining the stoichiometry of mPEG-Dye (M) and Al^{3+} in H_2O. The total con centration of mPEG-Dye and Al^{3+} was 20 μM (λ_{ex} = 408 nm, λ_{em} = 467 nm).

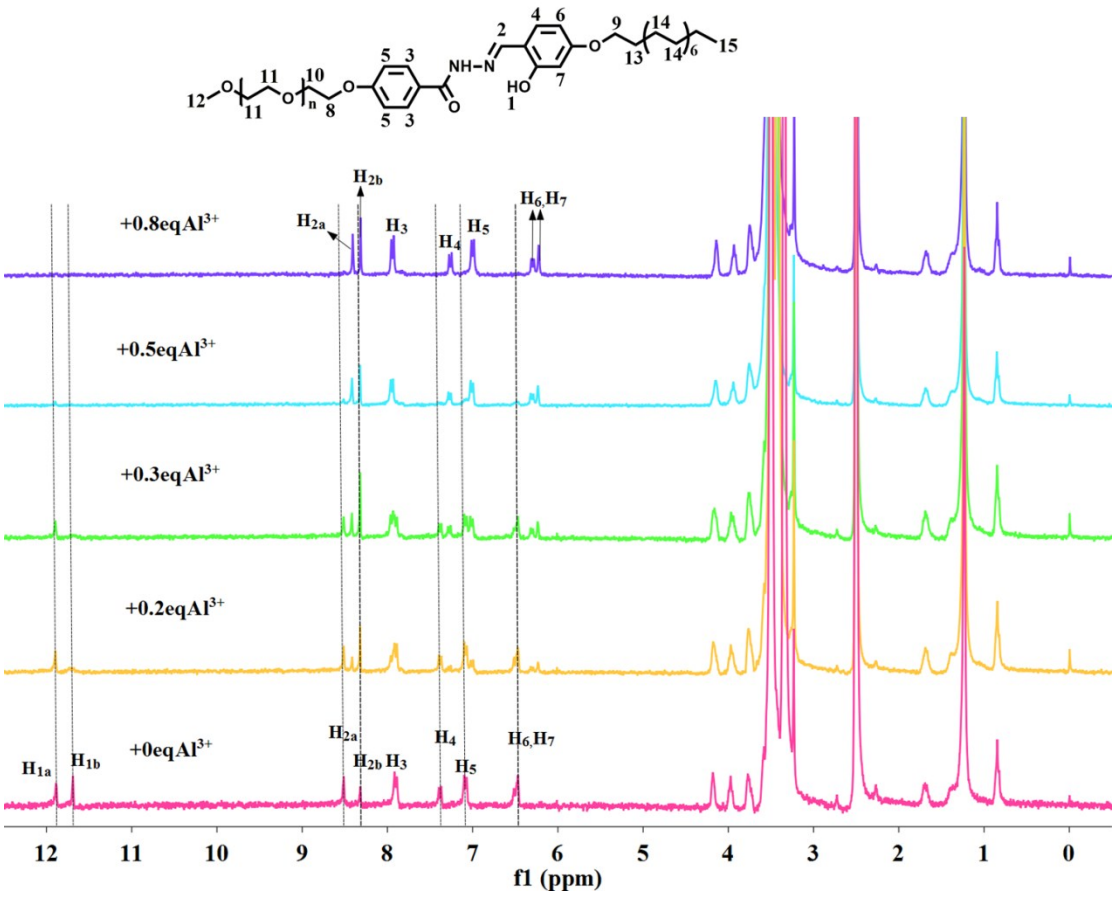

Figure S11. ^{1}H NMR of mPEG-Dye (10 mM) in DMSO-d_6 upon addition of various amount of Al^{3+} cation.

Table S1. Physicochemical properties of two micelles

Sample	TEM particle size(nm)	Hydrodynamic particle size(nm)	PDI
mPEG-Dye	15±3	18±0.05	0.213±0.01
mPEG-Dye-Biotin	18±3	21±0.04	0.201±0.01

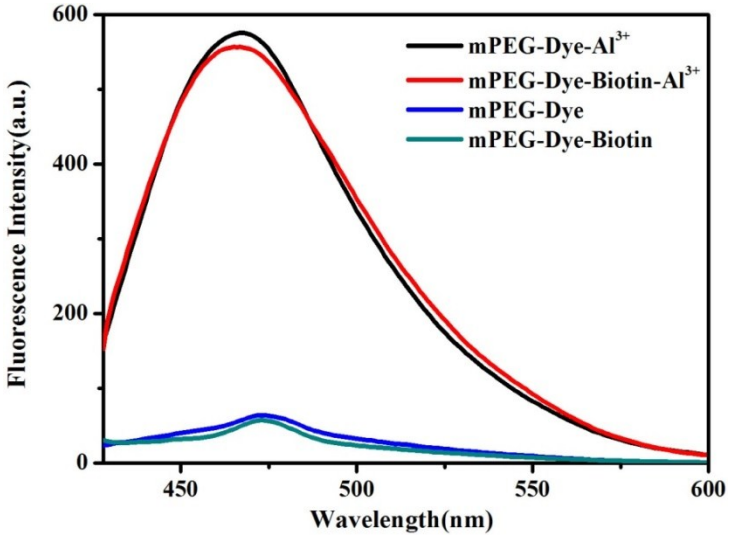

Figure S12. Fluorescence spectra of mPEG-Dye (20 μM) alone, mPEG-Dye-Biotin (20 μM) alone, mPEG-Dye (20 μM) with Al^{3+} (200 μM) and mPEG-Dye-Biotin (20 μM) with Al^{3+} (200 μM) in H_2O.

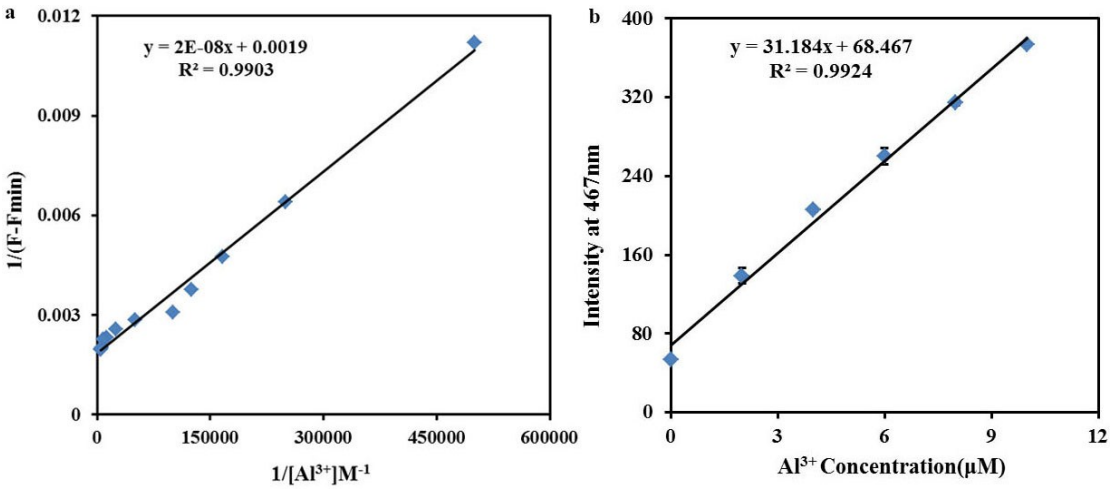

Figure S13. (a) Benesi-Hildebrand analysis of the emission changes for the complexation between mPEG-Dye-Biotin and Al^{3+}. (b) Linear fluorescence enhancement of mPEG-Dye-Biotin (20 μM) response to Al^{3+} concentration (0-10 μM).

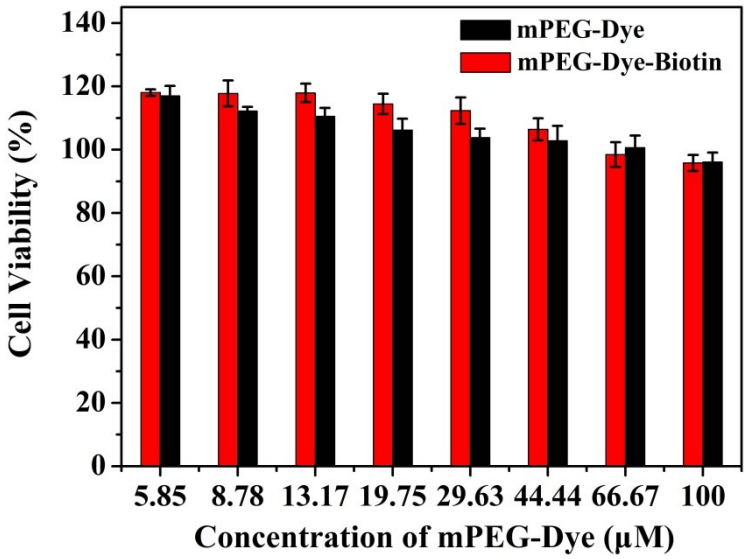

Figure S14. Cytotoxicity of mPEG-Dye-Biotin and mPEG-Dye against HeLa cells. Data are presented as ±SD (n=4).

Table S2 Comparison of some schiff base probes for Al^{3+} detection.

Probe	Testing media	Association Constant (M^{-1})	Detection limit (M)	Imaging Al^{3+} in live cells
Present work (mPEG-Dye-Biotin)	Aqueous solution	9.5×10^4	2.02×10^{-8}	Yes
Diarylethene-based fluorescentchemosensor (1O)[1]	Acetonitrile	4.90×10^4	2.7×10^{-8}	No
Nitrogen heterocycle platformbased fluorescence chemosensor(L)[2]	Methanol	4.72×10^4	1.24×10^{-5}	No
Fluorene-based Schiff-base fluorescent chemosensor(F3)[3]	CH_3CN	5.44×10^4	3.1×10^{-7}	No
Tetra(3-[benzoylhydrazone]-methyl-4-hydroxyphenyl) ethene (IV)[4]	DMSO: H_2O (9:1, v/v)	9.44×10^2	5×10^{-7}	No
Oligothiophene-phenylamine-based fluorescence sensor (3TP)[5]	THF: H_2O (7:3, v/v)	8.66×10^5	1.77×10^{-7}	No
2-amino-4,5-imidazoledicarbo-nitrile and 8-hydroxy-julolidine-9-carboxaldehyde(1)[6]	MeOH**:** H_2O (5:15, v/v)	2.7×10^3	3.44×10^{-6}	No
Fluorescence chemosensor based on rhodamine and azobenzene moieties(L)[7]	C_2H_5OH:H_2O (4:1, v/v)	7.03×10^3	1.1×10^{-7}	No
Schiff base fluorescence probe (STH)[8]	EtOH:H_2O (9:1, v/v)	6.74×10^3	$1.07 \times 1\ 0^{-6}$	Yes
Unsymmetrical azine derivative (NDEA)[9]	DMSO: H_2O: MeOH (0.1 : 1.9 :8.0, v/v)	2.47×10^4	1.65×10^{-7}	Yes
Schiff base-type fluorescent chemosensor[10]	Aqueous solution	7.80×10^4	0.17×10^{-6}	Yes

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