Supporting Information

A Highly Sensitive and Selective Turn-on Fluorescent Probe

for Pb(II) ion based on Coumarin-quinoline Platform

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Materials and Instrument

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using TMS as internal standard. Mass spectra were obtained with Waters GCT premier, LCMS-2010 and GCT CA127 Micronass UK, Waters LCT Premier XE. Steady-state emission spectra were recorded at ambient temperature on a Hitachi F-7000 Spectrophotometer and UV/Vis spectra were recorded on a Perkin-Elmer Lambda 950 UV-visible spectrophotometer. IR spectra were obtained on a Nicolet AVATAR 360FT-IR.

Preparation of T1



Scheme S1 Synthesis route of T1

8-BnT-HQC^{S1} (1 mmol, 0.34 g) and 3-AC^{S2} (1.1 mmmol, 0.18 g) acetic acid (0.4 mL) were added to the solution of dry methanol (10 mL), refluxing for 3 h and cooling to room temperature. Obtained residue by filtrate was further refined by refluxing in absolute CH₃OH, affording the faint yellow solid (0.28 g, 68%). ¹H NMR (400 MHz, CD₃CN, TMS), δ H [ppm]: 8.39 (dd, J = 13.7, 8.5 Hz, 2H), 7.76 (dd, J = 9.6, 8.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.58 (s, 1H), 7.53 (d, J = 6.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.31-7.35 (m, 4H), 7.07 (dd, J = 12.6, 8.5 Hz, 2H), 6.08 (d, J = 5.7 Hz, 2H), 5.07 (s, 2H), 5.06 (s, 2H). ESI-Mass (m/z): [M+H⁺]⁺ Calcd. for C₂₉H₂₁N₅O₃, 488.51, found 489.73.

Characterization of T1



Fig. S1 ¹H NMR spectra of T1 in the absence and presence of Pb^{2+} in CD₃CN



Fig. S3 IR spectra of T1 and its Pb2+-complex

Job's plot



Fig. S4. The Job's plot of T1 with Pb²⁺, where the difference in I₄₆₆ nm was plotted against the χ_{Pb} at an invariant total concentration of 20 μ M in buffer solution (CH₃CN:H₂O = 95:5, v/v, 10 mM HEPES, pH 7.2).

Determination of K_d

The apparent dissociation constants (K_d) of **T1** with Pb²⁺ was determined using the nonlinear least-squares analysis⁸³ based on a 1:1 complex expression:

$$F = F_0 + \frac{F_{\text{max}} - F_0}{2} \left\{ 1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L} - \left[\left(1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L} \right)^2 - 4 \frac{C_M}{C_L} \right]^{\frac{1}{2}} \right\}$$

Where F and F_0 are the fluorescence intensities of **T1** in the presence and absence of Pb²⁺, C_M and C_L are the concentrations of Pb²⁺ and **T1**, and K_s is the stability constant.



Fig. S5 A nonlinear fitting curve of fluorescence intensity of T1 versus [Pb²⁺]/[T1] at 466 nm.

Detection limit

The calibration curve was obtained by plotting $[Pb^{2+}]$ -I₄₆₆ when adding different concentration of Pb²⁺ (from 6 μ M to 20 μ M) to T1 (20 μ M) in buffer solution (CH₃CN:H₂O = 95:5, v/v, pH 7.2) under room temperature. The results were summarized based on 15 measurements.



Fig. S6 A linear fitting curve of fluorescence intensity of T1 versus [Pb²⁺] at 466 nm.

Stability of imine of T1



Figure S7. The fluorescence intensity at 466 nm of T1 and T1-Pb²⁺ with 3 h. Black squre: T1 (20 μ M) was stored in CH₃CN/H₂O (95/5) for 3 h. The fluorescence intensity at 466 nm was recorded for 3 h. Red round: Pb²⁺ (40 μ M) was added to fresh prepared T1 solution (20 μ M), the fluorescence intensity was recorded for 3 h. Blue triangle: T1 (20 μ M) was stored in CH₃CN/H₂O (95/5) for 3 h, followed by the addition of Pb²⁺ (40 μ M). Then the fluorescence intensity at 466 nm was recorded for 3 h.

Fluorescence quantum yields of T1

The quantum yields were calculated according to the following equation: S4-S5

$$\Phi = \Phi_R \frac{A_R F_S n_S^2}{A_S F_R n_R^2}$$

in which the subscript R and S stand for standard samples (quinine sulfate in 0.1 M H_2SO_4) and target sample (T1), respectively. Φ is the quantum yield, F is the integrated emission spectrum. n is the refractive index for the solvent. Quantum yields of T1 were determined using quinine sulfate as the reference. Quinine sulfate in 0.1 M H_2SO_4 was estimated to 0.54.

Sensing material	Target	Medium	pН	K _d (µM)	Reference
4,4-dimethyl-4H-5-oxa-1,3-dithia-6,11- diazacyclopenta[a]anthracen-2-one	Pb ²⁺	MeOH/H ₂ O/ NEt ₄ OH (2/1/7)	<mark>4-1</mark> 0	23	S6
Leadfluor-1	Pb ²⁺	HEPES	7	23±4	S 7
2-Ferrocenylimidazo[4,5-b]pyridine	Pb ²⁺	CH ₃ CN	-	1.6	S 8
4-(4-Pyridineethenyl) tetrathiafulvalene	Pb ²⁺	CH ₃ CN	-	3.8	S 9
Ferrocene-imidazophenazine dyad	Pb ²⁺	CH ₃ CN/H ₂ O (9/1)	-	0.28	S10
Coumarin-quinoline Platform	Pb ²⁺	CH ₃ CN/H ₂ O (95/5)	7.2	0.1	This work

Table S1 Disassociation constant (K_d) some fluorescent probes for Pb(II) detection

Reference:

[S1] A. B. Mandal, N. R. Chereddy and S. Thennarasu, *Dalton Trans.*, 2012, 41, 11753-11759.

[S2] G. Kokotos and C. Tzougraki, J. Heterocyclic Chem., 1986, 23, 87-92.

[S3] a) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, 32, 1133-1139;

b) A. R. Reddi, T. R. Guzman, R. M. Breece, D. L. Tierney and B. R. Gibney, *J. Am. Chem. Soc.*, 2007, **129**, 12815-12827.

[S4] G. A. Crosby and J. N. Demas, J. Phys. Chem., 1971, 75, 991-1024.

[S5] E. Cogné-Laage, J. F. Allemand, O. Ruel, J. B. Baudin, V. Croquette, M. Blanchard-Desce and L. Jullienet, *Chem. Eur. J.*, 2004, **10**, 1445-1455.

- [S6] L. Marbella, B. Serli-Mitasev and P. Basu, Angew. Chem., Int. Ed., 2009, 48, 3996-3998.
- [S7] Q. He, E. W. Miller, A. P. Wong and C. J. Chang, J. Am. Chem. Soc., 2006, 128, 9316-9317.
- [S8] F. Zapata, A. Caballero, A. Espinosa, A. Tárraga and P. Molina, Org. Lett., 2008, 10, 41-44.

[S9] H. Xue, X. J. Tang, L. Z. Wu, L P. Zhang and C. H. Tung, J. Org. Chem., 2005, 70, 9727-9734.

[S10] M. Alfonso, A. Tárraga and P. Molina, J. Org. Chem., 2011, 76, 939-947.