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## Supporting Information Highly selective ratiometric fluorescent probe based on

## diketopyrrolopyrrole for Au<sup>3+</sup>: an experimental and theoretical study

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**Fig. S1.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of compound **1** (DMSO- $d_{\delta}$ ).



**Fig. S2.** Partial <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of compound **1** (in DMSO- $d_{\delta}$ ).



Fig. S3. HRMS-ESI spectra of compound 1.



Fig. S4. The fluorescent intensity of probe 1 (10  $\mu$ M) in various solvents. ( $\lambda_{ex}$ : 485 nm).



Fig. S5: The influence of water content to the fluorescent intensity of probe 1 (10  $\mu$ M). ( $\lambda_{ex}$ : 485 nm).



Fig. S6. Absorption (left) and emission (right) spectra of compound 1 (1×10<sup>-5</sup> M) in DMF/0.01 M PBS buffer (v/v, 4:1,

pH 7.4).



Fig. S7. Reaction time profile of probe 1 (10  $\mu$ M) in the presence of Au<sup>3+</sup> (200  $\mu$ M). The fluorescence intensity ratio ( $I_{610}/I_{555}$ ) of probe 1 was continuously monitored at time intervals in DMF/0.01 M PBS buffer (v/v, 4:1, pH 7.4). ( $\lambda_{ex}$ : 485 nm).



**Fig. S8.** Effect of pH on the fluorescence intensity of **1** (10  $\mu$ M) in DMF/0.01 M PBS buffer (v/v, 4:1, pH 7.4) in the absence (black dot) and presence of Au<sup>3+</sup> (red dot). ( $\lambda_{ex}$ : 485 nm).



**Fig. S9.** Emission spectra of **1** (10  $\mu$ M) in DMF/0.01 M PBS buffer (v/v, 4:1, pH 7.4) (black line); upon addition of 200  $\mu$ M of Au<sup>3+</sup> under the inert gas (red line); upon addition of 200  $\mu$ M of Au<sup>3+</sup> under the atmosphere of oxygen (blue line).  $\lambda_{ex}$ : 485 nm.



Fig. S10. HRMS-ESI spectra of DPP-AL.

Synthesis of DPP-AC: AuCl<sub>3</sub> (10 mmol %) was added to the solution of **1** (25 mg, 0.031 mmol) in 20 ml DMF-H<sub>2</sub>O (v/v = 4:1), and the reaction mixture was stirred for 4h. The solvent was evaporated and the mixture was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 20/1) to give the compound DPP-AC (16 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm) 8.19 (d, *J* = 8.4 Hz, 4H), 8.05 (d, *J* = 8.4 Hz, 4H), 3.94 (t, *J* = 5.2 Hz, 4H), 3.72 (t, *J* = 5.2 Hz, 4H), 3.57-3.55 (m, 12H), 3.50-3.48 (m, 4H), 3.37 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm) 167.8, 162.7, 148.4, 132.6, 131.2, 130.1, 129.9, 110.8, 71.8, 70.5, 68.8, 59.0, 42.5. HRMS-ESI: *m/z* calcd (%) for C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>O<sub>12</sub>: 669.2659 [M+H<sup>+</sup>], found: 669.2665.

The partial <sup>1</sup>H NMR of probe **1** and the isolated **DPP-AC** were shown in Fig. S11. The resonance signals corresponding to semithiocarbazone moiety protons ( $H_c$ ,  $H_d$ ,  $H_e$ ,  $H_f$ ,  $H_g$  and  $H_h$  at  $\delta$  8.23, 7.57, 7.40, 7.24, 12.04, and 10.27 ppm, respectively) of **1** disappeared, and the two doublet resonance signals which indentified as *meso*-aryl protons ( $H_a$  and  $H_b$ ) of **1** downfield shifted from 8.02 to 8.05 and from 8.13 to 8.19, respectively. On the other hand, <sup>13</sup>C resonance peaks of  $C_{\alpha}$  which indentified as carboxylic acid carbon of **DPP-AC** appeared at 167.8 (Fig. S12). Mass spectral analysis of the resulting mixture had shown a corroborative evidence for the product **DPP-AC** formation at *m/z* obsd 669.2665 (M+H<sup>+</sup>) (calcd 669.2659 for (M+H<sup>+</sup>)) (Fig. S13).



**Fig. S11.** (a) Synthesis route of **DPP-AC**; (b) Partial <sup>1</sup>H-NMR of **1** in DMSO-*d*<sub>6</sub>; (c) Partial <sup>1</sup>H-NMR of **DPP-AC** in CDCl<sub>3</sub>/CD<sub>3</sub>OD.



Fig. S12. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **DPP-AC** (CDCl<sub>3</sub>/CD<sub>3</sub>OD).



Fig. S13. HRMS-ESI spectra of DPP-AC.

![](_page_8_Figure_2.jpeg)

Fig. S14. The optimized ground-state and excited-state geometries of probe 1 and selected C=N or N-N or C-N or C-S

or C=S bond lengths (in Å).

![](_page_8_Figure_5.jpeg)

![](_page_8_Figure_6.jpeg)

geometries of product **DPP-AC**.

![](_page_9_Figure_0.jpeg)

![](_page_9_Figure_1.jpeg)

**Fig. S16.** The frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of **1** (enol isomer) and **1** (keto isomer). CT stands for conformation transformation. Excitation and radiative processes are marked as solid lines and the non-radiative processes are marked by dotted lines. For details please refer to **Fig. S11** and **Table** S1-S2.

Type of probe	LOD	Reference
turn-on	0.50 μΜ	Chem. Commun. 2009, 7218-7220
turn-on	50 nM	Org. Lett. 2009, 11, 5610-5613
ratiometric	No data for Au <sup>3+</sup>	Org. Lett. 2010, 12, 5310-5313
turn-on	64 ppb	Org. Lett. 2010, 12, 932-934
turn-on	0.4 ppm (Au <sup>+</sup> )	Org. Lett. 2010, 12, 401-403
turn-on	48 nM	Chem. Commun. 2011, 47, 12506-12508
turn-on	290 nM	Chem. Commun. 2011, 47, 4703-4705
ratiometric (FRET mechanism)	$3.9 \times 10^{-7} M$	Chem. Eur. J. 2011, 17, 9066-9069
turn-on	No data for Au <sup>3+</sup>	Analyst 2012, 137, 4411-4414
turn-on	0.4 µM	Org. Lett. 2012, 14, 5062-5065
on-off	1.50 × 10 <sup>-5</sup> M	Tetrahedron 2013, 69, 2048-2051
ratiometric	8.44 µM	Biosensors Bioelectronics 2013, 49, 438-441.
turn-on	0.6 ppm	Analyst 2013, 138, 3638-3641
ratiometric	8 nM	Chem. Eur. J. 2015, 21, 13201-13205
turn-on	44 nM	Chem. Commun. 2014, 50, 5884-5886
turn-on	65 nM	Chem. Commun. 2014, 50, 1119-1121
turn-on	0.5 ppb	Org. Lett. 2014, 16, 1374-1377
turn-on	95 ppb	Dyes and Pigments 2015, 112, 236-238
turn-on	0.5 nM	J. Org. Chem., 2015, 80, 8530-8538
turn-on	23 nM	Biosensors Bioelectronics 2016, 80, 288-293
ratiometric	18 nM	Present work

Table S1. Comparison of the present probe with existing Au<sup>3+</sup> probes

The detection limit of compound **1** for  $Au^{3+}$  was 18 nM, much lower than that of existing probes except for probe (LOD 0.5 nM) reported by Adhikari *et al.* (Table S3), indicating compound **1** could be used as a high sensitivity probe for  $Au^{3+}$  ions detection.