Electronic Supplementary Information (ESI)

Learn from T-Hg-T and C-Ag-T: Four-input Dual-core Molecular Logic Gate and Its New Application in Cryptography

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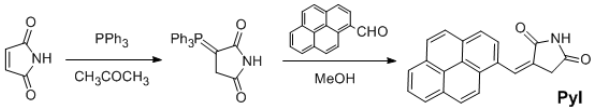
Material & Instrumentation

Maleimide was purchased from Energy-Chemical (China). PPh_3 and Benzaldehyde were purchased from GuangFu (China). 1-Formylpyrene was purchased from TCI. Quinine sulphate was purchased from Alfa Aesar. All other common reagents and solvent were received from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were measured in DMSO-*d6* on Bruker-Avance (400 MHz for ^1H and 101 MHz for ^{13}C) with TMS as an internal reference. HPLC-HRMS were measured with Bruker MicrOTOF QII. UV-vis absorption spectra were obtained using a Varian-Cary50. All the fluorescence measurements were acquired on a Varian-FLR006 and Edinburgh Instrument FLS920.

Synthesis of PyI



A mixture of maleimide (116 mg, 1.2 mmol), PPh_3 (315 mg, 1.2 mmol), and acetone (3 ml) was heated under reflux for 2 h. After cooling, the precipitate was filtered and washed with acetone (20 ml), then dried in vacuo and got a colorless solid (308 mg, 0.86 mmol, yield 72%). It was used for the next step without further purification and mixed with 1-Formylpyrene (198 mg, 0.86 mmol) and methanol (5 ml). The mixture was heated under reflux for 3 h, then cooled at room temperature. The resulting precipitate was filtered, washed with methanol (20 mL) and dried in vacuo to give a yellow power **PyI**: 204 mg, 76% yield. Metamorphosed into brown over 260 ^oC. ^1H NMR (400 MHz, DMSO) δ 11.56 (s, 1H), 8.52 – 8.19 (m, 9H), 8.13 (t, J = 7.6 Hz, 1H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 175.85, 171.80, 131.57, 130.78, 130.17, 129.50, 129.27, 128.62, 128.53, 128.09, 127.81, 127.29, 126.63, 126.27, 126.10, 125.91, 125.03, 123.95, 123.66, 122.64, 34.76. HRMS ($M+H^+$): Cald. For $C_{21}H_{14}NO_2$ 312.1019; Found: 312.1014.

Synthesis of PhI

This imide derivative was synthesized according to the literature method.[1]

Synthesis of PhI-Ag-PhI

PhI (187 mg, 1.0 mmol) was dissolved in 5 mL methanol / DMF. Triethylamine (TEA) (1 equiv.) and $AgNO_3$ solution (85 mg, 0.5 mmol, in DMF) were then added. The resulting precipitate was filtered, washed with methanol / H_2O and dried in vacuo to give a white power **PhI-Ag-PhI**: 52 mg, yield 22%.

Method for making PyI fluorescent paper

The filter papers were soaked in the ethanol solution of 10 mM **PyI**. After 0.5 h, they were removed out of solution and dried at room temperature.

(1) (a) Y. Luo, L. Ma, H. Zheng, L. Chen, R. Li, C. He, S. Yang, X. Ye, Z. Chen, Z. Li, Y. Gao, J. Han, G. He, L. Yang and Y. Wei, *J. Med. Chem.*, 2010, **53**, 273; (b) H. M. Albers, L. J. Hendrickx, R. J. van Tol, J. Hausmann, A. Perrakis and H. Ovaa, *J. Med. Chem.*, 2011, **54**, 4619.

Emission spectra of PyI in EtOH / H_2O mixture

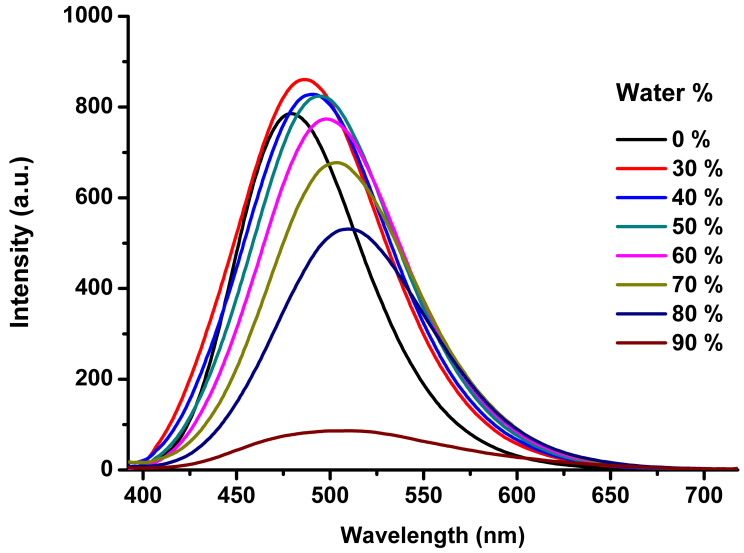


Fig. S1 Emission spectra of the **PyI** (5 μM) in EtOH and 30~90 % water in EtOH.

Photo of PyI in the solid and EtOH solution under UV lamp

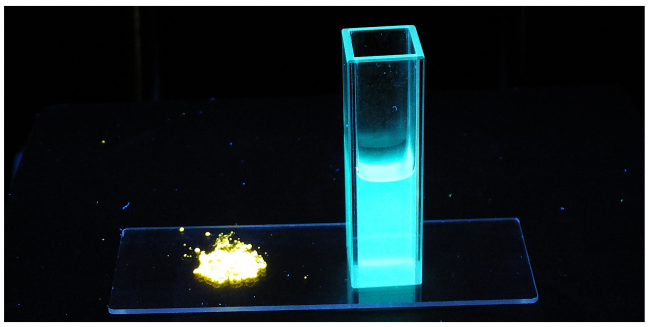


Fig. S2 Fluorescence of **PyI** under UV lamp (365 nm) (left) in the solid (right) 5 μM in EtOH solution.

Quenching effect by Hg^{2+} and Ag^{+} in different pH

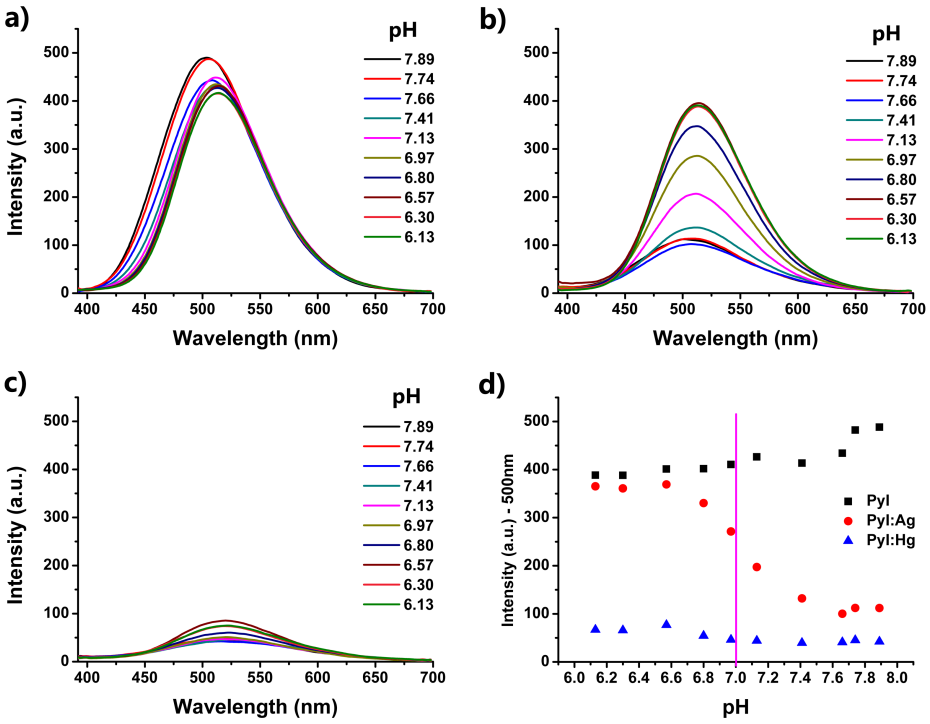


Fig. S3 Emission spectra of **PyI** (5 μM) in EtOH-PBS buffer (5 mM) (1:4, v/v) (a) in pH 6.13~7.89, without Ag^{+} and Hg^{2+}; (b) adding 5 μM Ag^{+} or Hg^{2+} in pH 6.13~7.89; (c) adding 5 μM Hg^{2+} in pH 6.13~7.89; (d) The fluorescence intensity at 500 nm without and with 5 μM Ag^{+} or Hg^{2+} vs pH, (λ_{ex} = 375 nm).

Fluorescence quantum yield (Φ) and % fluorescence quenching of PyI.

pH	Compound	Fluorescence quantum yield[a] Φ	% Fluorescence quenching[b,c]
6	**PyI**	0.39	-
6	**PyI**:Hg^{2+}	0.08	77 (92)
8	**PyI**	0.45	-
8	**PyI**:Ag^{+}	0.10	85 (90)
8	**PyI**:Hg^{2+}	0.09	87 (93)

Table. S1 [a]Quinine sulphate was used as standard whose quantum yield is 0.63 in 0.1N H_2SO_4 at λ_{ex}= 375 nm; [b]calculated at 0.5 equiv. of metal ions; [c]values in parentheses correspond to 1.0 equiv. of metal ions. (EtOH-PBS buffer (5 mM) (1:4, v/v))

Emission spectra of PyI versus Hg^{2+} or Ag^{+} concentration

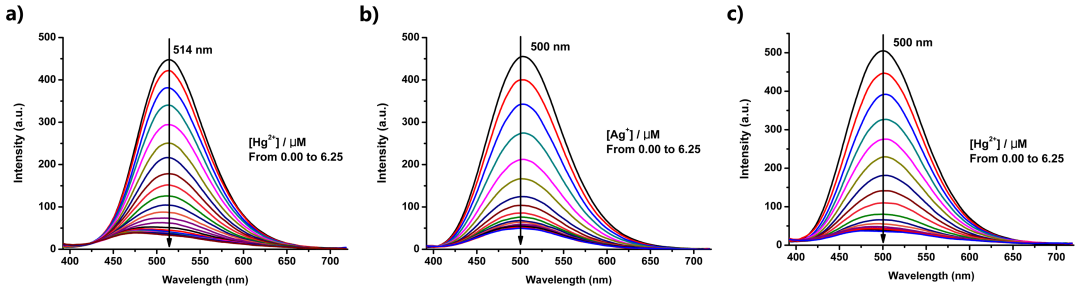


Fig. S4 Emission spectra of **PyI** (5 μM) in EtOH-PBS buffer (5 mM) (1:4, v/v) (a) in pH 6.0, adding different concentrations of Hg^{2+}; (b) in pH 8.0, adding different concentrations of Ag^{+}; (c) in pH 8.0, adding different concentrations of Hg^{2+}, (λ_{ex} = 375 nm).

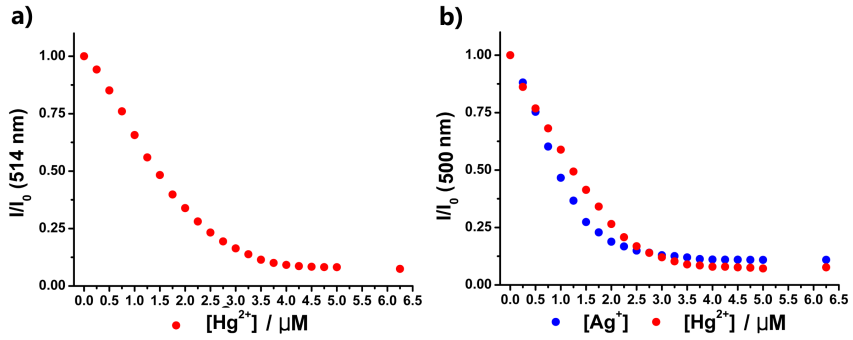


Fig. S5 Plots of fluorescence intensity **PyI** (5.0 μM) at (a) 514 nm versus Hg^{2+} concentration in EtOH-PBS buffer (5 mM, pH = 6.0) (1:4, v/v); (b) 500 nm versus Hg^{2+} and Ag^{+} concentration EtOH-PBS buffer (5 mM, pH = 8.0) (1:4, v/v). (λ_{ex} = 375 nm).

Job plot of Hg^{2+} and Ag^{+} complex formation

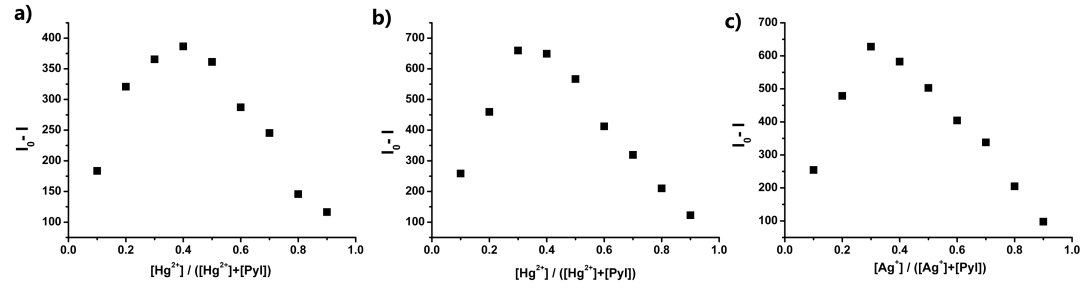


Fig. S6 Job plot of Hg^{2+} and Ag^{+} complex formation. I_0 is the fluorescence intensity ((a) at 500 nm in pH 6.0; (b, c) at 514 nm in pH 8.0) when [Hg^{2+}] or [Ag^{2+}] = 0. [Hg^{2+}] + [**PyI**] = 0.01 mM or [Ag^{+}] + [**PyI**] = 0.01 mM.

Emission spectra of logic gate PyI with different inputs

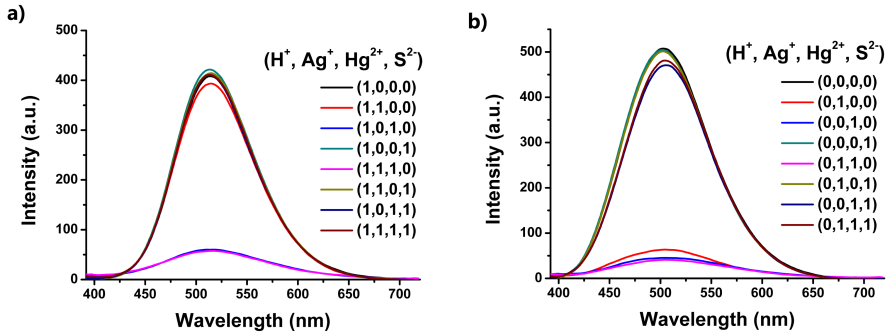


Fig. S7 Emission spectra of **PyI** (5 μM) in EtOH-PBS buffer (5 mM) (1:4, v/v) with different inputs (5 μM $Hg(NO_3)_2$, 5 μM $AgNO_3$ and 15 μM Na_2S) (a) in pH 6.0; (b) in pH 8.0, (λ_{ex} = 375 nm).

Photos of the reversibility of logic gate PyI

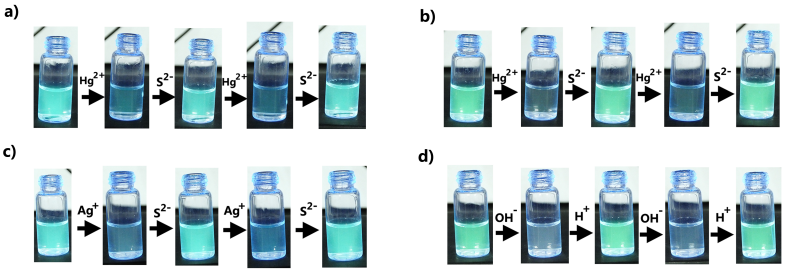


Fig. S8 Fluorescence of **PyI** (5 μM) under UV lamp (365 nm) in EtOH-PBS buffer (5 mM) (1:4, v/v) by alternating addition of (a) Hg^{2+} and S^{2-} in pH 6.0; (b) Hg^{2+} and S^{2-} in pH 8.0; (c) Ag^{+} and S^{2-} in pH 8.0; (d) a little dilute HNO_3 and NaOH in the presence of 5 μM Ag^{+}.

UV-Vis spectra of PyI for Hg^{2+} and Ag^{+} in different pH

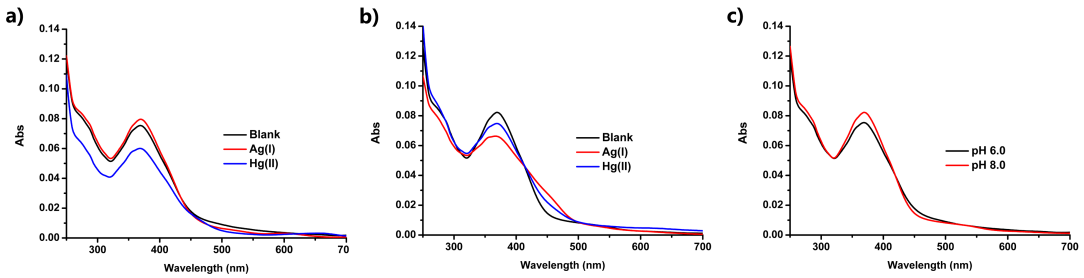


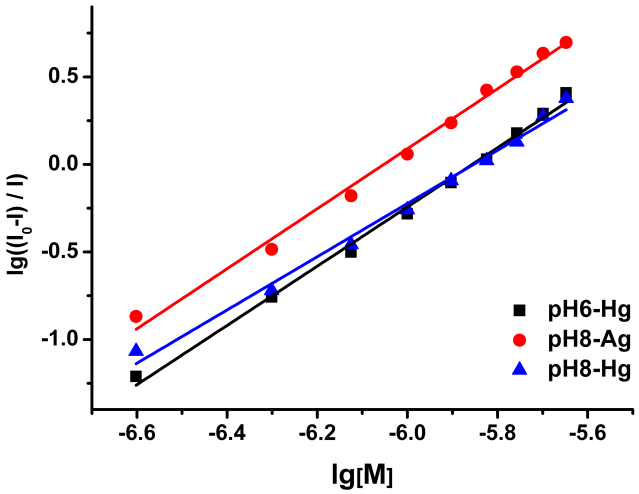
Fig. S9 UV-Vis spectra of **PyI** (0.02 mM) in EtOH-PBS buffer (20 mM) (1:4, v/v) (a) in pH 6.0, adding 0.02 mM Ag^{+} or Hg^{2+}; (b) in pH 8.0, adding 0.02 mM Ag^{+} or Hg^{2+}; (c) in pH 6.0 or pH 8.0, without Ag^{+} or Hg^{2+}.

Hill equation[2]

Hill equation describes the quantitative relationship between the ligand with receptor. Because the quenching efficiency of Ag^{+} or Hg^{2+} to fluorescent probe **PyI** are high, the **Hill equation** can be described as the following:

$$\lg\frac{I_0 - I}{I} = n\lg[M] + \lg K_{app}$$

where I_0 and I are fluorescence intensities of **PyI** in the absence and presence of Ag^{+} or Hg^{2+} and **[*M*]** is the concentration of Ag^{+} or Hg^{2+} respectively. By fitting the fluorescence quenching data, the apparent association constant K_{app} and Hill coefficient n (the binding of **PyI** to Ag^{+} or Hg^{2+}) can then be obtained. (n>1, positive cooperativity; n=1, noncooperativity and n<1, negative cooperativity.)



pH	Compound	lgK_{app}	n	R^2
6	**PyI**:Hg^{2+}	9.91	1.7	0.994
8	**PyI**:Ag^{+}	10.4	1.7	0.992
8	**PyI**:Hg^{2+}	8.90	1.5	0.990

Fig. S10 / Table S2. Fluorescence quenching data of **PyI** by Hg^{2+} and Ag^{+} fitted with **Hill equation** (solid line).

(2) J. Gao, Y. Lai, C. Wu and Y. Zhao, *Nanoscale*, 2013, **5**, 8242.

PyI in different pH

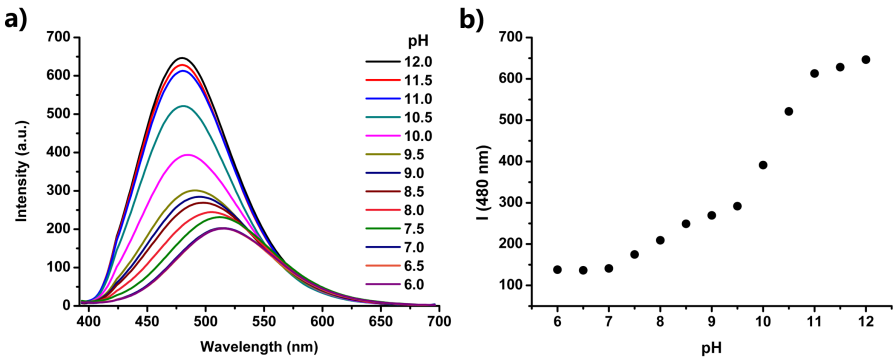
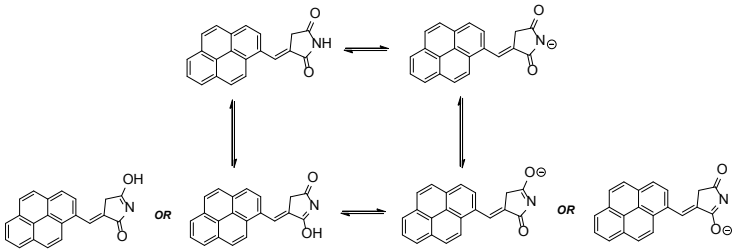


Fig. S11 (a) Emission spectra of **PyI** (5 μM) in EtOH-PBS buffer (5 mM) (1:4, v/v) in pH 6.0~12.0; (b) The fluorescence intensity at 480 nm vs pH, (λ_{ex} = 375 nm).



Scheme S1 The conversion of **PyI** (5 μM) in the base environment.

Fluorescence lifetime spectra of PyI

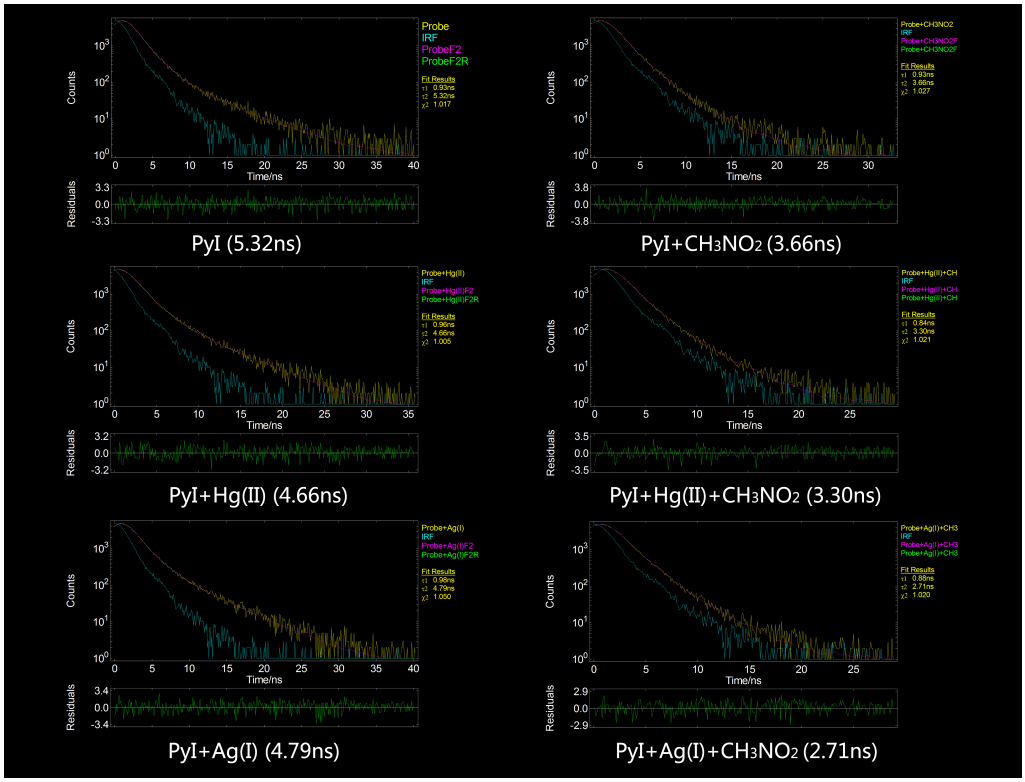


Fig. S12 Fluorescence lifetime spectra of **PyI**, **PyI** + CH_3NO_2, **PyI** + Hg^{2+}, **PyI** + Hg^{2+} + CH_3NO_2, **PyI** + Ag^+, **PyI** + Ag^+ + CH_3NO_2 in EtOH-PBS buffer (1:4, v/v) in pH 8.0.

The function of the logic gate PyI

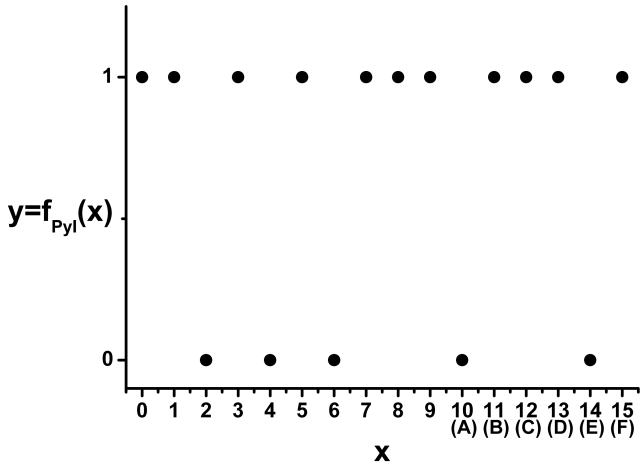


Fig. S13 The encryption function of the logic gate **PyI**.

Transcoded by the logic gate PyI

Table S3. Detailed steps.

Steps	Details
1	ABCD 2346 EAF (Secret letter)
2	A→1010 B→1011 C→1100 D→1101
	2→0010 3→0011 4→0100 6→0110
	E→1110 A→1010 F→1111 (Hexadecimal→Binary)
3	1010→0 1011→1 1100→1 1101→1
	0010→0 0011→1 0100→0 0110→0
	1110→0 1010→0 1111→1 (Outputs by **PyI**)
4[a]	0111→.--- 0100→.-.. 001→..-
5	.---→J .-..→L ..-→U (Transcoded by Morse alphabet)

[a] "0" = "." / "1" = "-"

The security and reliability of the encryption by PyI

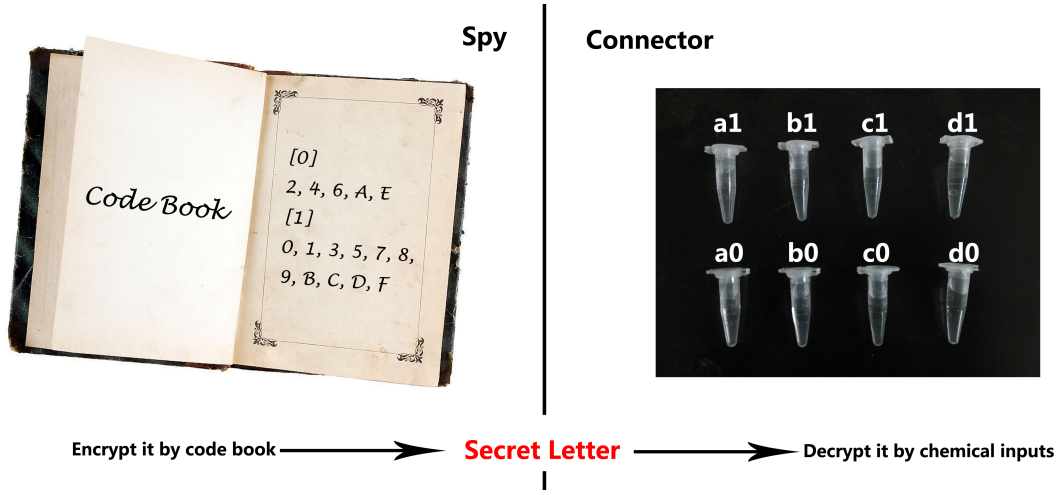


Fig. S14 The code book (spy) and the chemical inputs (connector).

Table S4. Chemical input tubes.

a1	b1	c1	d1	a0	b0	c0	d0
PBS	Ag^{+}	Hg^{2+}	S^{2-}	PBS	H_2O	H_2O	H_2O
pH=6.0	5 μM	5 μM	15 μM	pH=8.0	-	-	-

***Example*:**

(*Encryption*) When the the spy wanted to sent the message "0", he could write "A" in the fluorescent paper.

(*Decryption*) After getting the secret letter, the connector added (a1, b0, c1, d0) into the fluorescent paper to get the message "0".

Others: By changing the chemical input tubes as following, we could get 384 kinds of code systems by **PyI**.

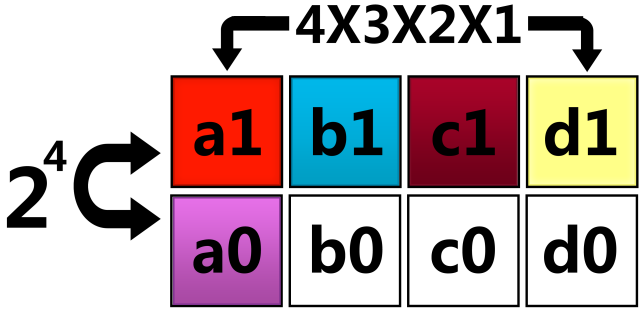


Fig. S15 The changing of the chemical input tubes.

International Morse Code alphabet[3]

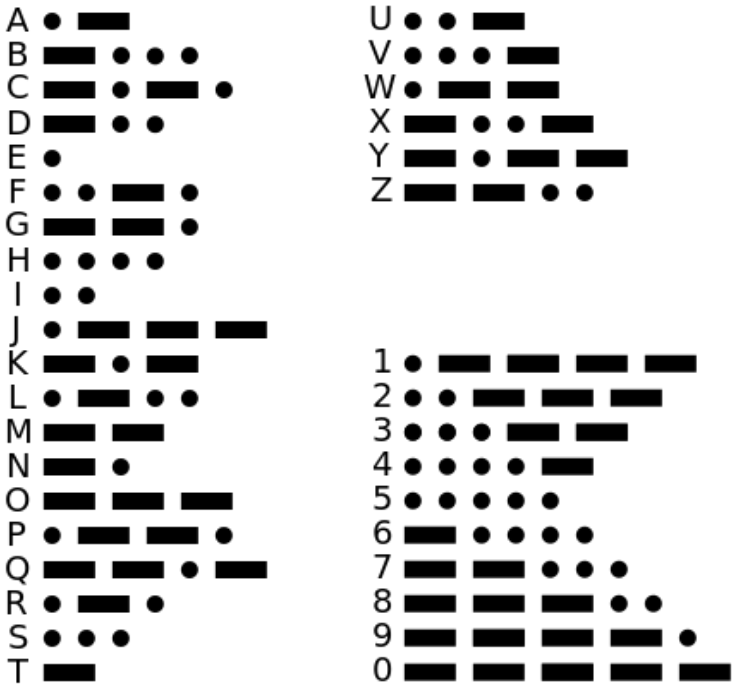


Fig. S16 International Morse Code alphabet

(3) http://en.wikipedia.org/wiki/Morse_code

Electronic engineering symbols for some double-input logic gates[4]

In_1	In_2	Out						
0	0	0	0	1	0	1	0	1
0	1	0	1	0	1	0	1	0
1	0	0	1	0	1	0	0	1
1	1	1	1	0	0	1	0	1
		AND	OR	NOR	XOR	XNOR	INH	IMP

Fig. S17 Names, truth tables, and electronic engineering symbols for some double-input logic gates which will be built-up into larger arrays in subsequent sections. INH = INHIBIT. IMP = IMPLICATION.

(4) A. P. de Silva, *Chem. Asian J.*, 2011, **6**, 750.

^{1}H NMR, ^{13}C NMR spectra of PyI

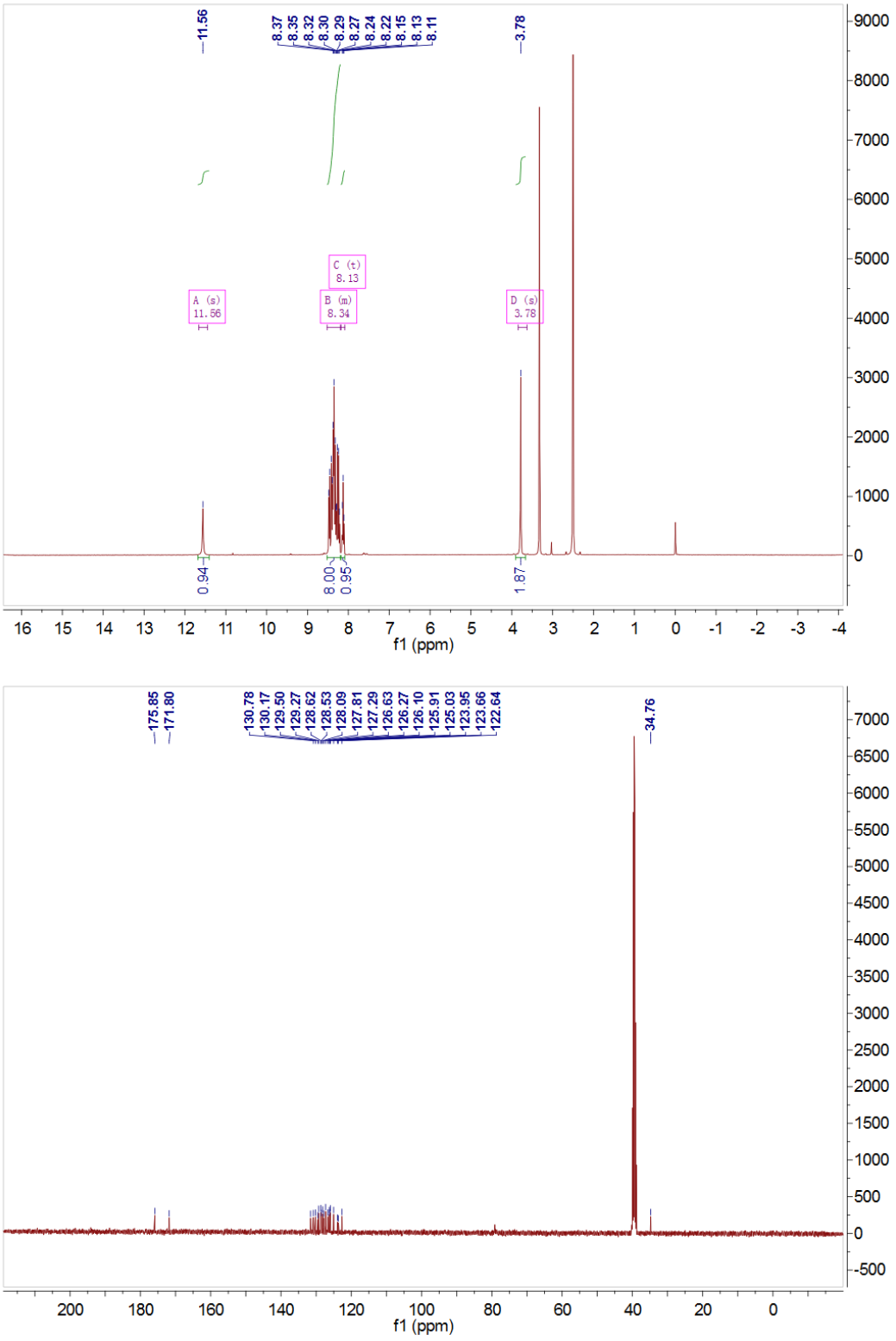


Fig. S18 ^{1}H NMR, ^{13}C NMR spectra of **PyI**.

HRMS data of PyI

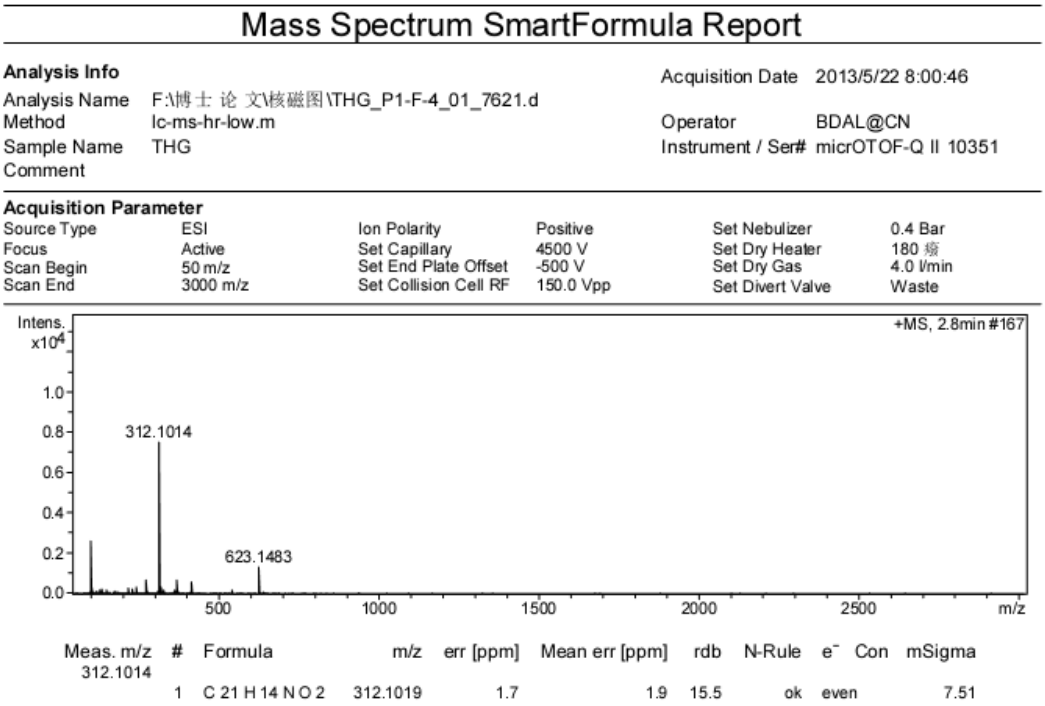


Fig. S19 HRMS data of **PyI**

HRMS data of PhI-Ag-PhI

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	tdy	Instrument / Ser#	micrOTOF-Q II 10351
Comment			

Acquisition Parameter

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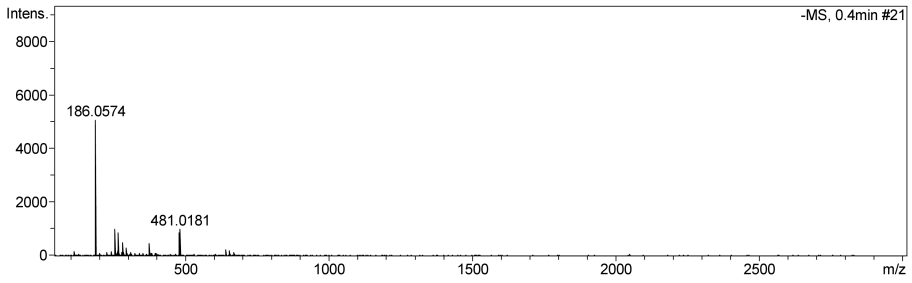
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Con	mSigma
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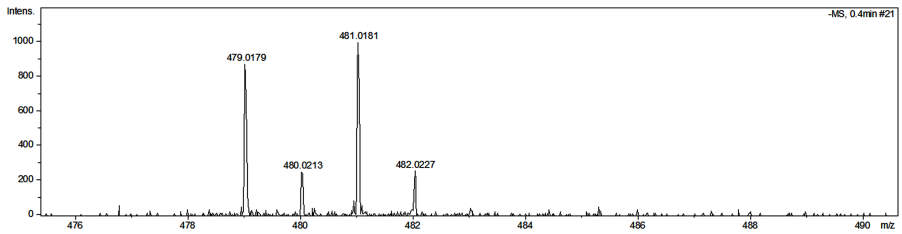

Bruker Compass DataAnalysis 4.0 printed: 2013/8/24 8:42:36 Page 1 of 1

Fig. S20 HRMS data of **PhI-Ag-PhI**.

^{1}H NMR spectra of PhI and PhI-Ag-PhI

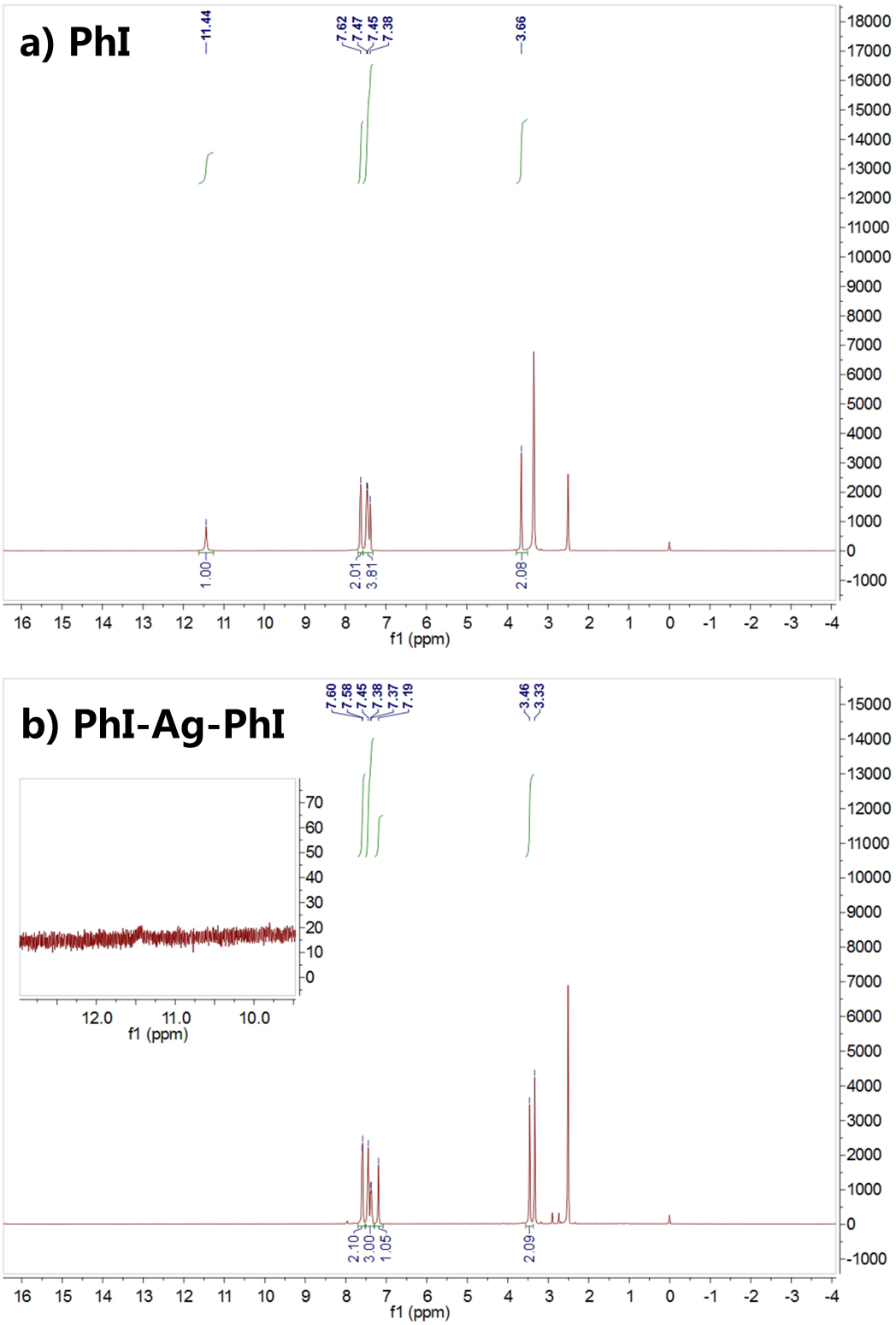

Fig. S21 ^{1}H NMR spectra of **PhI** and **PhI-Ag-PhI**.