Dual-Mode Unsymmetrical Squaraine-Based Sensor for Selective Detection of Hg^{2+} in Aqueous Medium

Cheng Chen, Haijun Dong, Yaqing Chen, Liangqia Guo,

Zhenyu Wang, Jian-Jun Sun, Nanyan Fu*

Key Laboratory of Analysis and Detection for Food Safety, Ministry of Education & Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, and Department of Chemistry, Fuzhou University, Fuzhou 350108, P. R. China

nanyan_fu@fzu.edu.cn

Supplementary Supporting Information

Contents:

1. The characterization of USQ-1.

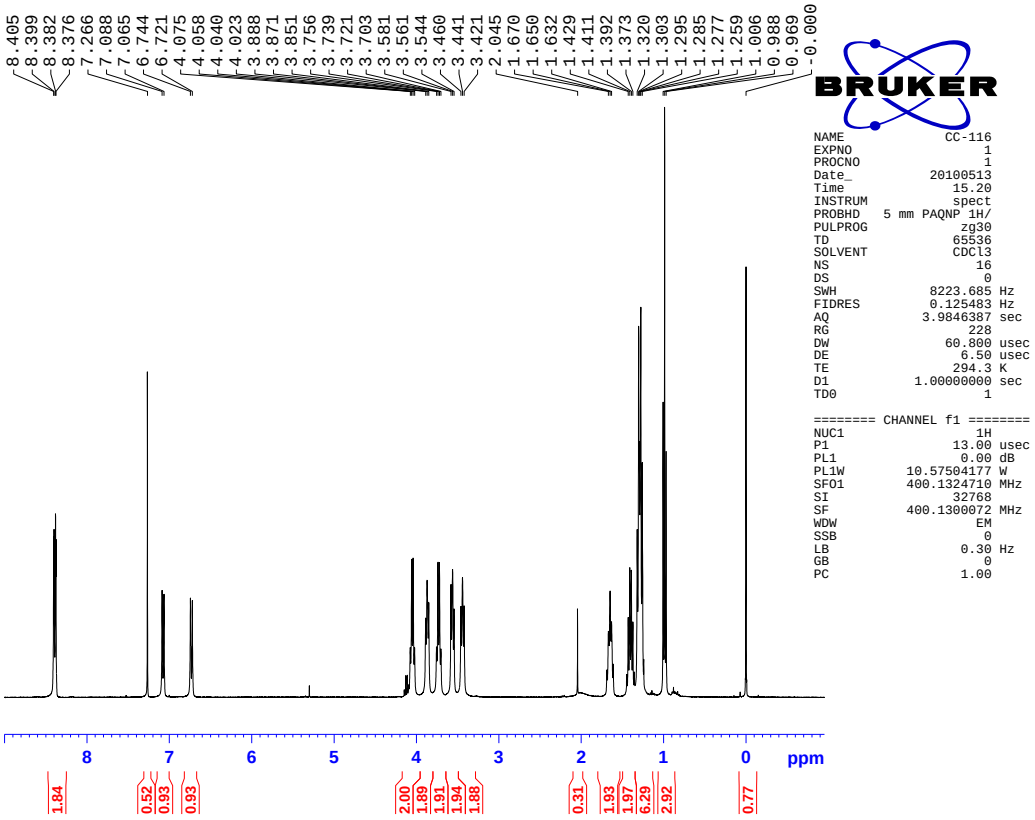

Fig. S1 The ^{1}H NMR spectrum of **USQ-1** in $CDCl_3$ (400MHz).

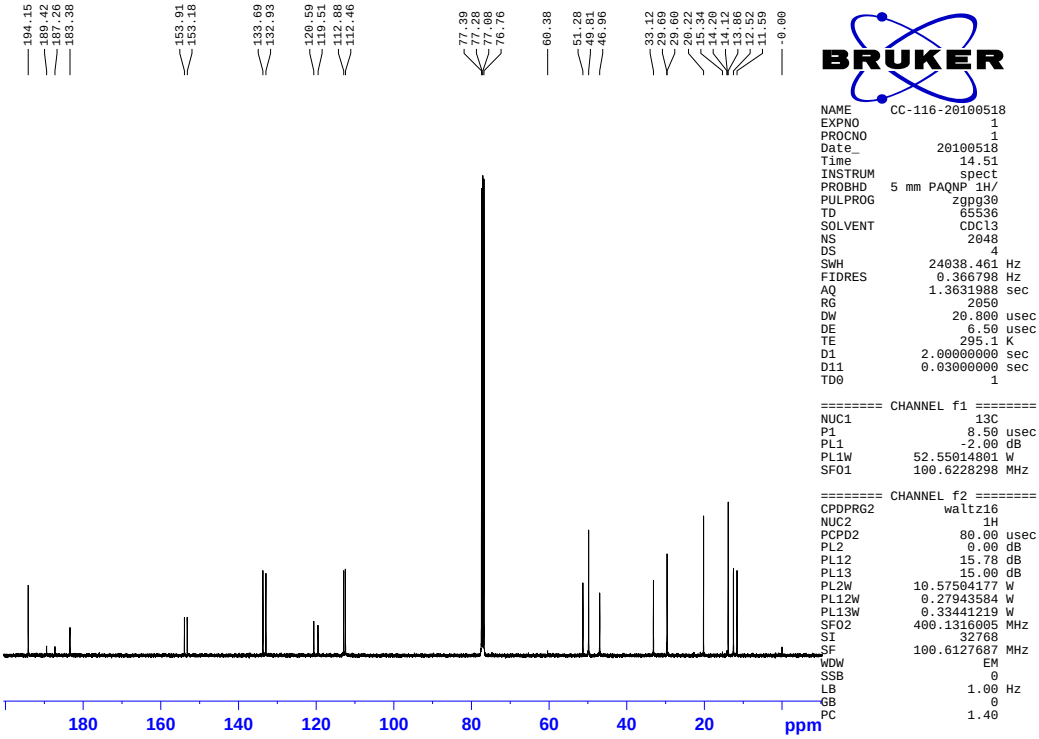

Fig. S2 The ^{13}C NMR spectrum of **USQ-1** in $CDCl_3$ (100 MHz).

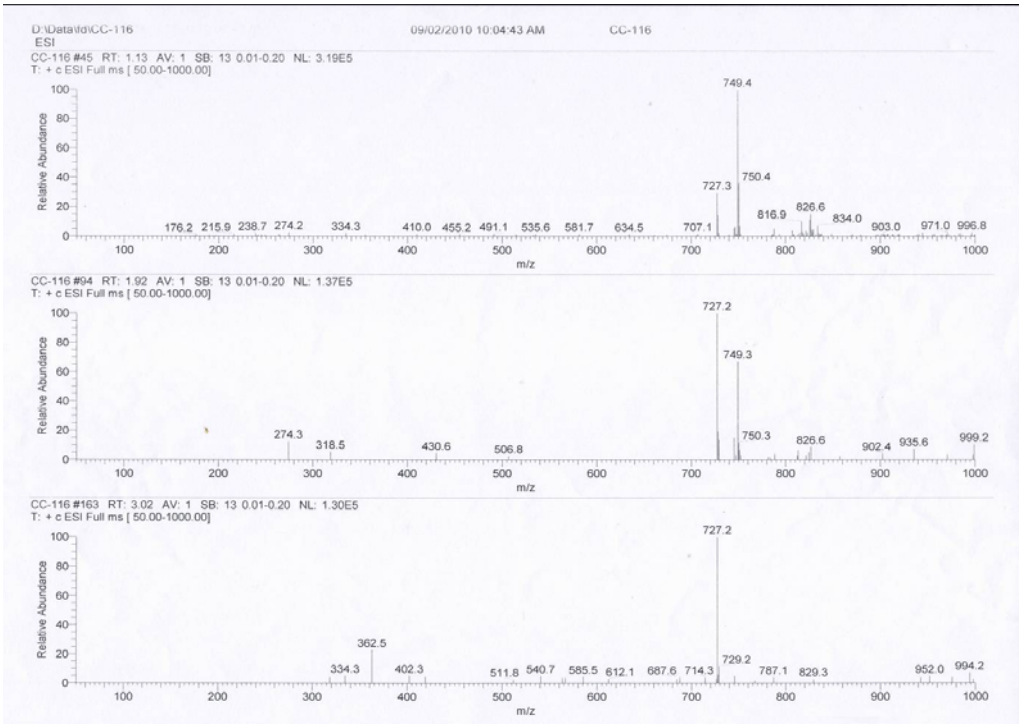

Fig. S3 The MS (ESI) spectrum of **USQ-1**.

2. The absorption responses of USQ-1 to metal ions.

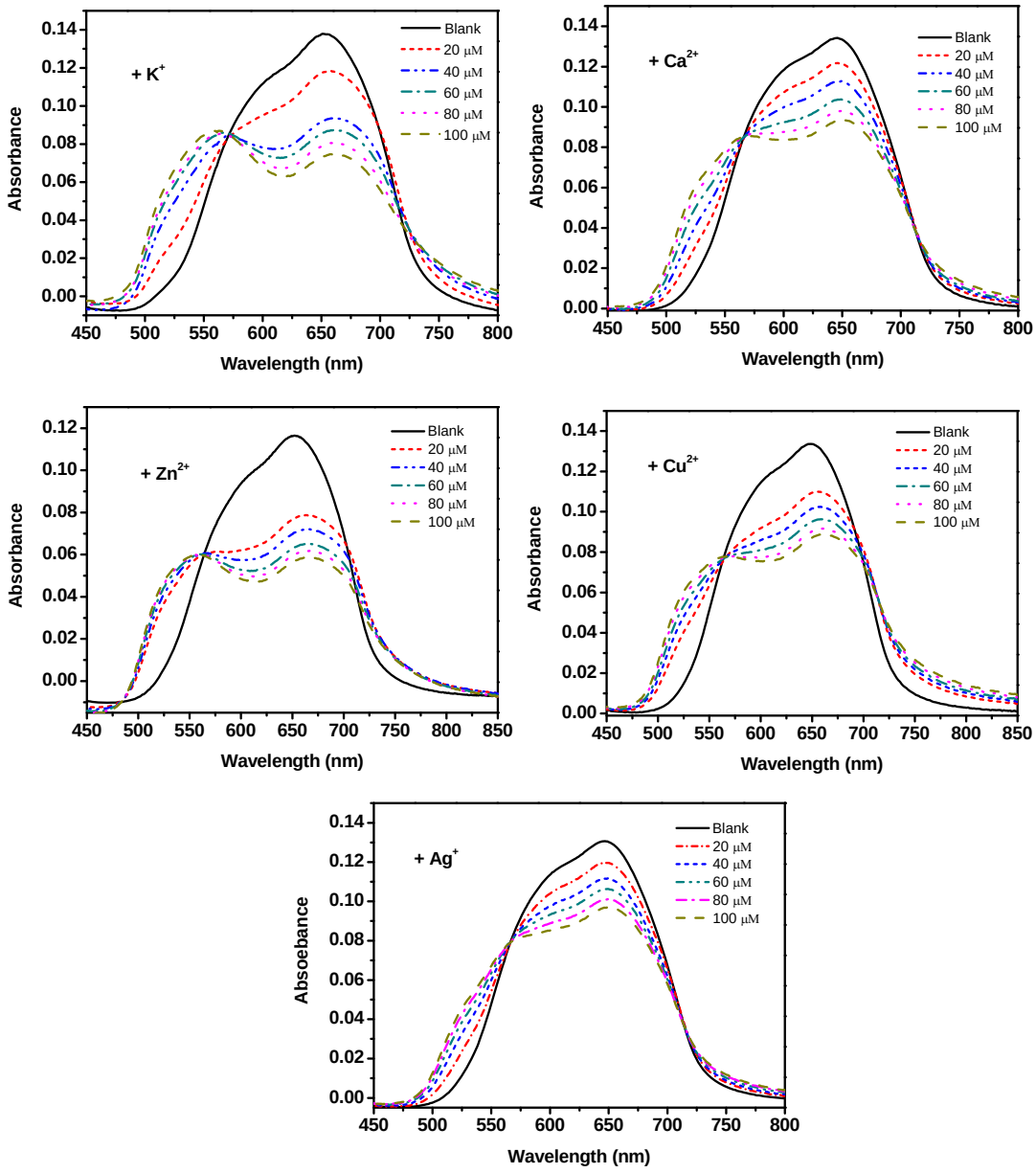

Fig. S4 The absorption spectra of **USQ-1** (2.5 μM) upon addition of K^+, Ca^{2+}, Zn^{2+}, Cu^{2+}, Ag^+ (0-100 μM) in AcOH-H_2O (10:90, v/v) solution.

3. Benesi-Hildebrand equation for 1:1 association.

When assuming a 1:*n* stoichiometry for interaction between **SQ** and Hg^{2+}, the equilibrium is given by the following equation:

$$SQ + nHg^{2+} \overset{K}{\longleftrightarrow} SQ \bullet nHg^{2+} \quad \cdots\cdots\cdots\cdots(1)$$

The association constant, *K*, is therefore expressed as:

$$K = \frac{\left[SQ \bullet nHg^{2+}\right]}{\left[SQ\right]\left[Hg^{2+}\right]^{n}} = \frac{\left[SQ \bullet nHg^{2+}\right]}{\left(\left[SQ\right]_0 - \left[SQ \bullet nHg^{2+}\right]\right)\left(\left[Hg^{2+}\right]_0 - n\left[SQ \bullet nHg^{2+}\right]\right)^{n}} \quad \cdots\cdots\cdots\cdots(2)$$

$[SQ \cdot nHg^{2+}]$, [SQ], and $[Hg^{2+}]$ represent the equilibrium concentrations of the complex, free SQ, and free Hg^{2+}, respectively. $[SQ]_0$ and $[Hg^{2+}]_0$ are the initial concentrations of SQ and Hg^{2+}, respectively. If $[Hg^{2+}]_0 >> [SQ \cdot nHg^{2+}]$, the eq 2 can be simplified as follows:

$$K = \frac{\left[SQ \bullet nHg^{2+}\right]}{\left(\left[SQ\right]_0 - \left[SQ \bullet nHg^{2+}\right]\right)\left(\left[Hg^{2+}\right]_0\right)^{n}} \quad \cdots\cdots\cdots\cdots(3)$$

Eq. 3 is transformed to:

$$\frac{1}{\left[SQ \bullet nHg^{2+}\right]} = \frac{1}{K\left[SQ\right]_0\left(\left[Hg^{2+}\right]_0\right)^{n}} + \frac{1}{\left[SQ\right]_0} \quad \cdots\cdots\cdots\cdots(4)$$

The fluorescence intensity is given by the Beer-Lambert law as follows:

$$I_0 = \varepsilon_0\left[SQ\right]_0 l \quad \cdots\cdots\cdots\cdots(5)$$

$$I = \varepsilon_0\left[SQ\right] l + \varepsilon_\infty\left[SQ \bullet nHg^{2+}\right] l \quad \cdots\cdots\cdots\cdots(6)$$

$$I_{max} = \varepsilon_0\left[SQ\right]_{max} l + \varepsilon_\infty\left[SQ \bullet nHg^{2+}\right]_{max} l \quad \cdots\cdots\cdots\cdots(7)$$

I_0 is the fluorescence intensity of **SQ** without cations, I is the fluorescence intensity of **SQ** obtained with Hg^{2+}, I_{max} is the fluorescence intensity of **SQ** in the presence of excess amount of Hg^{2+}. By means of eqs 5, 6, 7 the following equation is obtained:

$$\frac{I_{max} - I_0}{I - I_0} = \frac{\left[SQ \bullet nHg^{2+}\right]_{max}}{\left[SQ \bullet nHg^{2+}\right]} \quad \cdots\cdots\cdots\cdots(8)$$

In the presence of excess amount of Hg^{2+}, $[SQ \cdot nHg^{2+}]_{max}$ is almost equal to $[SQ]_0$. The eq 8 can therefore be replaced as follows:

$$\frac{I_{max} - I_0}{I - I_0} = \frac{\left[SQ\right]_0}{\left[SQ \bullet nHg^{2+}\right]} \quad \cdots\cdots\cdots\cdots(9)$$

Using eqs 4 and 9, the Benesi-Hildebrand equation is obtained as:

$$\frac{1}{I - I_0} = \frac{1}{K(I_{max} - I_0)\left[Hg^{2+}\right]_0^{n}} + \frac{1}{I_{max} - I_0} \quad \cdots\cdots\cdots\cdots(10)$$

4. The MS (ESI) spectrum of the complex of USQ-1 and Hg^{2+}.

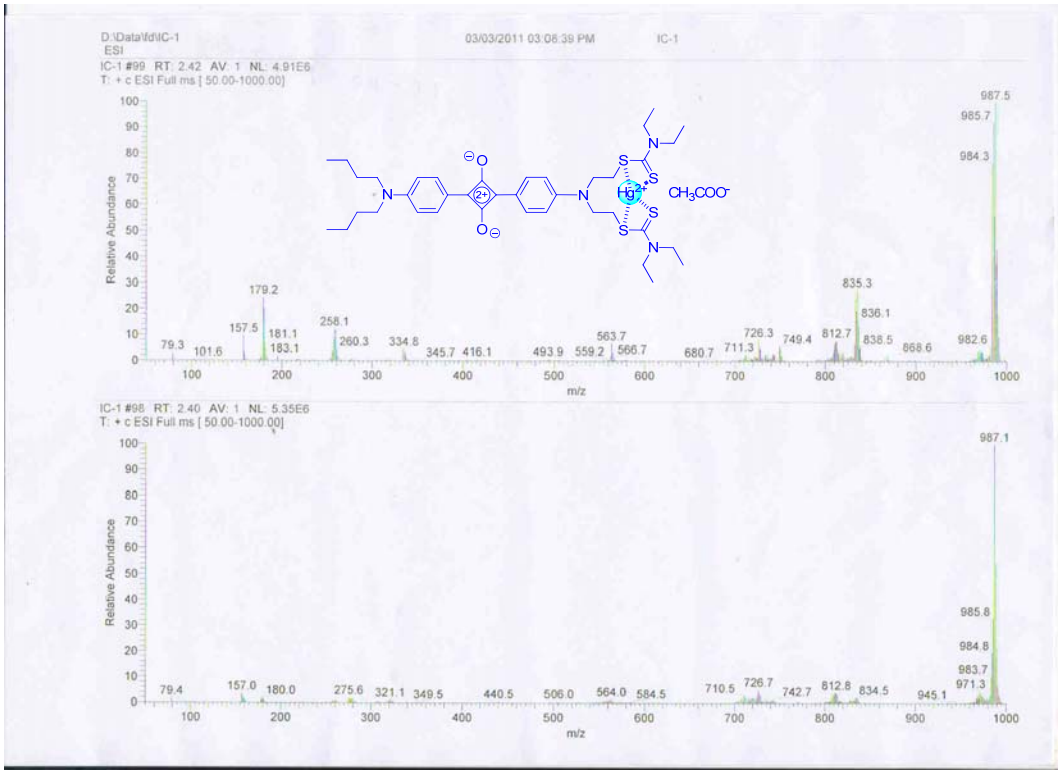

Fig. S5 The MS (ESI) spectrum of the complex of **USQ-1** and Hg^{2+}.

5. The ^{1}H NMR titration of USQ-1.

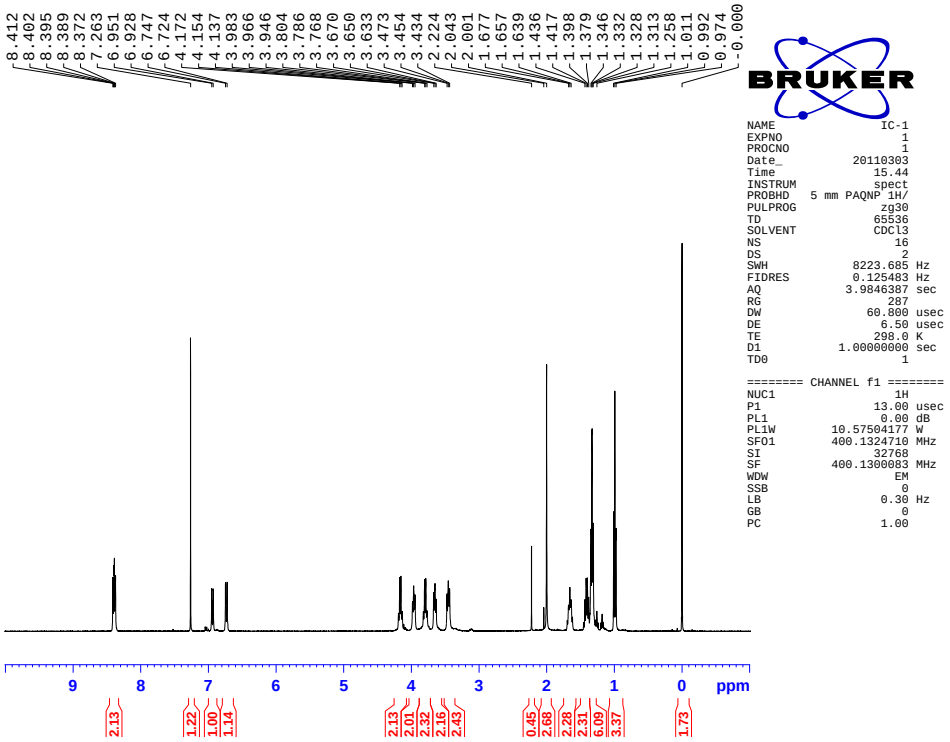

Fig. S6 ^{1}H NMR spectrum of **USQ-1** in $CDCl_3$. The mole ratio of $[(CH_3COO)_2Hg]$ to [**USQ-1**] is 0.5:1.0.

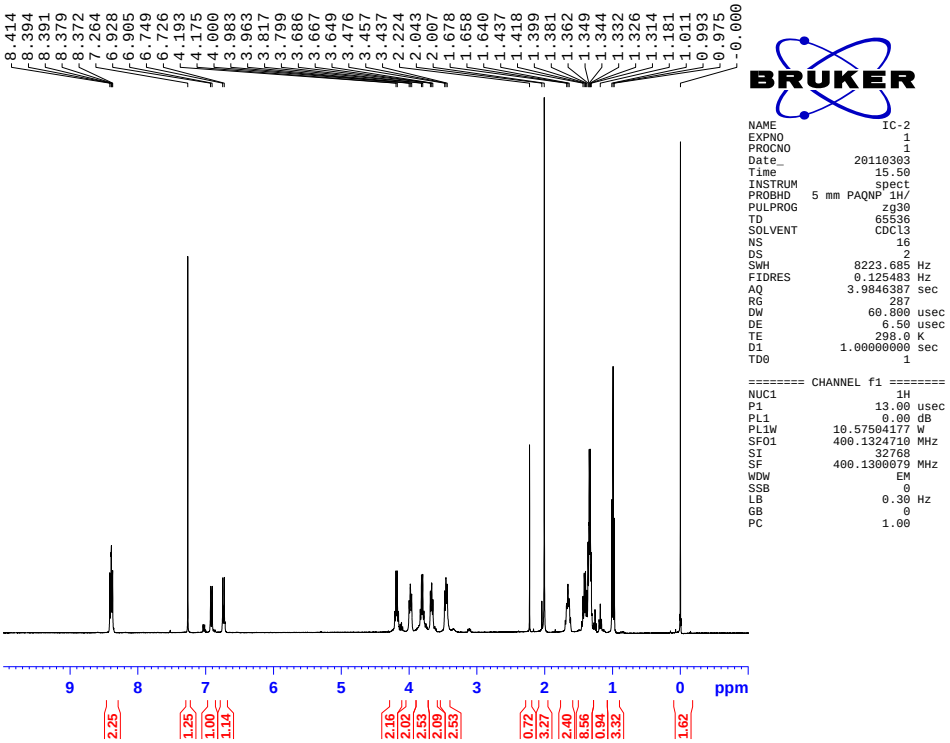

Fig. S7 ^{1}H NMR spectrum of **USQ-1** in $CDCl_3$. The mole ratio of $[(CH_3COO)_2Hg]$ to [**USQ-1**] is 1.2:1.0.

6. The X-ray crystal data and structure refinement for USQ-1.

Table S1 Crystal data and structure refinement for **USQ-1**.

Identification code	**USQ-1**
Empirical formula	C38H54N4O2S4
Formula weight	727.09
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.207(2) Å alpha = 70.90(3)°
	b = 12.542(3) Å beta = 85.07(3)°
	c = 15.394(3) Å gamma = 89.15(3)°
Volume	2036.9(7) $Å^3$
Z	2
Density (calculated)	1.186 g/cm^3
Absorption coefficient	0.269 mm^{-1}
F(000)	780
Crystal size	0.25 x 0.24 x 0.18 mm
Theta range for data collection	3.22° to 27.51°
Index ranges	$-11 \le h \le 14$; $-16 \le k \le 16$; $-19 \le l \le 19$
Reflections collected	17264
Independent reflections	8989 [R(int) = 0.0475]
Reflections observed (>2σ)	5357
Data Completeness	0.960
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8989 / 2 / 445
Goodness-of-fit on F^2	1.158
Final R indices [I > 2σ(I)]	R~1 = 0.1262 wR~2 = 0.2922
R indices (all data)	R~1 = 0.1860 wR~2 = 0.3362
Largest diff. peak and hole	0.704 and -0.512 $e.Å^{-3}$

Table S2 Hydrogen bond lengths (Å) and bond angles (º).

D-H···A		d(D-H)	d(H···A)	d(D···A)	∠DHA
C(8)-H(8A)···S(4)	**#1**	0.99	2.80	3.655(6)	144
C(14)-H(14)···O(2)	**#1**	0.95	2.53	3.182(6)	126
C(26)-H(26B)···S(2)		0.99	2.64	3.109(6)	109
C(28)-H(28A)···S(1)		0.99	2.52	2.879(6)	101
C(29)-H(29B)···S(1)		0.98	2.79	3.323(8)	115
C(30)-H(30B)···S(2)		0.99	2.62	3.037(8)	106
C(33)-H(33A)···S(4)		0.99	2.79	3.239(7)	109
C(35)-H(35A)···S(2)	**#3**	0.99	2.83	3.774(6)	160
C(35)-H(35A)···S(2)	**#2**	0.99	2.83	3.774(6)	161
C(35)-H(35B)···S(3)		0.99	2.39	2.840(6)	107
C(36)-H(36A)···S(3)	**#2**	0.98	2.84	3.578(8)	133
C(37)-H(37B)···S(4)		0.99	2.58	3.017(7)	107

Symmetry codes: **#1**: -x,2-y,-1-z; **#2**: -1-x,-y,-z; **#3**: -x,1-y,-z

Table S3 π-π Stacking Interactions for **USQ-1.**

Cg(I)…Cg(J)	Symmetry code	Dist. Centroids (Å)	Dihedral angle (°)	CgI_Perp dist. (Å)	CgJ_Perp dist. (Å)
Cg(1)→Cg(1)	-X,1-Y,-Z	4.603(3)	0	3.585(2)	3.585(2)
Cg(2)→Cg(2)	1-X,2-Y,-1-Z	4.733(3)	0	-3.578(2)	-3.578(2)

Ring Cg(1): C(19)→C(20)→C(21)→C(22)→C(23)→C(24)→

Ring Cg(2): C(9)→C(10)→C(11)→C(12)→C(13)→C(14)→