Supporting information

Gui-Xian Song[a,b], Qing Tang[a], Ying Huang[*,a,b], Ruibing Wang[c], Yun-Yun Xi[b], Xin-Long Ni[b], Zhu Tao[b], Sai-Feng Xue[b], Jian-Xin Zhang[*,d]

[a] *The Engineering and Research Center for Southwest Bio-Pharmaceutical Resources of National Education Ministry of China, Guizhou University, Guiyang 550025, China*

[b] *Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China*

[c] *State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Taipa, Macau SAR*

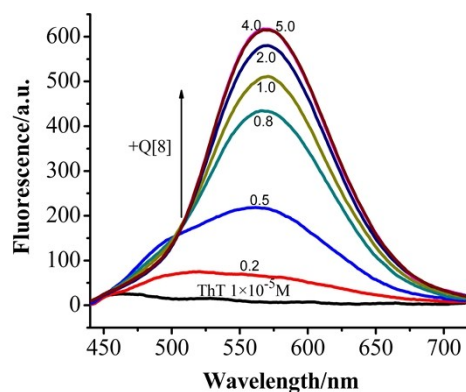[d] *Key Laboratory of Chemistry for Natural Products of Guizhou Province, Guiyang 550002, China*

Fig.1S Fluorescence spectra of ThT(C_{ThT}=2×10^{-5} mol L^{-1}) with Q[8] (0, 0.2, 0.5, 0.8, 1.0, 2.0, 4.0, and 5.0 equiv.) in aquous solution (λ_{ex}=406 nm, slit:10 nm/10 nm)

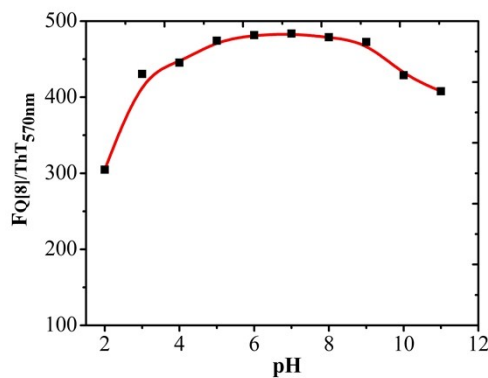**Fig.2S** Fluorescence spectra of Q[8]-ThT($C_{Q[8]}$=2×10^{-5} mol L^{-1}, C_{ThT}=2×10^{-5} mol L^{-1}) with different pH (λ_{ex}=406 nm, slit:10 nm/10 nm)
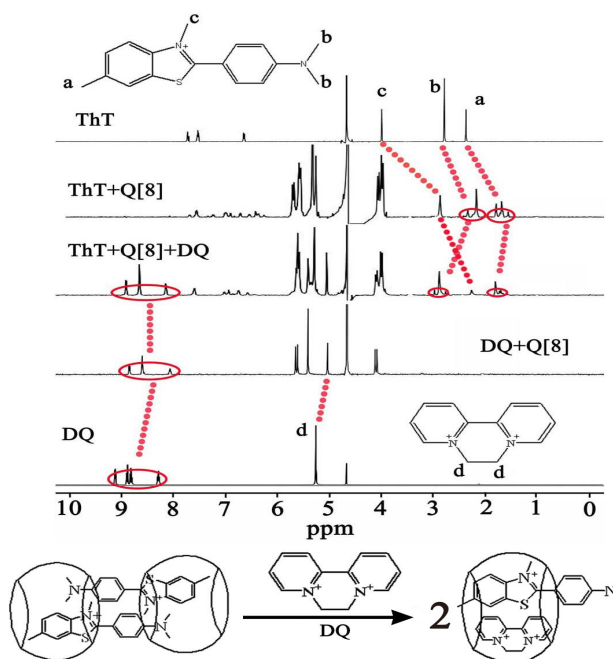
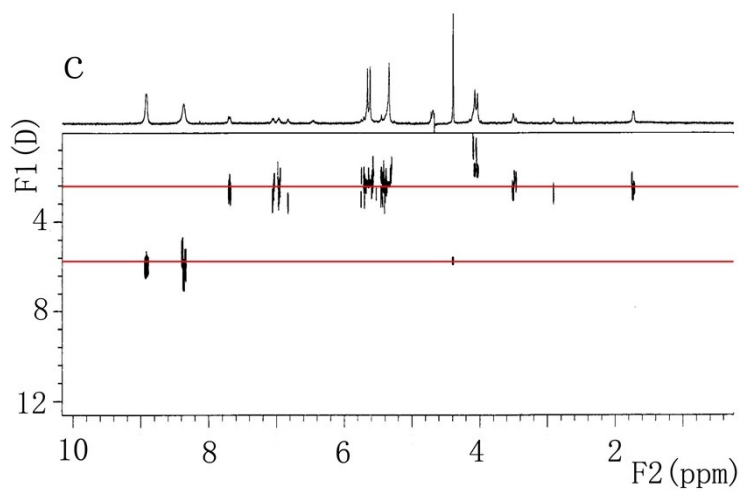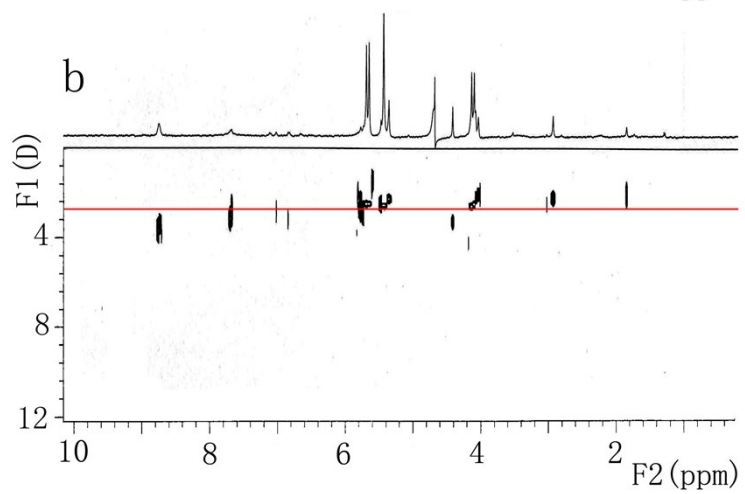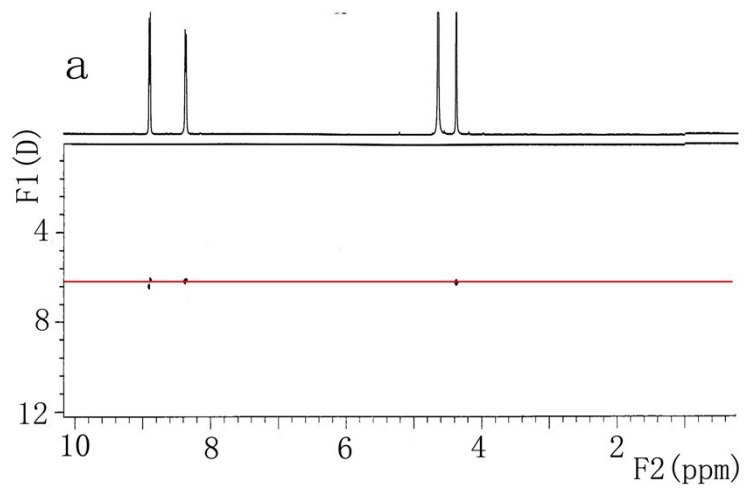**Fig.3S** ^{1}H NMR spectra (400 MHz, D$_2$O) of ThT, DQ in the absence and in the presence of 1 equivalent of Q[8].

DOSY-NMR experiments:

Both free PQ and DQ diffusion coefficients are around **6.2**×10^{-10} m^2/s with very narrow coefficient distribution (see the Fig.4S-a and Fig.4S-d for PQ and DQ DOSY spectra, respectively).

When 1 equivalent molar quantity of PQ or DQ was added into ThT-Q[8] system, the complexed PQ or DQ diffusion coefficient decreased to the range of **2.4 to 5.6** ×10^{-10} m^2/s with very broad diffusion coefficient value distribution, whereas the rest species (ThT-Q[8]) were centered around **2.4**×10^{-10} m^2/s. Therefore, PQ or DQ is likely shuttling rapidly in and out of the Q[8] cavity (where ThT is sitting in tightly due to its higher binding affinity with Q[8] than that of PQ or DQ based on ITC data) (see the Fig.4S-b and Fig.4S-e for PQ-ThT-Q[8] and DQ-ThT-Q[8] DOSY spectra, respectively)

When large excess of PQ or DQ was added into ThT-Q[8] system, the DQ diffusion coefficient moved to around **5.2** ×10^{-10} m^2/s and **4.8** ×10^{-10} m^2/s, respectively. Whereas the rest (ThT-Q[8]) were still centered around **2.4**×10^{-10} m^2/s, implying majority of PQ or DQ in this case is in the free form and only a portion of them is shuttling rapidly between free and complexed state (see the Fig.4S-c and Fig.4S-f for excess PQ or DQ with ThT-Q[8], respectively).

These collective evidence based on 2D DOSY-NMR spectra, as well as ^{1}H NMR spectra of these ternary systems presented in the main text and supporting information, suggest that these herbicides individually form ternary complex PQ(or DQ)-ThT-Q[8].

a

F1 (D)

4

8

12

10   8   6   4   2   F2 (ppm)

b

F1 (D)

4

8

12

10   8   6   4   2   F2 (ppm)

c

F1 (D)

4

8
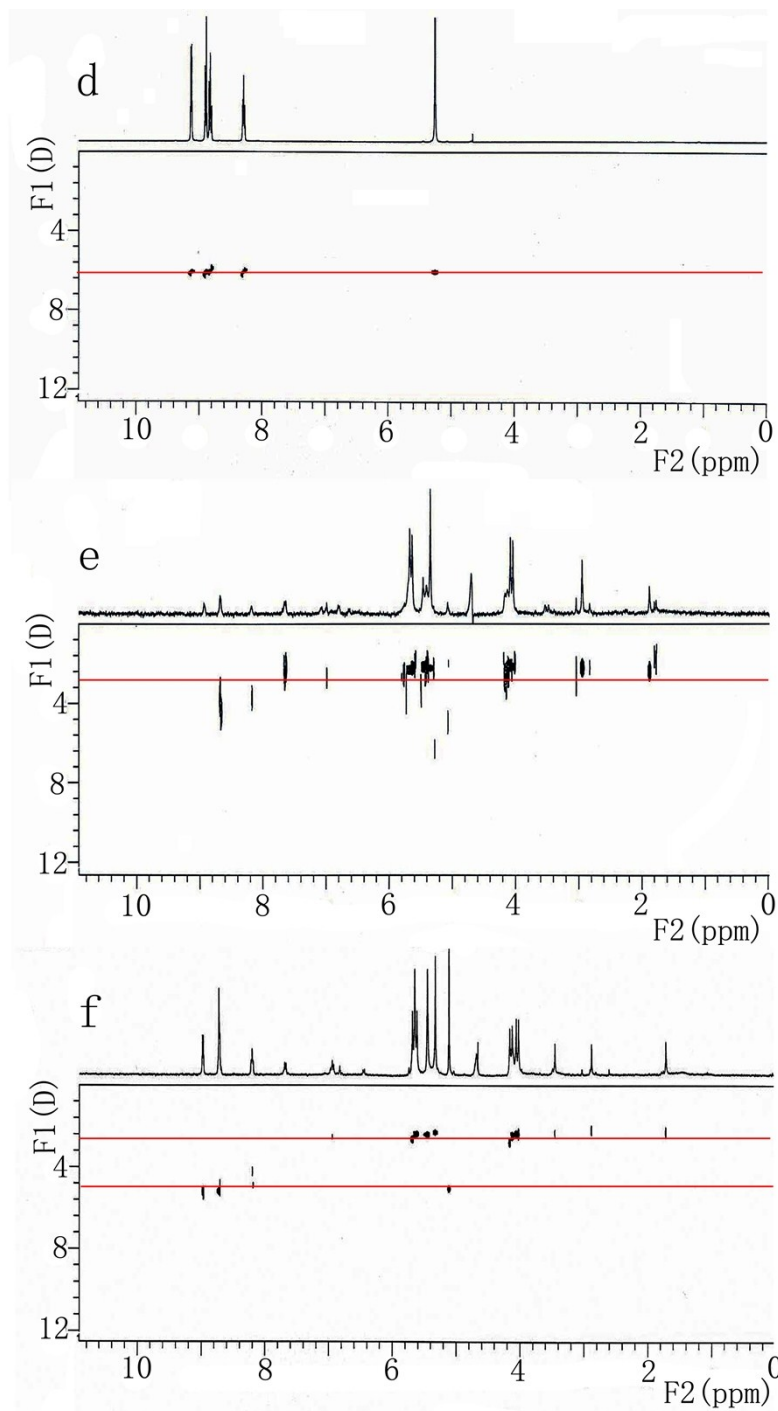
12

10   8   6   4   2   F2 (ppm)

Fig. 4S DOSY NMR spectral changes for Q[8]-ThT-PQ (a-c) and Q[8]-ThT-DQ(d-f) system in D_2O.
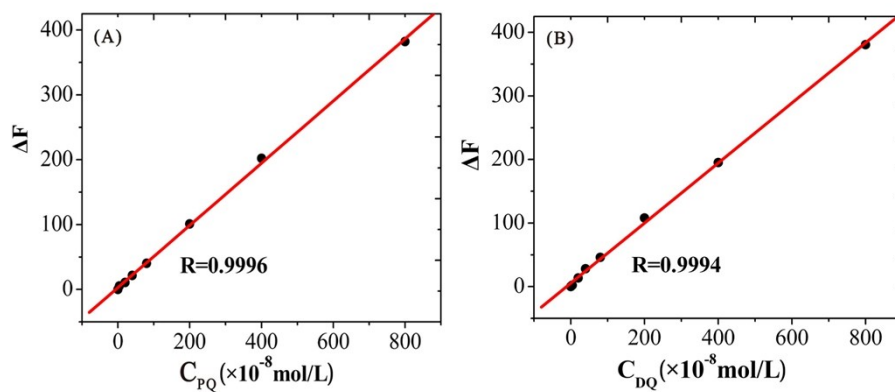

Fig. 5S a Stern-Volmer plot describing the PQ(A) and DQ(B) concentration dependence of the fluorescence intensity of the Q[8]-ThT complexes, a linearity is observed throughout the following range of PQ and DQ concentrations

Table 1S. Selectivity study[a]

Foreign species	Tolerated interference/analyte ratio (w/w)[b]
K^+, Mg^{2+}, SO_4^{2-}, Cl^-	60
Na^+, $H_2PO_4^-$	80
Cu^{2+}, NH_4^+	30
Ca^{2+}	6
Fe^{3+}	10

[a] $C_{ThT} = C_{Q[8]} = C_{herbicides} = 2\times10^{-5}$ mol L^{-1} in aqueous solution at 25.0 °C.
[b] Maximum concentration of interference causing a relative error of <5% in analytical signal.

Table 2S. Maximum concentration tolerated for other quaternary ammonium salt of herbicide to produce interference in PQ/DQ determination.

Interference of PQ	Maximum allowed concentration (mol L^{-1})	Interference of DQ	Maximum allowed concentration (mol L^{-1})
DQ	5×10^{-7}	PQ	5×10^{-7}
DF	5×10^{-7}	DF	5×10^{-7}

Table 3S. Recovery of PQ and DQ in water samples.[a]

Herbicides	Added	Found	This method		HPLC	
	(×10⁻⁶ mol)	(×10⁻⁶ mol)	Recovery[b] (%)	RSD (%)	Recovery[b] (%)	RSD (%)
PQ	10	10.53	105.3	3.89	92.6%	3.53
	20	21.77	108.8	4.01	91.5%	2.95
	40	42.01	105.0	3.75	92.2%	3.18
DQ	10	10.61	106.1	4.77	92.6%	2.98
	20	21.63	108.2	5.02	91.5%	3.53
	40	41.91	104.8	4.95	92.2%	3.61

[a] 2×10^{-5} mol L^{-1} Q[8], 2×10^{-5} mol L^{-1} ThT, in water at 25.0 °C. From the Huaxi river, Guizhou province, China.
[b] Recoveries were means from triplicate determinations.

Table 4S. Recovery of PQ and DQ in cabbage samples.[a]

Herbicides	Added	Found	This method		HPLC	
	(×10⁻⁶ mol)	(×10⁻⁶ mol)	Recovery[b] (%)	RSD (%)	Recovery[b] (%)	RSD (%)

PQ	10	10.72	107.2	4.13	92.3%	3.22
	20	21.22	106.1	4.58	91.1%	2.74
	40	41.96	104.9	5.07	91.5%	2.55
DQ	10	10.68	106.8	5.11	92.3%	4.01
	20	21.14	105.7	4.68	91.1%	3.36
	40	41.96	104.9	3.95	91.5%	3.05

[a] 2×10^{-5} mol L^{-1} Q[8], 2×10^{-5} mol L^{-1} ThT, in water at 25.0 °C. From the Huaxi river, Guizhou province, China.
[b] Recoveries corresponded to the average from triplicate determinations.