

Supplementary Information:

**Diaza-18-crown-6 Appended Dual
7-Hydroxyquinolines; Mercury Ion Recognition in
Aqueous Solution**

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General information and Materials. All solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated glassic sheets (0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV light at 254 nm and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). Infrared spectra were recorded on a Nicolet Magna II 550 FTIR apparatus with automatic background subtraction. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Unity 400 or Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constant (J) are recorded in Hertz (Hz). Low and high resolution mass spectra were recorded by Gas Chromatograph-Mass Spectrometer (Finnigan MAT TSQ-46C GC/MS/MS/ DS).

8,8'-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)bis(methylene)diquinolin-7-ol

(**TDBQ**, see the Figure S1-S2). A solution of anhydrous toluene (50 ml), 4, 13-diaza-18-crown-6 (100 mg, 0.38 mmol), 7-hydroxyquinoline (111 mg, 0.76 mmol), and paraformaldehyde (23 mg,

0.76 mmol) was refluxed for 20 hours. The solvent was evaporated under reduced pressure, and residue was separated by chromatography on silica gel using MeOH/NH₄OH (4/1) as eluant to afford **TDBQ** (132 mg, 60 %). ¹H NMR (400 MHz, CDCl₃, in ppm): δ 8.79 (dd, *J*₁ = 4.2 Hz, *J*₂ = 1.4 Hz, 2H), 8.04 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.4 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.22 (dd, *J*₁ = 8.1 Hz, *J*₂ = 4.2 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 4.60 (s, 4H), 3.77 (t, *J* = 5.4 Hz, 8H), 3.65 (s, 8H), 3.01 (t, *J* = 5.4 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃, in ppm): δ 159.91, 149.35, 147.86, 136.06, 127.86, 122.62, 120.16, 117.79, 114.37, 70.73, 68.92, 54.04, 52.64. MS (FAB) *m/z* 577 (M+H)⁺. HRMS calcd. for C₃₂H₄₁O₆N₄ 577.3026, found 577.3030.

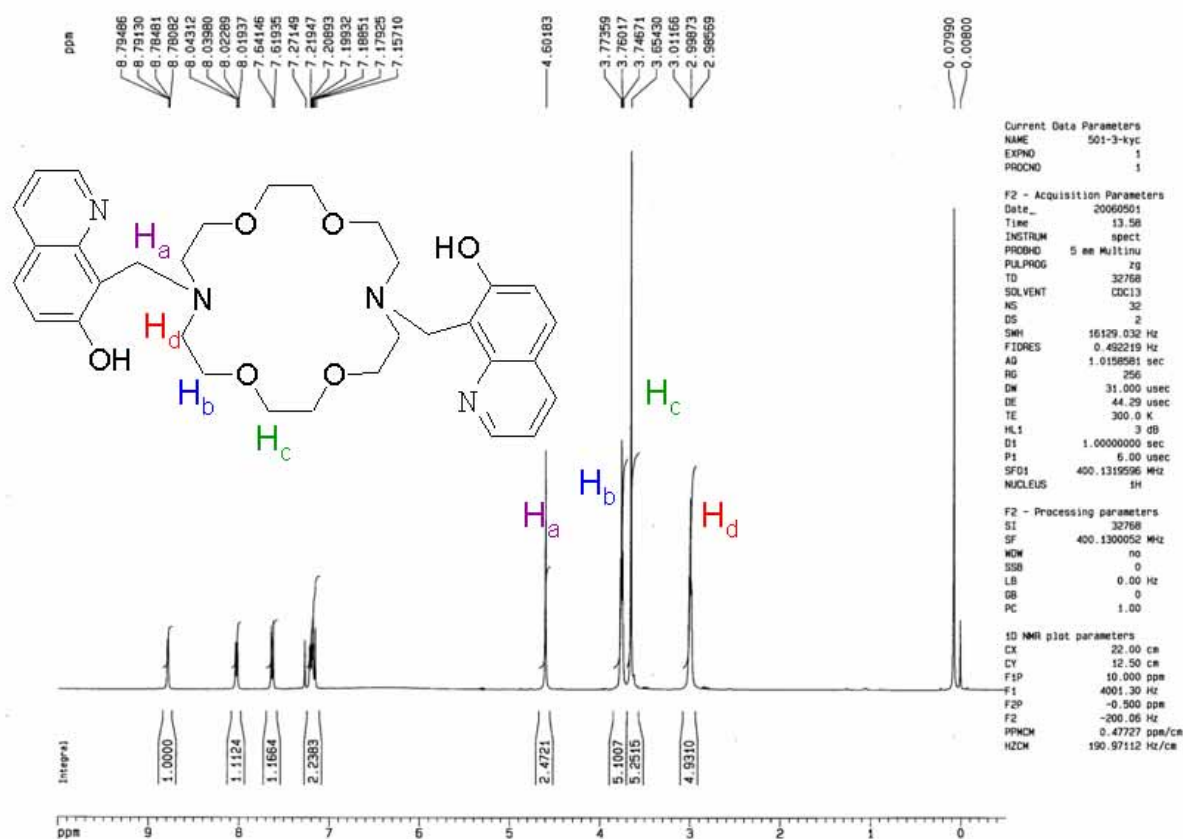


Figure S1. ¹H NMR spectra of **TDBQ** in CDCl₃.

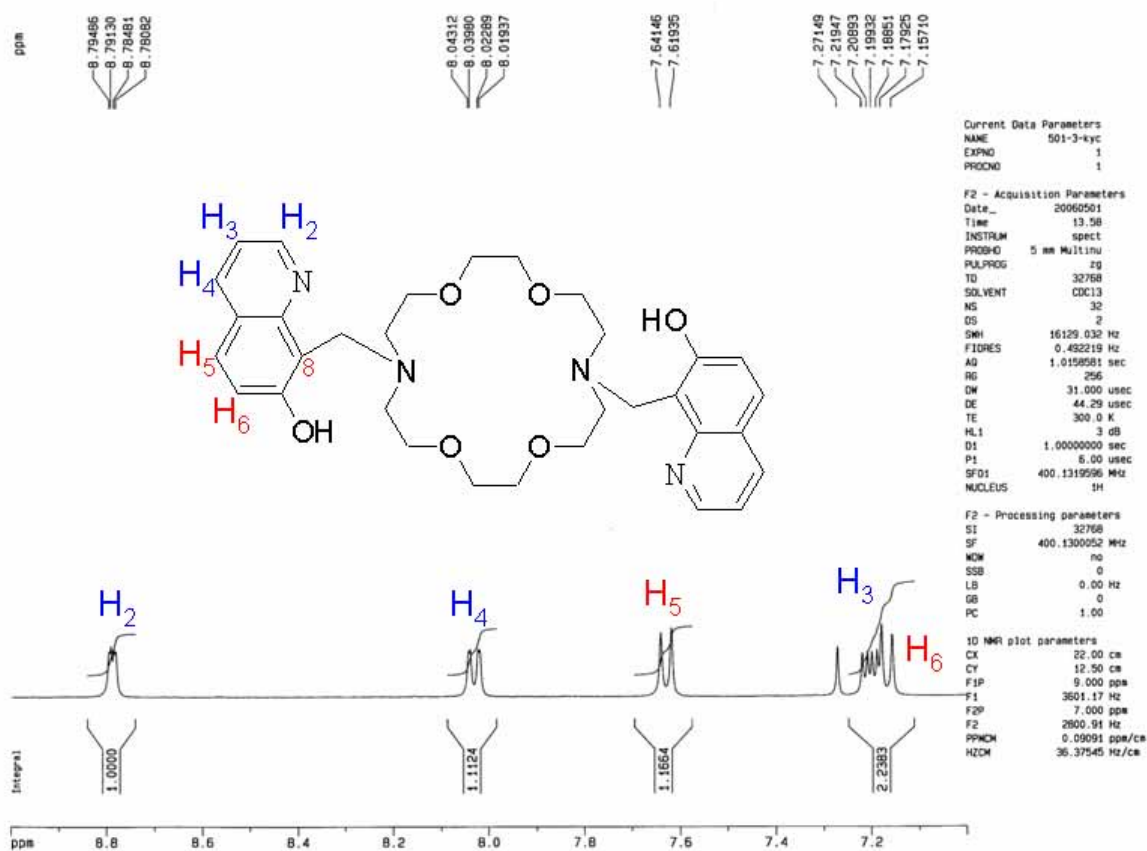


Figure S2. The extension of ^1H NMR spectra of TDBQ in CDCl_3 .

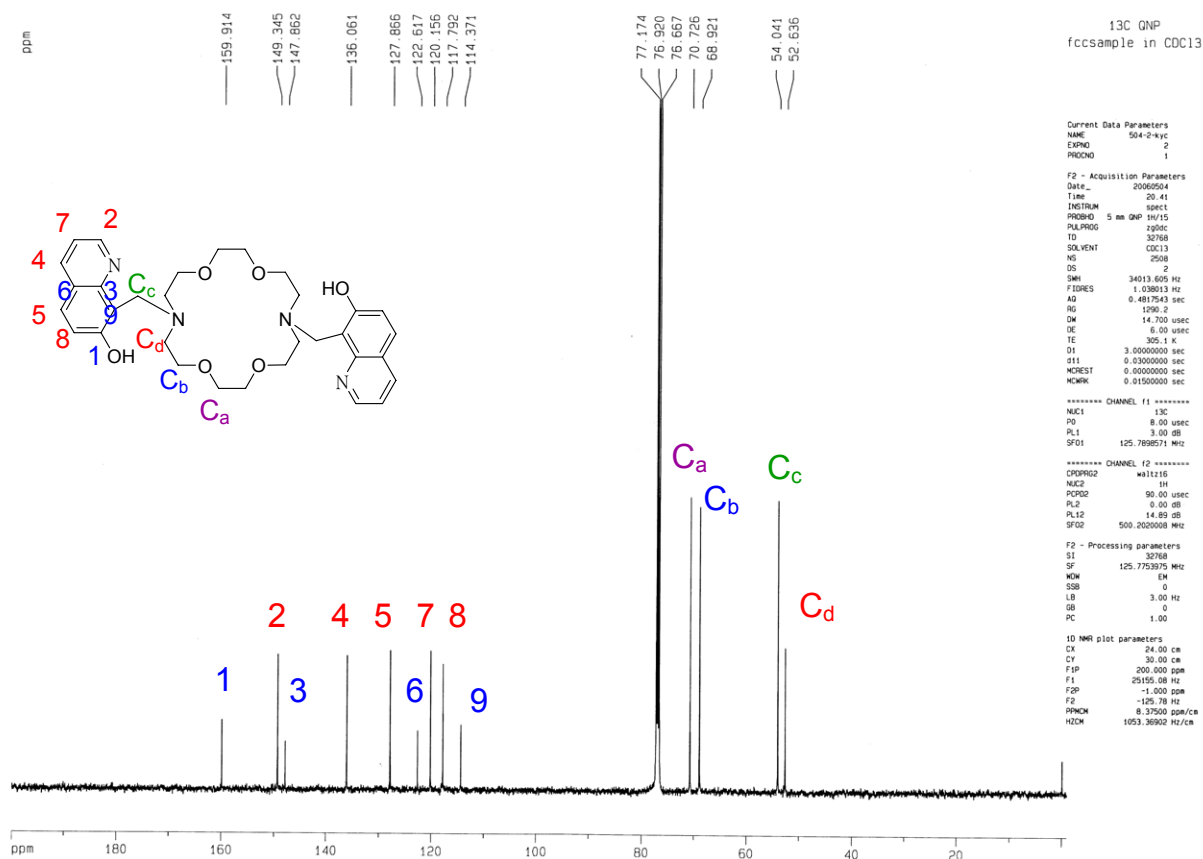


Figure S3. ¹³C NMR of TDBQ in CDCl₃. (125MHz)

[Elemental Composition] Page: 1
 Data : 2006Jun08_01HR-001 Date : 08-Jun-2006 11:17
 Sample: HQ-C-HQ
 Note : NBA
 Inlet : Direct Ion Mode : FAB+
 RT : 0.13 min Scan#: (1,6)
 Elements : C 400/0, H 800/0, O 6/6, N 4/4
 Mass Tolerance : 10mmu
 Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
577.3030	44.1	+0.7 / +0.4	14.5	C 32 H 41 O 6 N 4 = 577.3026

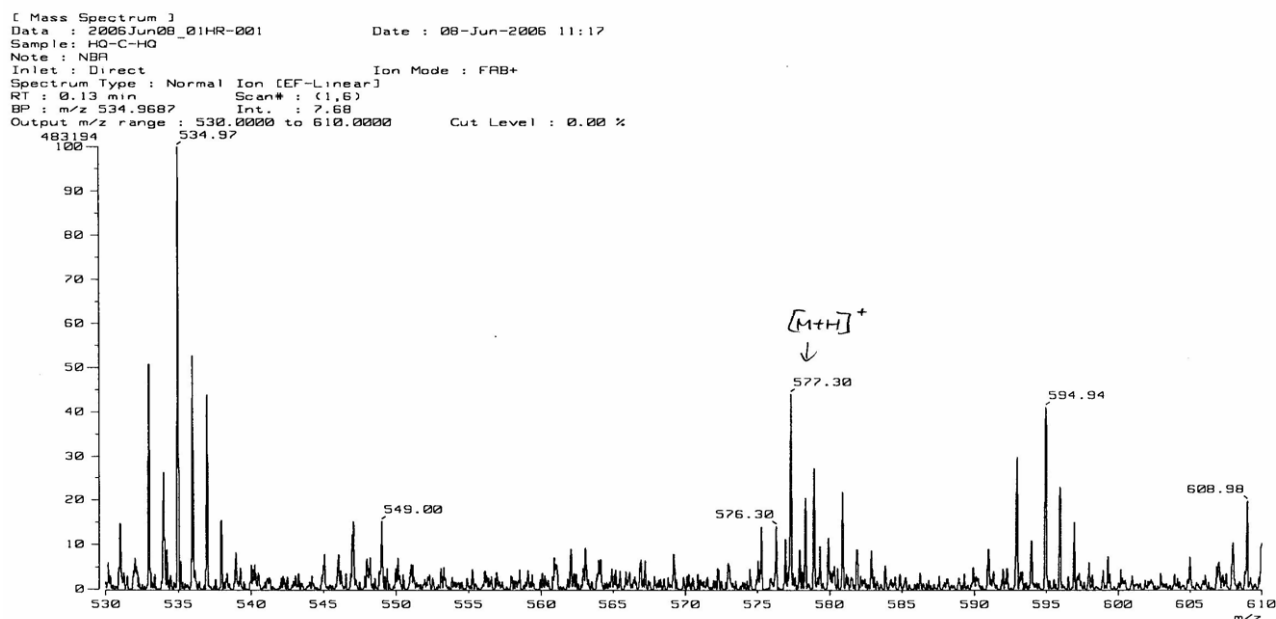
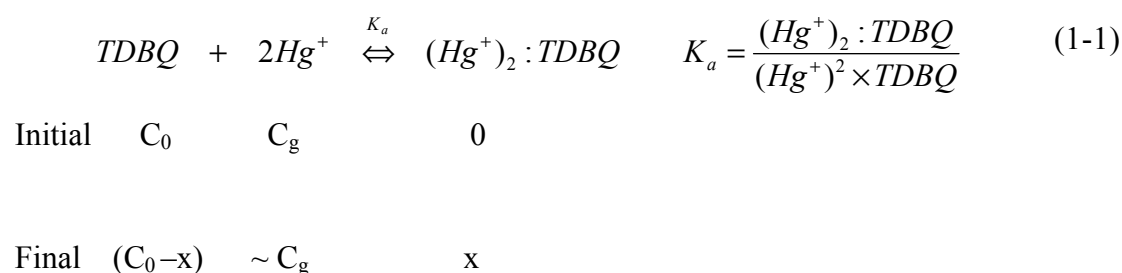


Figure S4. HRMS of TDBQ in CDCl₃. (125MHz)

UV-Vis and Fluorescence Titration of Compounds TDBQ with Hg²⁺ Ions. The stock solution of compound TDBQ (1.52×10^{-5} M) was prepared by using spectroscopic grade MeOH-H₂O (1:10, v/v). The solution of Hg²⁺ ions (1×10^{-2} M) was prepared by using mercury(II) perchlorate hydrate dissolved in H₂O. The absorption and emission spectra of TDBQ (1.5 mL of 7.8×10^{-6} M stock solution) in a quartz cell (1 cm width) were recorded at 298 K.

Absorption titration

The association constant K_a of 1:2 **TDBQ**/ Hg^+ complex formation obtained by the UV-Vis absorption method can be derived as follows:



where C_0 is the initially prepared concentration of **TDBQ**, C_g denotes the concentration of added Hg^{2+} . Note Hg^{2+} would be reduced to Hg^+ in the presence of **TDBQ**. Assuming that the concentration of the added guest molecule (Hg^{2+}) varies negligibly during the titration, the association constant K_a can thus be expressed by $K_a = x / C_g^2(C_0 - x)$, in which x denotes the amount of **TDBQ** being consumed for complexation. If the percentage of **TDBQ**- Hg^+ formation is less than of the initially prepared C_0 , then

$$\frac{1}{K_a} = \frac{C_g^2 C_0}{x} - C_g^2 \quad (1-2)$$

On the other hand, the absorbance, A_{ab} , of the **TDBQ** and $(\text{Hg}^+)_2 : \text{TDBQ}$ complex at a specific wavelength can be expressed by

$$A_{ab} = \epsilon_{\text{TDBQ}}(C_0 - x) + \epsilon_{\text{TDBQ-Hg}^+}x$$

$$x = \frac{A_{ab} - \epsilon_{\text{TDBQ}}C_0}{\epsilon_{\text{TDBQ-Hg}^+} - \epsilon_{\text{TDBQ}}} \Rightarrow \frac{1}{x} = \frac{\epsilon_{\text{TDBQ-Hg}^+} - \epsilon_{\text{TDBQ}}}{A_{ab} - \epsilon_{\text{TDBQ}}C_0} \quad 8$$

$$(1-3)$$

Plugging (1-3) into (1-2), we obtain

$$\frac{1}{K_a} + C_g^2 = \frac{C_g^2 C_0 (\epsilon_{TDBQ-Hg^+} - \epsilon_{TDBQ})}{(A_{ab} - \epsilon_{TDBQ} C_0)} \quad (1-4)$$

Both sides of (1-4) are divided by $C_g^2 (\epsilon_{TDBQ-Hg^+} - \epsilon_{TDBQ})$ to obtain

$$\frac{C_0}{A_{ab} - \epsilon_{TDBQ} C_0} = \left[\frac{1}{K_a (\epsilon_{TDBQ-Hg^+} - \epsilon_{TDBQ})} \right] \frac{1}{C_g^2} + \frac{1}{\epsilon_{TDBQ-Hg^+} - \epsilon_{TDBQ}} \quad (1)$$

where ϵ_{TDBQ} and $\epsilon_{TDBQ-Hg^+}$ are molar extinction coefficients of the **TDBQ** and $(Hg^+)_2 : \text{TDBQ}$

complex, respectively, at a specific wavelength. The validity of this approach can be examined from

a linear plot for $\frac{C_0}{A_{ab} - \epsilon_{TDBQ} C_0}$ versus $\frac{1}{C_g^2}$. The association constant K_a can thus be extracted

from intercept/[slope].

Preparation of TDBQ-mercury crystal. To the methanol solution (2 mL) of **TDBQ** (0.0056 g, mmol) was added to the aqua solution (2 mL) of $Hg(ClO_4)_2$ (0.0081 g, mmole) in a 1:2 equivalent **TDBQ** and metal salt ration at room temperature to give a clear solution (pH = 7). Colorless crystals were obtained after standing for several days in *ca.* 61 % yield. Anal. Calc. for $C_{32}H_{40}Cl_2Hg_2N_4O_{14}$: C 32.66, H 3.43, O 19.03; Found: C 32.64, H 3.41, O 19.01. IR (KBr) ν (cm^{-1}): 3052 (w), 1686 (m), 1589 (s), 1504 (vs), 1478 (vs), 1428 (s), 1351 (m), 1223 (m), 1211 (w).

Crystallographic Data Collection and Refinement. The chosen crystals of **TDBQ** and **TDBQ**-mercury crystal were both mounted on a glass fiber. Data collections were carried out on a Siemens SMART diffractometer with a CCD detector with Mo radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame correspond to a 0.3° scan in 10 s, following by spot integration and least-squares refinement. For each structure, data were measured using ω scans of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART^{S1} software and refined with SAINT^{S2} on all observed reflections. Data reduction was performed with the SAINT^{S2} software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.^{S3} Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinements. All Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The final full-matrix, least-squares refinement on F^2 was applied for all observed reflections [$I > 2\sigma(I)$]. All calculations were performed by using the SHELXTL-PC V 5.03 software package.^{S4} Crystallographic data and experimental details of refinements for structural analyses are given in Table S2.

Crystallographic data (excluding structure factors) of **TDBQ** and **TDBQ**-mercury crystal for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC***** and CCDC*****. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

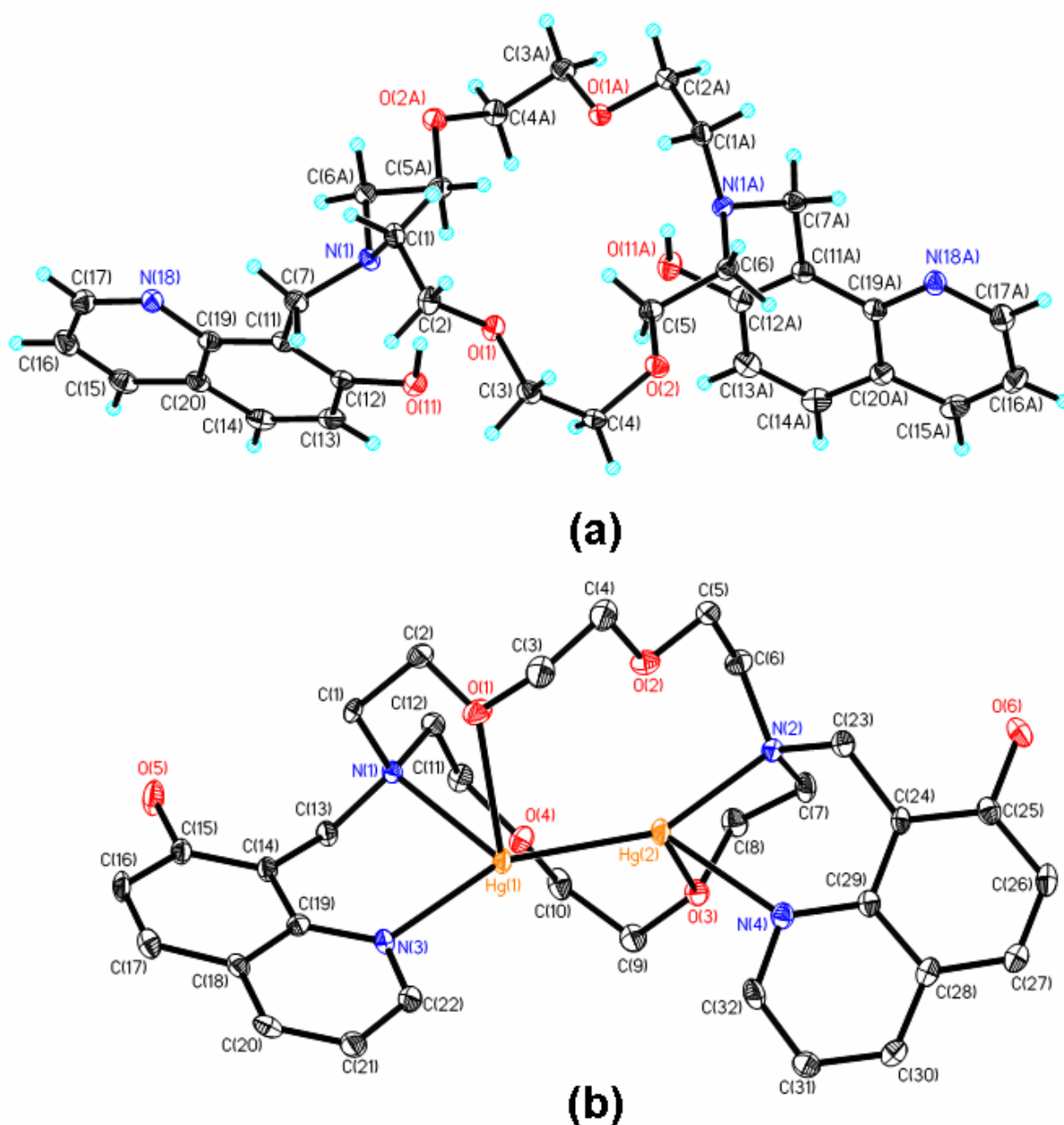


Figure S5. ORTEP diagram of (a) **TDBQ** and (b) **TDBQ-mercury** crystal with thermal ellipsoids shown at 30% probability level.

Table S1. Selected Bond Length (Å) and Angles (°) for **TDBQ-mercury** crystal

Hg(1)–N(1)	2.427(4)	Hg(2)–N(2)	2.349(4)
Hg(1)–N(3)	2.317(4)	Hg(2)–N(4)	2.401(4)

Hg(1)–O(1)	2.685(4)	Hg(2)–O(3)	2.643(4)
Hg(1)–Hg(2)	2.5207(3)		
N(3)–Hg(1)–N(1)	83.3(2)	N(2)–Hg(2)–N(4)	80.6(2)
N(3)–Hg(1)–Hg(2)	154.7(1)	N(2)–Hg(2)–Hg(1)	150.5(1)
N(1)–Hg(1)–Hg(2)	121.5(1)	N(4)–Hg(2)–Hg(1)	128.8(1)
N(3)–Hg(1)–O(1)	102.8(1)	N(2)–Hg(2)–O(3)	71.0(1)
N(1)–Hg(1)–O(1)	66.9(1)	N(4)–Hg(2)–O(3)	84.5(1)
Hg(2)–Hg(1)–O(1)	92.88(9)	Hg(1)–Hg(2)–O(3)	105.53(8)

Table S2. Crystallographic Data and Refinement Parameters for **TDBQ** and **TDBQ**-mercury crystal.

	TDBQ	TDBQ -mercury crystal
empirical formula	C ₃₂ H ₄₀ N ₄ O ₆	C ₃₂ H ₄₀ Cl ₂ Hg ₂ N ₄ O ₁₄
color	colorless	colorless
fw	576.68	1176.76
cryst syst	Orthorhombic	Triclinic
space group	<i>F</i> dd2	<i>P</i> -1
<i>a</i> (Å)	16.517(1)	9.3342(5)
<i>b</i> (Å)	34.853(3)	12.9306(7)
<i>c</i> (Å)	9.9291(7)	16.776(1)
α (°)	90.0	75.396(1)
β (°)	90.0	85.285(1)
γ (°)	90.0	69.475(1)

$V (\text{\AA}^3)$	5715.9(7)	1835.0(2)
Z	8	2
temp (K)	150 (1)	150 (2)
abs coeff (mm^{-1})	0.093	8.576
obsd rflns [$I > 2\sigma(I)$]	1797	7162
Final $R(F)$ [$I > 2\sigma(I)$] ^a	0.0274	0.0345
w $R(F^2)$ indices [$I > 2\sigma(I)$] ^a	0.0385	0.0775

$$^a R(F) = \sum |F_o - F_c| / \sum |F_o| \text{ and } wR(F^2) = [\sum w |F_o^2 - F_c^2|^2 / \sum w (F_o^4)]^{1/2}.$$

XANES

The X-ray absorption experiments were carried out at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. All spectra of Hg L_{III}-edge were recorded at room temperature at the wiggler beamline 17C with a double Si(111)-crystal monochromator. The energy resolution $\Delta E/E$ is 2×10^{-4} . High harmonics were removed by using Rh-coated mirrors. XANES spectrum of **TDBQ**-mercury powder was recorded in fluorescence mode. The spectra of reference compounds, HgCl₂ and Hg₂Cl₂, were recorded in transmission mode. Energy calibration of all spectra was based on HgCl₂ at 12284.1 eV.^{S5}

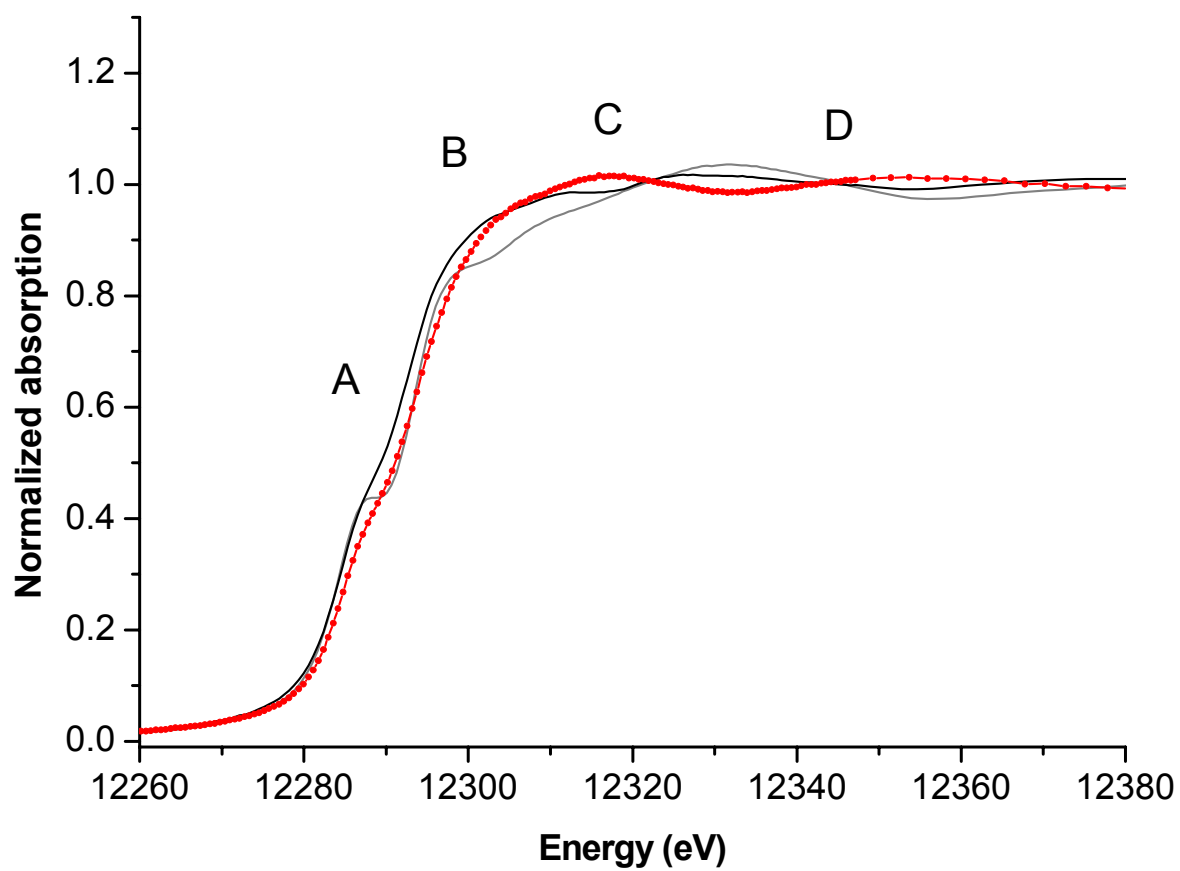


Figure S6. Normalized XANES spectra for **TDBQ-mercury crystal** (- · -), HgCl₂ (Gray), and Hg₂Cl₂ (black).

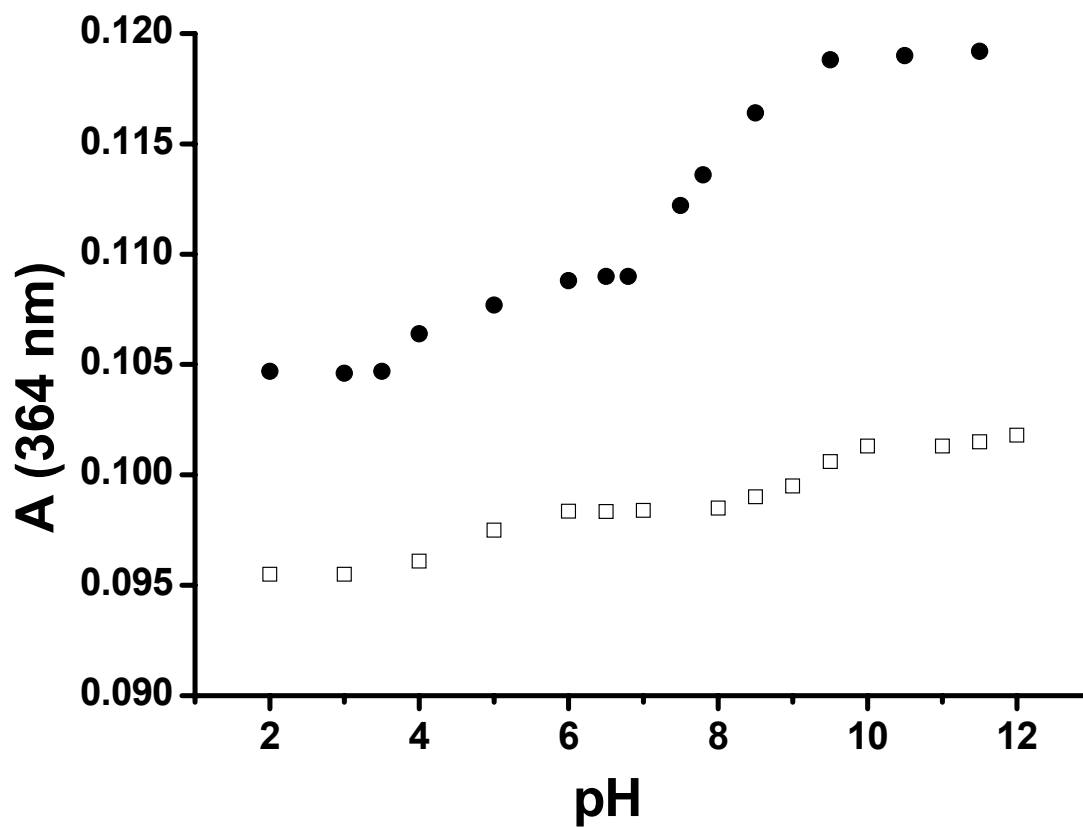


Figure S7. Absorbance (364 nm) of TDBQ (1.5 μM) in aqueous solution at various pH values : \square , TDBQ alone; \bullet , TDBQ with Hg^{2+} (1.5 μM).

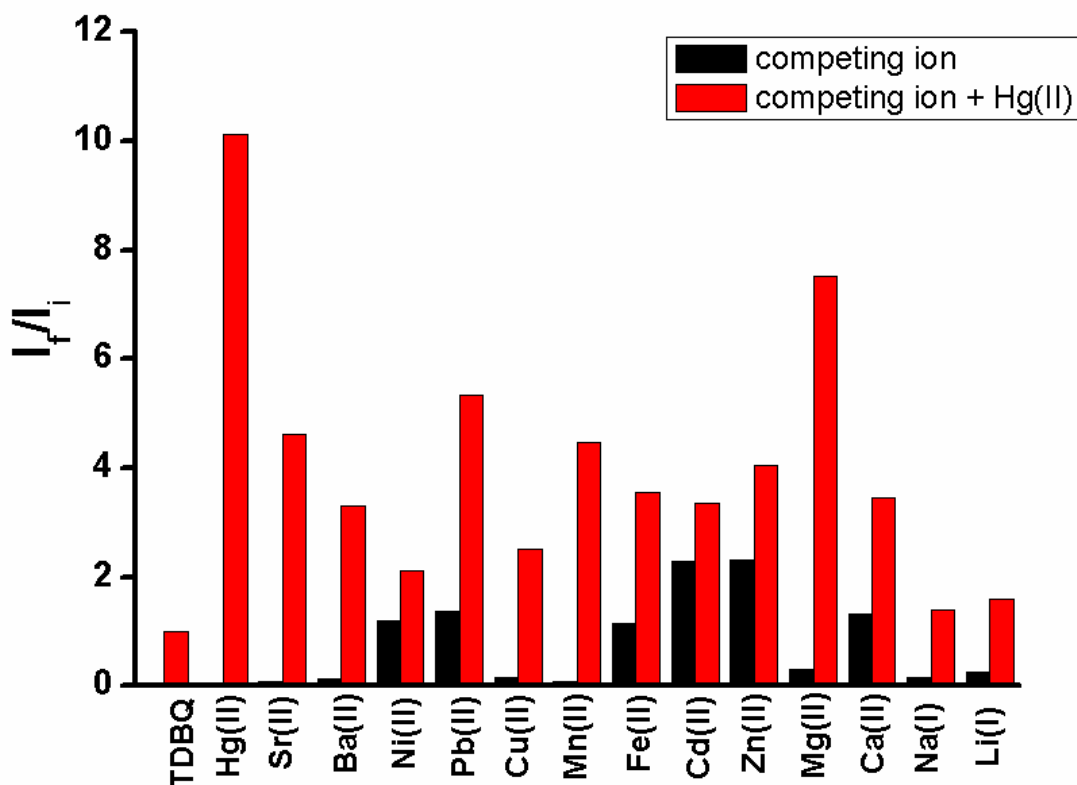


Figure S8. Fluorescence responses of **TDBQ** to various metal ions. Bars represent the final integrated fluorescence response (I_f) over the initial integrated emission (I_i). Initial spectrum was acquired in H_2O , pH 7. Black bars represent the addition of a 1 mM of the appropriate metal ion to a 1 μM solution of **TDBQ**. Red bars represent the addition of 1 mM Hg^{2+} to solutions containing **TDBQ**. Excitation was provided at 358 nm, and the emission was integrated over 400 to 700 nm.

References:

- S1. *SMART V 4.043 Software for CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
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- S5. A. Bernaus, X. Gaona, A. Ivask, A. Kahru and M. Valiente, *Anal. Bioanal. Chem.* 2005, **382**, 1541.