Electronic Supplementary Information

Anion induced multisignaling probe for Hg^{2+} and its application for fish kidney and liver tissue imaging studies

Sandip Mandal,[a] Arnab Banerjee,*[a] Debasree Ghosh,[b] Dipak Kumar Mandal,[b] Damir A. Safin,*[c] Maria G. Babashkina,[c] Koen Robeyns,[c] Mariusz P. Mitoraj,*[d] Piotr Kubisiak,[d] Yann Garcia[c] and Debasis Das*[a]

[a] *Department of Chemistry, The University of Burdwan, Burdwan, 713104, West Bengal, India. Fax: +91 342 2530452; Tel: +91 342 2533913; E-mail: ddas100in@yahoo.com*

[b] *Fish Biology Laboratory, Department of Zoology, School of Life Sciences, Visva-Bharati University, Santiniketan, 731 235, West Bengal, India*

[c] *Institute of Condensed Matter and Nanosciences, Molecules, Solids and Reactivity (IMCN/MOST), Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: +32(0) 1047 2330; Tel: +32(0) 1047 2831; E-mail: damir.a.safin@gmail.com*

[d] *Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland. Email: mitoraj@chemia.uj.edu.pl*

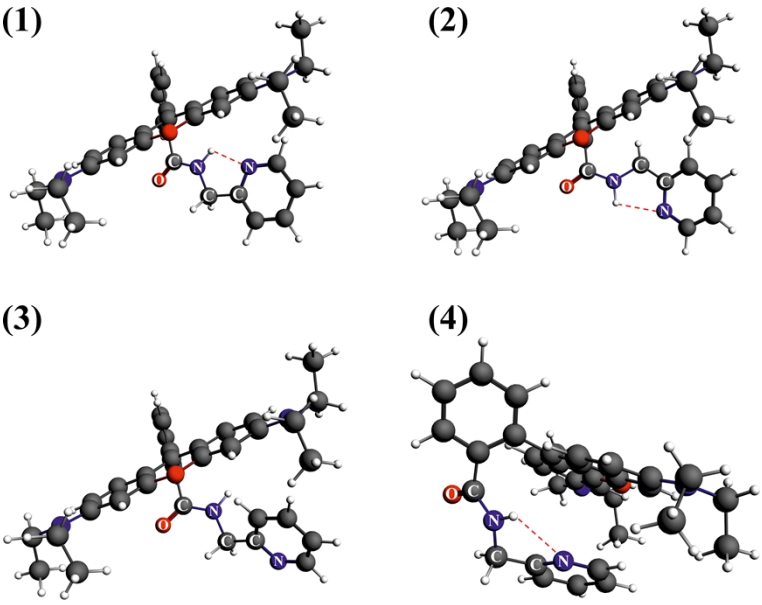

Fig. S1 The lowest energy structures of HL^+ obtained from the ADF/DFT/BLYP-D3/TZP calculations.

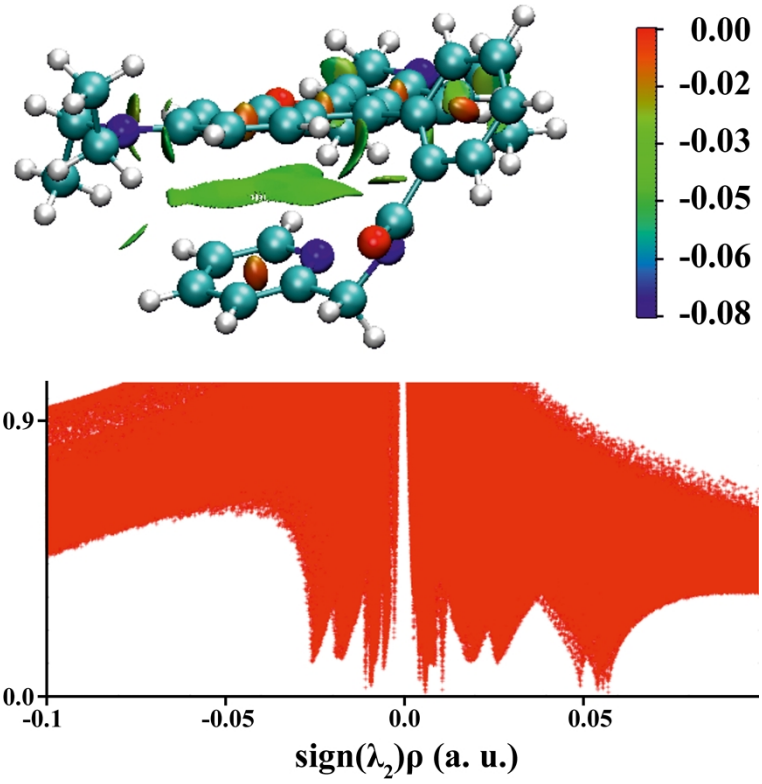

Fig. S2 The NCI isosurface for **HL**$^{+}$, indicating the reduced density gradient at an isovalue of 0.5 a. u. (A). The colour scheme used from blue, through green to red, reflects the following range density colored by Hessian eigenvalue λ_2: –0.08 a. u. < sign(λ_2)*ρ < 0.00 a. u. The 2D representation is also shown (B).

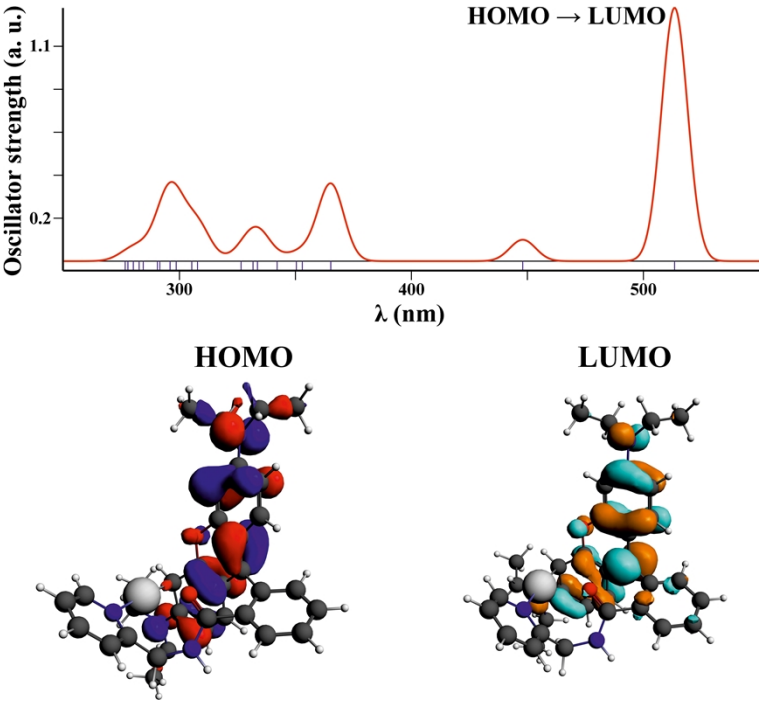

Fig. S3 The simulated TD-DFT/B3LYP/TZP spectrum of [**HL**$^{+}$–Hg^{2+}] in water (top) together with the contours of molecular orbitals (0.03 a. u.) involved in the dominant HOMO → LUMO transition (bottom).

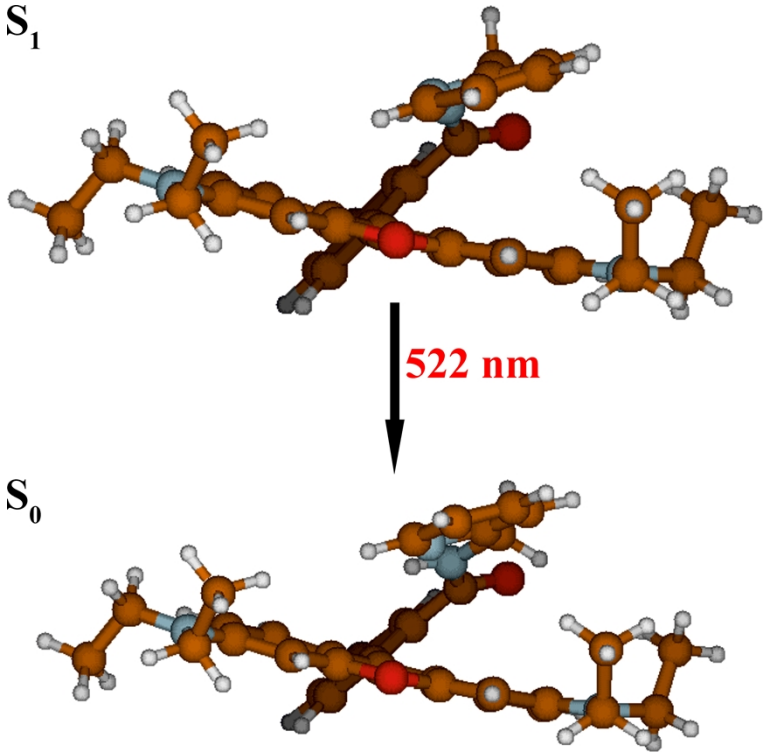

Fig. S4 Structures of the ground S_0 and excited S_1 states obtained from the TD-DFT (B3LYP/6-31++g**) calculations together with the differences in energy for **HL**$^+$.

Table S1 Selected bond lengths (Å) and bond angles (°) for **1**.

Bond lengths					
O(1)–C(2)	1.373(9)	C(2)–C(7)	1.373(11)	C(21)–C(22)	1.513(14)
O(1)–C(14)	1.362(9)	C(3)–C(4)	1.377(12)	C(23)–C(24)	1.474(14)
O(33)–C(32)	1.240(9)	C(4)–C(5)	1.389(11)	C(25)–C(26)	1.523(10)
N(8)–C(4)	1.480(10)	C(5)–C(6)	1.379(11)	C(26)–C(27)	1.387(12)
N(8)–C(9)	1.508(12)	C(6)–C(7)	1.402(12)	C(26)–C(31)	1.373(11)
N(8)–C(11)	1.518(11)	C(7)–C(25)	1.541(10)	C(27)–C(28)	1.407(12)
N(20)–C(16)	1.480(10)	C(9)–C(10)	1.513(15)	C(28)–C(29)	1.399(13)
N(20)–C(21)	1.530(12)	C(11)–C(12)	1.512(16)	C(29)–C(30)	1.366(13)
N(20)–C(23)	1.510(11)	C(14)–C(15)	1.393(11)	C(30)–C(31)	1.418(12)
N(34)–C(25)	1.495(9)	C(14)–C(19)	1.387(10)	C(31)–C(32)	1.470(11)
N(34)–C(32)	1.370(10)	C(15)–C(16)	1.374(11)	C(35)–C(36)	1.509(11)
N(34)–C(35)	1.447(10)	C(16)–C(17)	1.370(11)	C(36)–C(41)	1.358(12)
N(37)–C(36)	1.357(11)	C(17)–C(18)	1.392(12)	C(38)–C(39)	1.362(13)
N(37)–C(38)	1.341(11)	C(18)–C(19)	1.395(11)	C(39)–C(40)	1.375(14)
C(2)–C(3)	1.400(10)	C(19)–C(25)	1.525(10)	C(40)–C(41)	1.396(13)
Bond angles					
N(8)–C(4)–C(3)	118.3(7)	C(25)–N(34)–C(32)	111.7(6)	C(14)–C(19)–C(18)	118.2(7)
N(8)–C(4)–C(5)	120.0(7)	C(25)–N(34)–C(35)	122.5(6)	C(14)–C(19)–C(25)	122.1(7)
N(8)–C(9)–C(10)	112.0(8)	C(32)–N(34)–C(35)	122.4(6)	C(15)–C(14)–C(19)	120.6(7)
N(8)–C(11)–C(12)	111.4(8)	C(36)–N(37)–C(38)	123.2(7)	C(15)–C(16)–C(17)	122.2(8)
N(20)–C(16)–C(15)	119.7(7)	O(1)–C(2)–C(3)	114.3(7)	C(16)–C(17)–C(18)	118.0(7)
N(20)–C(16)–C(17)	118.2(7)	O(1)–C(2)–C(7)	124.0(7)	C(17)–C(18)–C(19)	121.7(7)
N(20)–C(21)–C(22)	111.9(7)	O(1)–C(14)–C(15)	115.7(7)	C(18)–C(19)–C(25)	119.7(7)
N(20)–C(23)–C(24)	112.8(8)	O(1)–C(14)–C(19)	123.6(7)	C(19)–C(25)–C(26)	111.9(6)
N(34)–C(25)–C(7)	112.4(6)	O(33)–C(32)–N(34)	123.0(8)	C(25)–C(26)–C(27)	129.4(7)
N(34)–C(25)–C(19)	108.3(6)	C(2)–O(1)–C(14)	118.7(6)	C(25)–C(26)–C(31)	109.2(6)
N(34)–C(25)–C(26)	101.3(6)	O(33)–C(32)–C(31)	130.0(8)	C(27)–C(26)–C(31)	121.4(7)
N(34)–C(32)–C(31)	107.0(6)	C(2)–C(3)–C(4)	118.3(7)	C(26)–C(27)–C(28)	117.7(8)
N(34)–C(35)–C(36)	113.7(7)	C(2)–C(7)–C(6)	118.2(7)	C(26)–C(31)–C(30)	120.8(7)
N(37)–C(36)–C(35)	118.5(7)	C(2)–C(7)–C(25)	121.8(7)	C(26)–C(31)–C(32)	109.7(7)
N(37)–C(36)–C(41)	118.1(7)	C(3)–C(2)–C(7)	121.7(7)	C(27)–C(28)–C(29)	120.8(8)
N(37)–C(38)–C(39)	119.6(8)	C(3)–C(4)–C(5)	121.7(7)	C(28)–C(29)–C(30)	120.9(8)
C(4)–N(8)–C(9)	112.0(7)	C(4)–C(5)–C(6)	118.6(8)	C(29)–C(30)–C(31)	118.3(8)

C(4)–N(8)–C(11)	112.5(6)	C(5)–C(6)–C(7)	121.4(7)	C(30)–C(31)–C(32)	129.5(7)
C(9)–N(8)–C(11)	112.1(7)	C(6)–C(7)–C(25)	119.9(7)	C(35)–C(36)–C(41)	123.4(8)
C(16)–N(20)–C(21)	112.3(6)	C(7)–C(25)–C(19)	109.6(6)	C(36)–C(41)–C(40)	120.0(9)
C(16)–N(20)–C(23)	112.7(6)	C(7)–C(25)–C(26)	113.0(6)	C(38)–C(39)–C(40)	119.2(8)
C(21)–N(20)–C(23)	113.0(7)	C(14)–C(15)–C(16)	119.2(7)	C(39)–C(40)–C(41)	119.8(9)

Table S2 Selected hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(8)–H(8)···O(81)$^{\#1}$	1	1.74	2.727(10)	167
N(20)–H(20)···Cl(53)$^{\#2}$	1	2.2	3.199(7)	175
N(37)–H(37)···O(82)$^{\#3}$	0.88	1.82	2.673(10)	162
O(81)–H(81A)···Cl(62)$^{\#4}$	0.82	2.41	3.207(8)	165
O(81)–H(81B)···Cl(62)$^{\#3}$	0.82	2.58	3.384(8)	168
O(82)–H(82A)···Cl(53)$^{\#5}$	0.82	2.47	3.216(7)	152
O(82)–H(82B)···Cl(54)$^{\#6}$	0.82	2.42	3.208(7)	163

Symmetry transformations used to generate equivalent atoms: #1 $1-x, 1-y, 1-z$; #2 $2-x, 1-y, 1-z$; #3 x, y, z; #4 $2-x, 1-y, -z$; #5 $-1+x, y, z$; #6 $1-x, 2-y, 1-z$.

Table S3 The relative energies from DFT/BLYP-D3/TZP for the isomers **1–4** shown in Fig. S1. The Gibbs-free energies at 298.15 K are given for the two lowest energy isomers **1** and **4**.

Isomer	Δ*E*	ΔG
1	+2.80	+2.55
2	+7.60	
3	+49.0	
4	0.0	0.00

Table S4 Bond energies (ΔE_{total}), describing the interaction between three fragments $Hg^{2+}/X^{-}/X^{-}$ ($X^{-} = NO_3^{-}$, OAc^{-}, Cl^{-}). The ETS energy decomposition is shown according to Ziegler-Rauk scheme.

	$Hg(NO_3)_2$	$Hg(OAc)_2$	$HgCl_2$
ΔE_{total}	–593.74	–625.6	–619.15
ΔE_{orb}	–195.98	–194.27	–199.94
ΔE_{elstat}	–578.15	–606.56	–620.99
ΔE_{Pauli}	184.25	178.91	202.14
$\Delta E_{dispersion}$	–3.86	–3.86	–0.35

$\Delta E_{total} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{dispersion}$