

Electronic Supplementary Information

A multiresponsive two-arm ferrocene-based chemosensor molecule for selective detection of mercury

Tomás Romero, Antonio Caballero, Arturo Espinosa, Alberto Tárraga* and Pedro Molina*

Departamento de Química Orgánica, Facultad de Química, Campus de Espinardo, Universidad de Murcia, E-30100, Spain. Fax: +34 968 364 149; Tel: +34 968 367 496; E-mail: pmolina@um, atarraga@um.es.

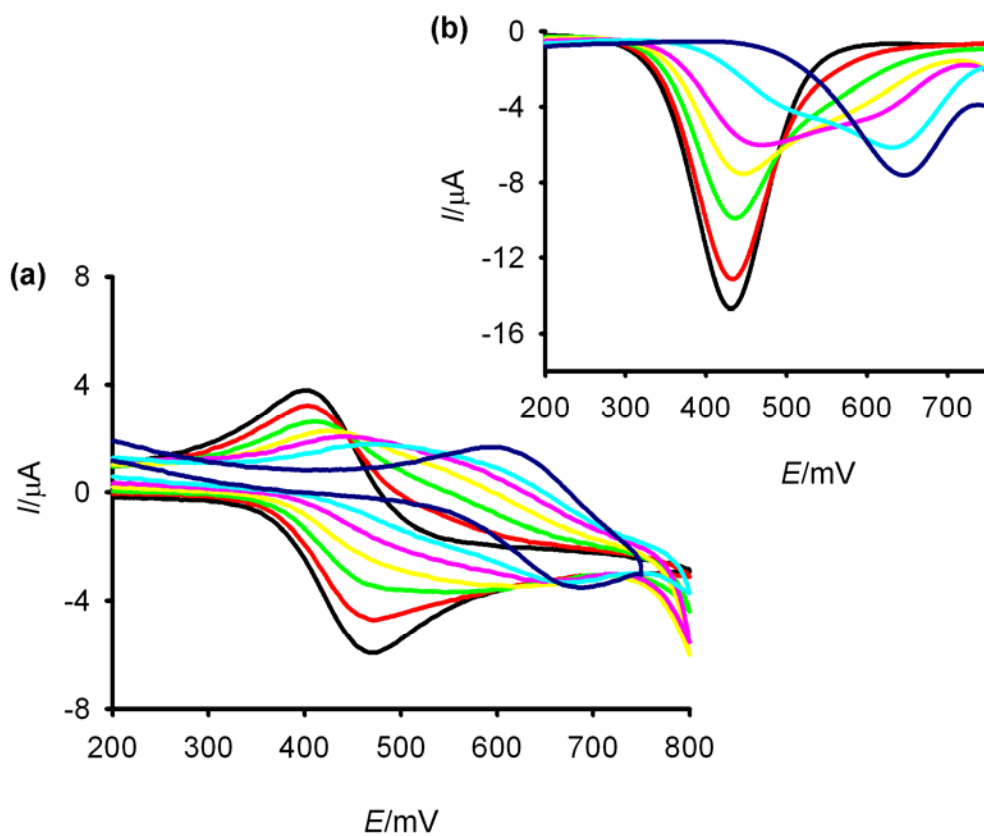


Figure S1. Evolution of the CV (a) and OSWV (b) of **4** (1×10^{-3} M) in CH_3CN using $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ as supporting electrolyte when $\text{Hg}(\text{OTf})_2$ is added: from 0 (black) to 1 equiv (deep blue).

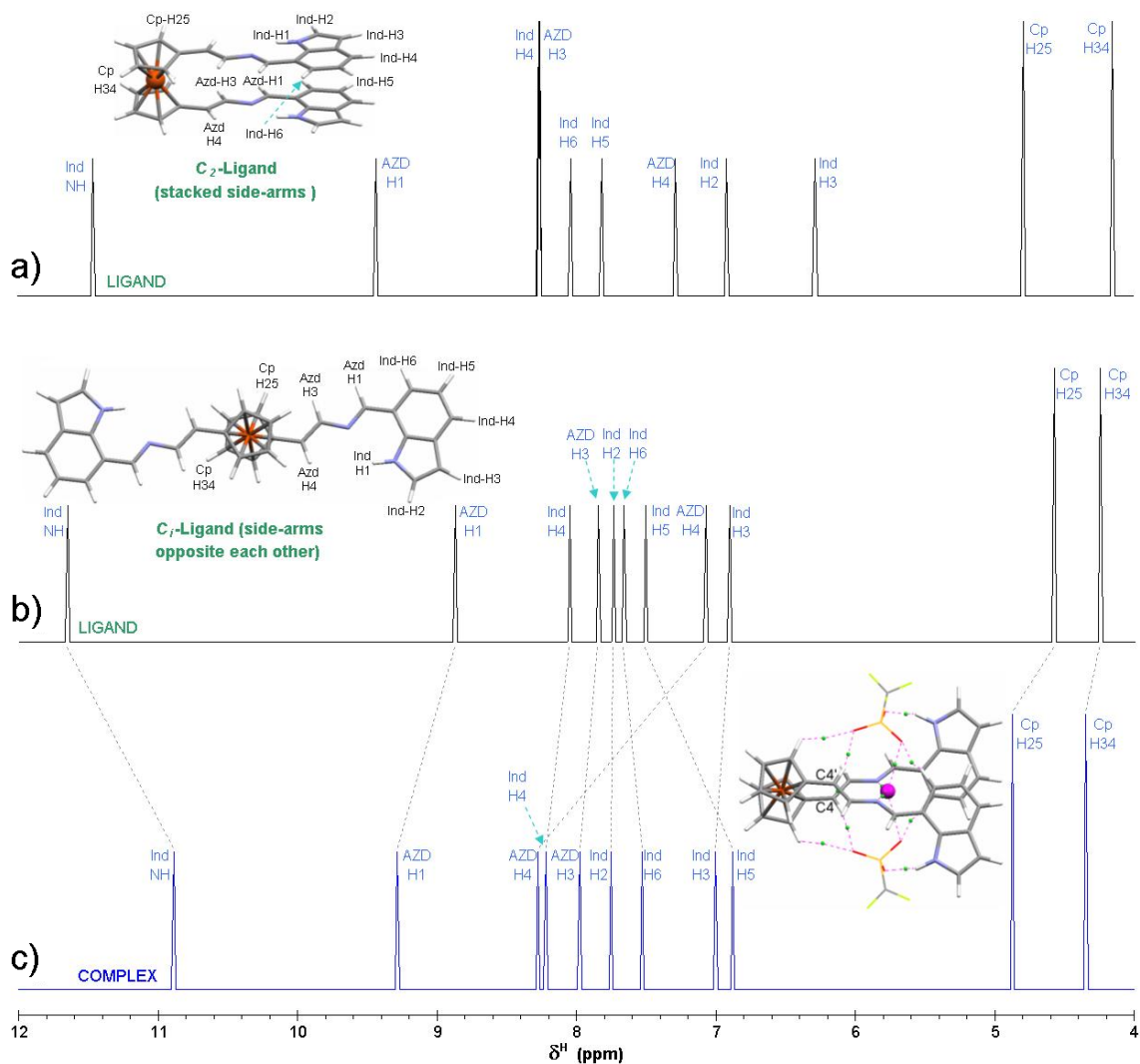
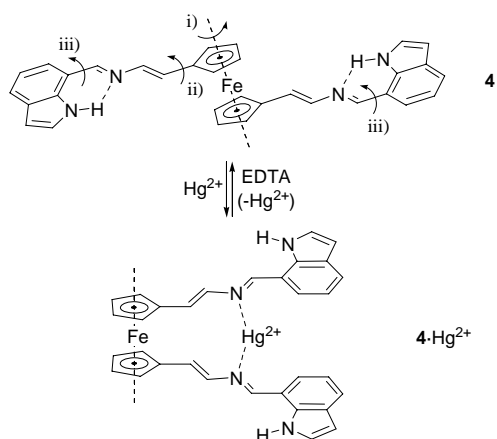


Figure S2. Calculated (GIAO/CPCM_{chloroform}/B3LYP/aug6-311G**/SDDecp // mPW1B95/aug6-311G**/SDDecp) ¹H NMR spectra for the C₂-stacked (a) and C_i (b) conformers of ligand 4 and for the 4^{C₂-st}.Hg(OTf)₂ complex (c). Every signal is represented as a singlet with a height proportional to the number of equivalent nuclei



Scheme S1. Ligand motion on complexation

Calculated structures: cartesian coordinates (in Å) and energies (au) computed for
Hg(OTf)₂, compounds **4** and complex **4**·Hg(OTf)₂.

Hg(OTf)₂ (C_i):

E_{MeCN} = -2076.803083 au

Hg	0.00000000	0.00000000	0.00000000	O	-4.02850166	-1.45706400	-0.53379533
O	2.06653316	0.00000000	0.00000000	S	-2.67317671	-1.49922080	-0.00000000
S	2.67317671	1.49922080	0.00000000	O	-2.06653317	0.00000000	-0.00000000
O	4.02850165	1.45706400	0.53379533	O	-1.64367212	-2.43537922	-0.48796019
O	1.64367211	2.43537922	0.48796018	C	-2.78656489	-1.77760012	1.88319397
C	2.78656489	1.77760012	-1.88319397	F	-3.16032496	-3.03432310	2.12787952
F	1.55310500	1.56460381	-2.40583732	F	-1.55310501	-1.56460381	2.40583732
F	3.16032496	3.03432310	-2.12787952	F	-3.65126902	-0.92211152	2.42912718
F	3.65126901	0.92211152	-2.42912718				

Compound 4^{C2-st}:

E_{MeCN} = -2717.969984 au

E_{gas-phase} = -2717.979293 au

C	4.86834324	1.67190907	0.00000000	H	0.74110242	-2.33944276	2.53751784
C	5.85217141	1.72133114	1.05657236	C	-1.08751725	2.15030638	-1.37613297
C	7.15564281	1.66617666	0.47137435	C	-1.73196525	1.88712782	-0.14493293
C	6.99870431	1.55348322	-0.94808102	N	-1.18762422	1.57516282	1.07120252
C	5.59833312	1.53868534	-1.23963847	C	-2.20461922	1.38168820	1.98981062
H	5.62800809	1.80074752	2.11670053	C	-3.41970726	1.58670130	1.37850642
H	8.09823049	1.68129896	1.01061386	C	-3.14986494	1.90736129	0.00690894
H	7.80158917	1.46417898	-1.67409533	C	-3.94363867	2.18928350	-1.11798291
H	5.15792299	1.43890882	-2.22741674	C	-3.32531824	2.44254711	-2.34417545
Fe	6.08083605	0.00000000	0.00000000	C	-1.92887734	2.42445477	-2.47168238
C	4.86834324	-1.67190907	0.00000000	H	-0.18082519	1.47319734	1.19283656
C	5.85217141	-1.72133114	-1.05657235	H	-1.97483342	1.09767538	3.01062472
C	7.15564281	-1.66617666	-0.47137434	H	-4.39155688	1.49884129	1.85094557
C	6.99870431	-1.55348321	0.94808103	H	-5.03112628	2.20771833	-1.03559222
C	5.59833312	-1.53868534	1.23963847	H	-3.93653392	2.66156262	-3.21981583
H	5.62800809	-1.80074753	-2.11670053	H	-1.47070786	2.63215907	-3.44055041
H	8.09823049	-1.68129895	-1.01061386	C	-1.08751725	-2.15030639	1.37613296
H	7.80158917	-1.46417898	1.67409533	C	-1.73196525	-1.88712783	0.14493293
H	5.15792299	-1.43890882	2.22741674	N	-1.18762422	-1.57516283	-1.07120253
C	3.43505533	1.69516807	0.19051972	C	-2.20461922	-1.38168822	-1.98981063
C	2.51644050	1.90290187	-0.78874888	C	-3.41970725	-1.58670132	-1.37850643
N	1.16128357	1.89058131	-0.53122530	C	-3.14986494	-1.90736131	-0.00690894
C	0.34627640	2.13175380	-1.52400360	C	-3.94363867	-2.18928351	1.11798290
H	3.06241034	1.53311619	1.20454728	C	-3.32531824	-2.44254712	2.34417545
H	2.84326774	2.09998974	-1.82296523	C	-1.92887734	-2.42445478	2.47168238
O	0.74110242	2.33944276	-2.53751784	H	-0.18082519	-1.47319735	-1.19283656
C	3.43505533	-1.69516807	-0.19051972	H	-1.97483342	-1.09767540	-3.01062473
C	2.51644050	-1.90290188	0.78874888	H	-4.39155688	-1.49884131	-1.85094558
N	1.16128357	-1.89058132	0.53122530	H	-5.03112628	-2.20771834	1.03559221
C	0.34627640	-2.13175381	1.52400360	H	-3.93653392	-2.66156263	3.21981582
H	3.06241034	-1.53311620	-1.20454728	H	-1.47070786	-2.63215908	3.44055041
H	2.84326774	-2.09998974	1.82296523	X	0.27855737	1.64758438	0.51661477

X	0.27855737	-1.64758438	-0.51661477	X	-1.44597951	0.20977467	-0.85701429
X	-3.27176458	-0.23194851	0.85522368	X	-1.44597951	-0.20977467	0.85701429
X	-3.27176458	0.23194851	-0.85522368				

Compound **4^{Gi}** :

$E_{\text{MeCN}} = -2717.970916$ au

$E_{\text{gas-phase}} = -2717.976489$ au

C	-0.71357338	-1.00613139	1.65418872	C	-5.73179947	-4.50636248	2.14117382
C	0.73025709	-1.02279346	1.59832993	C	-5.22348149	-5.80745426	1.92131667
C	1.20563730	0.32418352	1.61142346	N	-3.93793397	-6.20146892	1.66213498
C	0.06661200	1.19239975	1.65344543	C	-3.90491699	-7.57731157	1.51353549
C	-1.11146833	0.38233068	1.66427728	C	-5.17334968	-8.08615079	1.67647599
H	1.34285480	-1.91911732	1.55283216	C	-6.04122277	-6.97444269	1.93971208
H	2.24405045	0.63799349	1.55998282	C	-7.41745224	-6.82758957	2.18897476
H	0.09357665	2.27803932	1.64169944	C	-7.93769166	-5.55056502	2.40861928
H	-2.13284543	0.75109795	1.66138680	C	-7.11495424	-4.41455251	2.38567886
Fe	0.00000000	0.00000000	0.00000000	H	-3.18056569	-5.52020241	1.60402837
C	0.71357338	1.00613139	-1.65418872	H	-2.96962617	-8.08370974	1.30200941
C	-0.73025709	1.02279346	-1.59832993	H	-5.45150663	-9.13246532	1.61498259
C	-1.20563730	-0.32418352	-1.61142346	H	-8.07175959	-7.69992257	2.21060470
C	-0.06661200	-1.19239975	-1.65344543	H	-9.00349931	-5.43059307	2.60256103
C	1.11146833	-0.38233068	-1.66427728	H	-7.54885063	-3.42866092	2.56151110
H	-1.34285480	1.91911732	-1.55283216	C	5.73179947	4.50636248	-2.14117382
H	-2.24405045	-0.63799349	-1.55998282	C	5.22348149	5.80745426	-1.92131667
H	-0.09357665	-2.27803932	-1.64169944	N	3.93793397	6.20146892	-1.66213498
H	2.13284543	-0.75109795	-1.66138680	C	3.90491699	7.57731157	-1.51353549
C	-1.55286826	-2.18485682	1.66167100	C	5.17334968	8.08615079	-1.67647599
C	-2.89132930	-2.20873223	1.89669136	C	6.04122277	6.97444269	-1.93971208
N	-3.60677841	-3.38888779	1.88829308	C	7.41745224	6.82758957	-2.18897476
C	-4.89208118	-3.33408958	2.11943657	C	7.93769166	5.55056502	-2.40861928
H	-1.05862354	-3.14278394	1.48155405	C	7.11495424	4.41455251	-2.38567886
H	-3.43665489	-1.27533141	2.10987013	H	3.18056569	5.52020241	-1.60402837
H	-5.38860747	-2.36386013	2.31040923	H	2.96962617	8.08370974	-1.30200941
C	1.55286826	2.18485682	-1.66167100	H	5.45150663	9.13246532	-1.61498259
C	2.89132930	2.20873223	-1.89669136	H	8.07175959	7.69992257	-2.21060470
N	3.60677841	3.38888779	-1.88829308	H	9.00349931	5.43059307	-2.60256103
C	4.89208118	3.33408958	-2.11943657	H	7.54885063	3.42866092	-2.56151110
H	1.05862354	3.14278394	-1.48155405	X	-3.38831944	-4.73704824	1.71599370
H	3.43665489	1.27533141	-2.10987013	X	3.38831944	4.73704824	-1.71599370
H	5.38860747	2.36386013	-2.31040923				

Complex **4·Hg(OTf)₂** (C_2):

$E_{\text{MeCN}} = -4794.835372$ au

$E_{\text{BSSE}} = 0.01323344$ au

C	1.20649024	1.68249274	0.00000000	C	7.10028758	-2.72449542	-1.47269462
C	0.37841944	1.63222451	-1.17631795	C	7.97296437	-2.84409087	-2.57552829
C	-0.98486374	1.63557033	-0.76532043	N	7.71715899	-2.68764815	-3.91594473
C	-1.01640167	1.66351163	0.66283042	C	8.90680126	-2.85590802	-4.61020457
C	0.32736757	1.68276563	1.13702632	C	9.91987450	-3.16283391	-3.74317324
H	0.74635878	1.61035779	-2.19383924	C	9.35631256	-3.14124559	-2.42049242
H	-1.84608537	1.60520603	-1.41981836	C	9.87638500	-3.28961787	-1.12678782
H	-1.90565632	1.64995085	1.27948833	C	9.03465531	-3.12188956	-0.02679127
H	0.63643657	1.67485494	2.17402182	C	7.67105590	-2.84464977	-0.18925645
Fe	0.00000000	0.00000000	0.00000000	H	6.94094955	-2.12316301	-4.25834418
C	1.20649024	-1.68249274	-0.00000000	H	8.92417922	-2.73949157	-5.68488585
C	0.37841944	-1.63222451	1.17631795	H	10.94852351	-3.36582256	-4.00682320
C	-0.98486374	-1.63557033	0.76532042	H	10.92791162	-3.52234695	-0.98010222
C	-1.01640167	-1.66351163	-0.66283042	H	9.43114266	-3.23302175	0.97778366
C	0.32736757	-1.68276563	-1.13702632	H	7.03199986	-2.78842973	0.68572370
H	0.74635878	-1.61035779	2.19383924	Hg	5.55946593	0.00000000	0.00000000
H	-1.84608537	-1.60520603	1.41981836	O	6.55738803	0.50177927	-2.12231298
H	-1.90565632	-1.64995085	-1.27948833	S	5.56606503	0.53038504	-3.26790596
H	0.63643657	-1.67485494	-2.17402182	O	5.79812519	-0.52208080	-4.27835546
C	2.65987187	1.67566208	-0.02399387	O	4.17128527	0.70643223	-2.81858049
C	3.46886229	2.10193646	0.96622604	C	6.01492923	2.12874132	-4.10610508
N	4.86457191	1.98325909	0.85778670	F	5.17439468	2.36708825	-5.11582197
C	5.66553332	2.63257257	1.65185372	F	7.26304302	2.07473264	-4.57743246
H	3.11920073	1.31336241	-0.94257822	F	5.92825997	3.13585167	-3.22246216
H	3.09461284	2.57379926	1.87465824	O	6.55738801	-0.50177927	2.12231298
H	5.22118787	3.19320671	2.48172188	S	5.56606501	-0.53038504	3.26790596
C	2.65987187	-1.67566208	0.02399387	O	5.79812516	0.52208080	4.27835547
C	3.46886230	-2.10193647	-0.96622603	O	4.17128525	-0.70643223	2.81858048
N	4.86457191	-1.98325909	-0.85778668	C	6.01492919	-2.12874132	4.10610509
C	5.66553333	-2.63257258	-1.65185370	F	5.17439463	-2.36708825	5.11582196
H	3.11920073	-1.31336242	0.94257823	F	7.26304298	-2.07473264	4.57743247
H	3.09461284	-2.57379926	-1.87465823	F	5.92825993	-3.13585167	3.22246216
H	5.22118788	-3.19320671	-2.48172186	X	5.20429741	1.05838178	0.43578264
C	7.10028757	2.72449542	1.47269465	X	5.20429741	-1.05838178	-0.43578263
C	7.97296436	2.84409087	2.57552832	X	2.67983990	0.00000001	0.00000001
N	7.71715897	2.68764815	3.91594476	X	6.06412785	0.26830185	-1.15600162
C	8.90680124	2.85590802	4.61020461	X	6.06412784	-0.26830185	1.15600163
C	9.91987449	3.16283391	3.74317327	X	6.53555618	-1.50880847	-4.22207527
C	9.35631255	3.14124559	2.42049246	X	6.53555615	1.50880847	4.22207528
C	9.87638500	3.28961787	1.12678785	X	3.58481159	1.07561973	-1.66274113
C	9.03465531	3.12188955	0.02679130	X	3.58481158	-1.07561972	1.66274112
C	7.67105590	2.84464976	0.18925648	X	6.83423737	1.78601709	-1.19765280
H	6.94094953	2.12316301	4.25834420	X	6.83423736	-1.78601709	1.19765281
H	8.92417919	2.73949157	5.68488589	X	6.56321339	2.89627487	-1.77980927
H	10.94852350	3.36582256	4.00682324	X	6.56321336	-2.89627487	1.77980928
H	10.92791161	3.52234695	0.98010226				
H	9.43114267	3.23302175	-0.97778366				
H	7.03199986	2.78842973	-0.68572370				