Electronic Supplementary Information (ESI)

Induced Phosphorescence from Pt→Ag and Ag(I)···Ag(I) Metallophilic Interactions in Benzenedithiolatodiimine-Pt2 /Ag2 cluster: A Combined Experimental and Theoretical Investigation

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Table of Contents

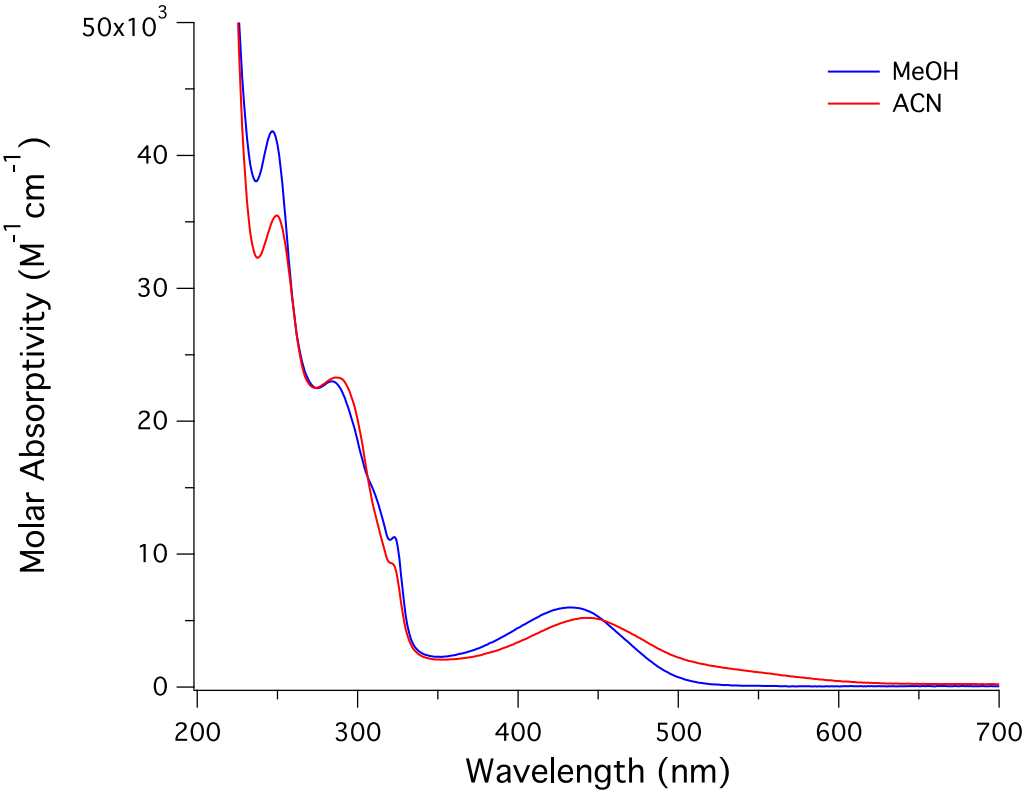

Figure S1. Absorption spectra of **2** in CH_3OH (blue line) and CH_3CN (red line) solution at room temperature.

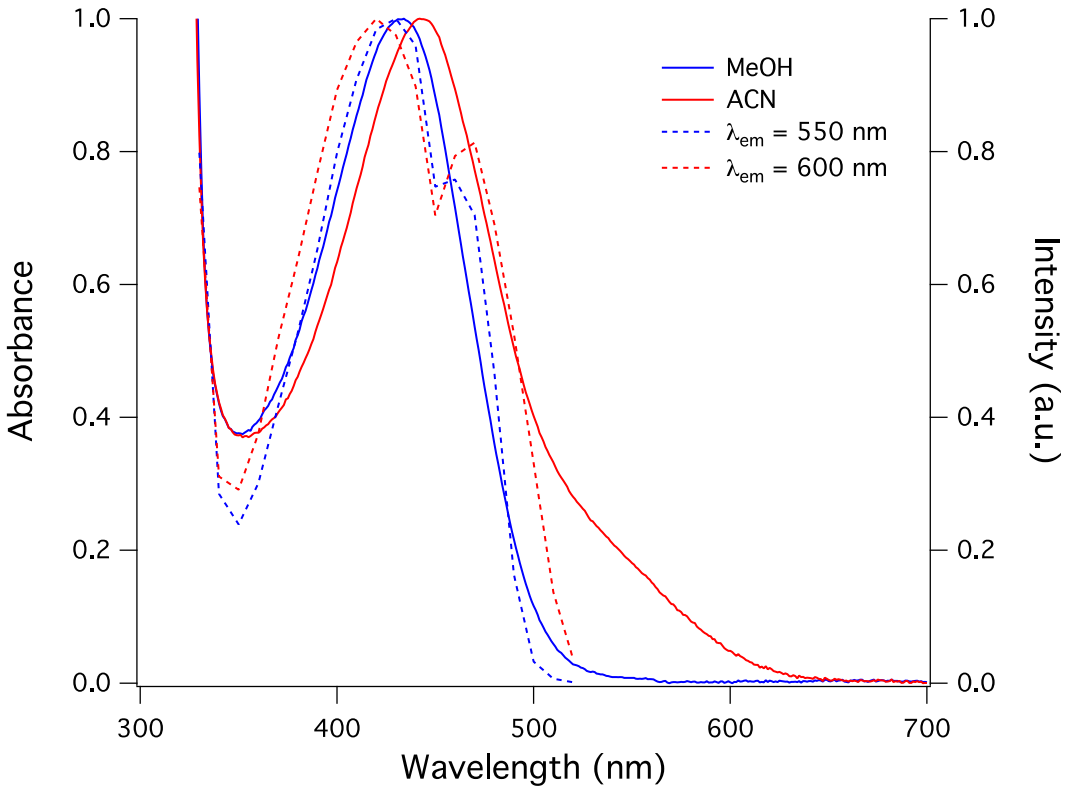

Figure S2. Comparison between the normalized absorbance spectra in MeOH (full blue line) and ACN (full red line) solution at room temperature and the excitation spectra of **2** in MeOH:EtOH (1:4) mixture at 77 K (dashed lines) taken at two different emission wavelengths, indicated in figure.

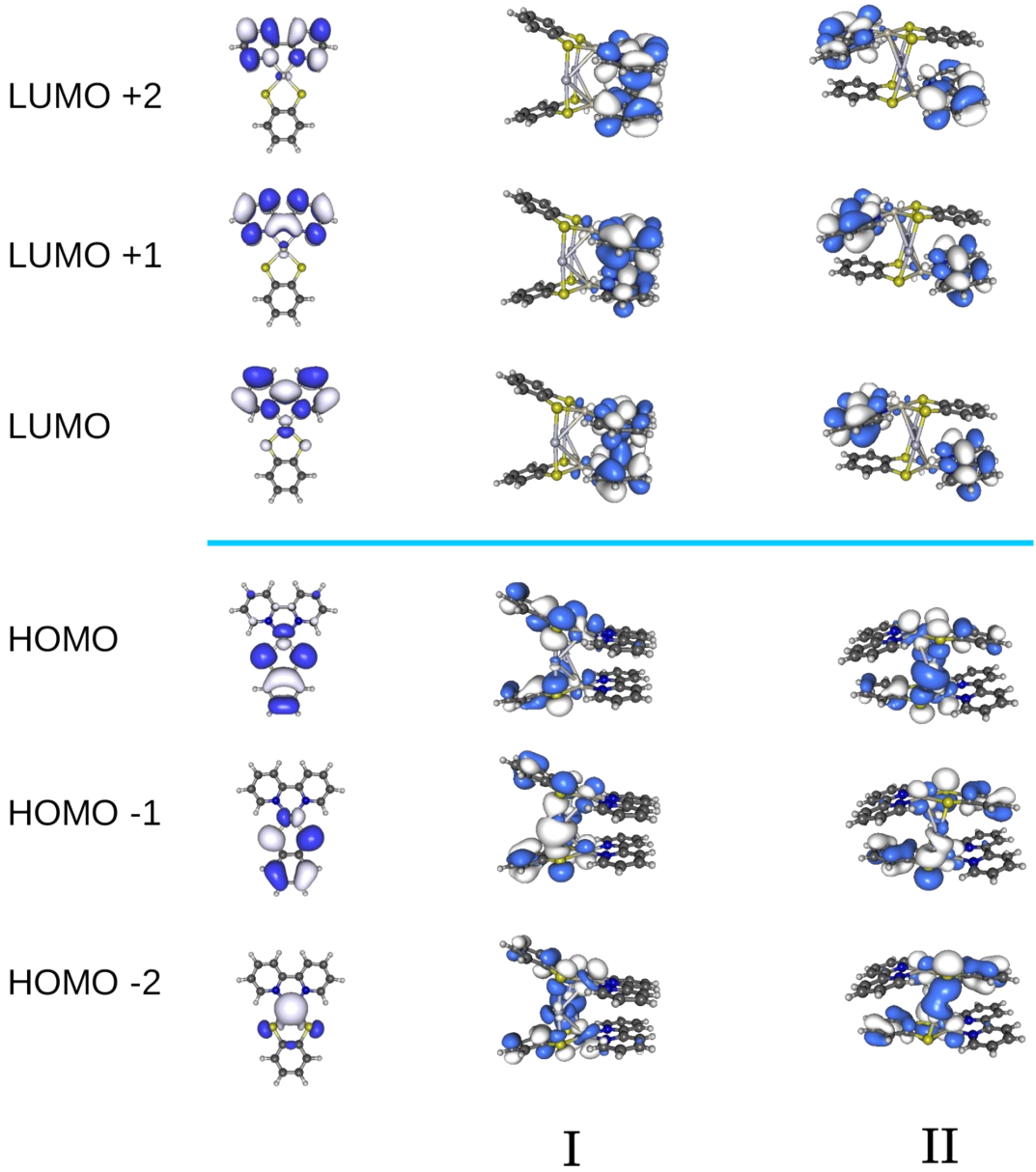

Figure S3. Comparison among the three high occupied and three low virtual MOs of I and II in their ground state calculated in acetonitrile solution. Those of Pt(*o*-bdt)(bpy) are also reported.

Table S1. Crystallographic data for $[(Pt2Ag2(o\text{-}bdt)_2(bpy)_2][CF_3SO_3]_2 \cdot 0.33\ H_2O \cdot 0.67\ CH_3CN$

Empirical formula	$C_{35}H_{26.67}Ag_2F_6N_{4.67}O_{6.33}Pt_2S_6$
Formula weight	1526.22 g/mol
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 13.508(4) Å
	b = 15.370(4) Å
	c = 16.789(4)Å
	α = 80.705(10)°
	β = 79.560(11)°
	γ = 89.233(11)°
Volume	3382.7(16) $Å^3$
Z	3
Density (calculated)	2.248 Mg/m^3
Absorption coefficient	7.391 mm^{-1}
F(000)	2160
Reflections collected	47069
Independent reflections	15241 [R(int) = 0.0210]
Final R indices [I>2sigma(I)]	R1 = 0.0533, wR2 = 0.1217
Final R indices [all data]	R1 = 0.0707, wR2 = 0.1362
Goodness-of-fit on F2	1.060
Largest diff. peak and hole ($e.Å^{-3}$)	5.610 and -2.24

Table S2. $S_0 \rightarrow S_n$ transitions of I in CH_3CN. ΔE (eV), wavelength λ (nm), oscillator strengths (f_{osc}) and the two most significant excitations of each transition are reported: h_n = HOMO $-n$ and l_n = LUMO $+n$.

n	ΔE / λ	f_{osc}	excitations	
1	2.53 / 490	0.0014	+0.69 $h_0 \rightarrow l_0$	
2	2.59 / 478	0.0036	+0.65 $h_1 \rightarrow l_0$	+0.22 $h_2 \rightarrow l_0$
3	2.66 / 466	0.1147	+0.64 $h_2 \rightarrow l_0$	–0.23 $h_1 \rightarrow l_0$
4	2.80 / 443	0.0061	+0.62 $h_3 \rightarrow l_0$	–0.26 $h_1 \rightarrow l_1$
5	2.95 / 420	0.0423	+0.58 $h_0 \rightarrow l_1$	–0.25 $h_2 \rightarrow l_1$
6	3.00 / 413	0.0142	+0.44 $h_4 \rightarrow l_0$	+0.37 $h_2 \rightarrow l_1$
7	3.08 / 402	0.0011	+0.61 $h_1 \rightarrow l_1$	+0.28 $h_3 \rightarrow l_0$
8	3.14 / 395	0.0007	+0.52 $h_2 \rightarrow l_1$	–0.43 $h_4 \rightarrow l_0$
9	3.26 / 380	0.0003	+0.63 $h_3 \rightarrow l_1$	+0.13 $h_4 \rightarrow l_0$
10	3.27 / 379	0.0004	+0.36 $h_0 \rightarrow l_5$	+0.29 $h_0 \rightarrow l_3$
11	3.35 / 370	0.0008	+0.34 $h_2 \rightarrow l_6$	+0.29 $h_0 \rightarrow l_6$
12	3.42 / 362	0.0091	+0.30 $h_1 \rightarrow l_3$	+0.25 $h_1 \rightarrow l_4$
13	3.44 / 360	0.0032	+0.61 $h_4 \rightarrow l_1$	–0.14 $h_7 \rightarrow l_0$
14	3.45 / 359	0.0019	+0.32 $h_1 \rightarrow l_6$	–0.30 $h_0 \rightarrow l_2$
15	3.46 / 358	0.0004	+0.61 $h_0 \rightarrow l_2$	+0.14 $h_3 \rightarrow l_5$
16	3.57 / 347	0.0037	+0.50 $h_1 \rightarrow l_2$	–0.45 $h_2 \rightarrow l_2$
17	3.57 / 346	0.0039	+0.50 $h_2 \rightarrow l_2$	+0.45 $h_1 \rightarrow l_2$
18	3.68 / 336	0.0007	+0.43 $h_0 \rightarrow l_3$	+0.25 $h_4 \rightarrow l_5$
19	3.74 / 331	0.0061	+0.48 $h_3 \rightarrow l_2$	–0.29 $h_5 \rightarrow l_0$
20	3.77 / 328	0.0085	+0.30 $h \rightarrow l_5$	+0.23 $h_2 \rightarrow l_3$
21	3.81 / 325	0.0011	+0.25 $h_4 \rightarrow l_6$	+0.25 $h_0 \rightarrow l_6$
22	3.84 / 323	0.0091	+0.37 $h_2 \rightarrow l_3$	–0.36 $h_3 \rightarrow l_2$
23	3.88 / 319	0.0010	+0.34 $h_2 \rightarrow l_3$	+0.28 $h_3 \rightarrow l_2$
24	3.89 / 318	0.0299	+0.49 $h_1 \rightarrow l_3$	+0.21 $h_7 \rightarrow l_0$
25	3.95 / 314	0.0521	+0.37 $h_6 \rightarrow l_0$	+0.32 $h_7 \rightarrow l_0$
26	3.98 / 311	0.0272	+0.34 $h_6 \rightarrow l_0$	+0.33 $h_1 \rightarrow l_8$
27	3.98 / 311	0.0175	–0.38 $h_1 \rightarrow l_8$	+0.27 $h_6 \rightarrow l_0$
28	4.00 / 309	0.0744	+0.47 $h_0 \rightarrow l_8$	+0.34 $h_1 \rightarrow l_8$
29	4.03 / 307	0.0008	+0.46 $h_8 \rightarrow l_0$	–0.30 $h_9 \rightarrow l_0$
30	4.05 / 306	0.0279	–0.53 $h_4 \rightarrow l_2$	–0.21 $h_2 \rightarrow l_4$
31	4.07 / 304	0.0100	–0.37 $h_0 \rightarrow l_4$	+0.24 $h_3 \rightarrow l_3$
32	4.08 / 304	0.0122	–0.54 $h_2 \rightarrow l_8$	+0.28 $h_0 \rightarrow l_4$

Table S3. $S_0 \rightarrow S_n$ transitions of II in CH_3CN. ΔE (eV), wavelength λ (nm), oscillator strengths (f_{osc}) and the two most significant excitations of each transition are reported: h_n = HOMO $-n$ and l_n = LUMO $+n$.

n	ΔE / λ	f_{osc}	excitations	
1	2.81 / 440	0.0000	+0.61 $h_0 \rightarrow l_1$	−0.32 $h_1 \rightarrow l_0$
2	2.82 / 439	0.1374	+0.61 $h_0 \rightarrow l_0$	−0.33 $h_1 \rightarrow l_1$
3	2.86 / 433	0.0000	+0.52 $h_1 \rightarrow l_0$	−0.39 $h_2 \rightarrow l_0$
4	2.86 / 433	0.0013	+0.52 $h_1 \rightarrow l_1$	−0.39 $h_2 \rightarrow l_1$
5	2.94 / 421	0.0000	+0.56 $h_2 \rightarrow l_0$	+0.33 $h_1 \rightarrow l_0$
6	2.94 / 421	0.0150	+0.57 $h_2 \rightarrow l_1$	+0.33 $h_1 \rightarrow l_1$
7	3.21 / 386	0.0000	+0.57 $h_3 \rightarrow l_1$	−0.28 $h_0 \rightarrow l_4$
8	3.21 / 385	0.0017	+0.57 $h_3 \rightarrow l_0$	+0.25 $h_0 \rightarrow l_5$
9	3.24 / 383	0.0000	+0.43 $h_0 \rightarrow l_4$	+0.37 $h_3 \rightarrow l_1$
10	3.24 / 383	0.0017	+0.38 $h_0 \rightarrow l_5$	−0.37 $h_3 \rightarrow l_0$
11	3.38 / 367	0.0003	+0.45 $h_2 \rightarrow l_4$	−0.32 $h_1 \rightarrow l_4$
12	3.38 / 366	0.0000	+0.39 $h_2 \rightarrow l_5$	−0.37 $h_3 \rightarrow l_4$
13	3.49 / 355	0.0074	+0.65 $h_4 \rightarrow l_1$	−0.22 $h_5 \rightarrow l_0$
14	3.49 / 354	0.0000	+0.65 $h_4 \rightarrow l_0$	−0.22 $h_5 \rightarrow l_1$
15	3.70 / 334	0.0000	+0.61 $h_0 \rightarrow l_2$	−3.31 $h_1 \rightarrow l_3$
16	3.72 / 333	0.0070	+0.55 $h_1 \rightarrow l_2$	−0.39 $h_0 \rightarrow l_3$
17	3.73 / 332	0.0000	+0.35 $h_4 \rightarrow l_5$	+0.27 $h_2 \rightarrow l_5$
18	3.73 / 332	0.0038	+0.40 $h_4 \rightarrow l_4$	+0.29 $h_2 \rightarrow l_4$
19	3.83 / 323	0.0091	+0.64 $h_2 \rightarrow l_2$	−0.18 $h_0 \rightarrow l_3$
20	3.88 / 319	0.0000	+0.51 $h_1 \rightarrow l_3$	+0.27 $h_0 \rightarrow l_2$
21	3.89 / 318	0.0130	+0.49 $h_0 \rightarrow l_3$	+0.40 $h_1 \rightarrow l_2$
22	3.94 / 314	0.0000	+0.56 $h_2 \rightarrow l_3$	+0.22 $h_1 \rightarrow l_3$
23	4.03 / 307	0.0124	+0.56 $h_0 \rightarrow l_6$	−0.28 $h_0 \rightarrow l_5$
24	4.06 / 305	0.0000	+0.40 $h_1 \rightarrow l_6$	−0.28 $h_1 \rightarrow l_5$
25	4.09 / 303	0.0000	+0.51 $h_2 \rightarrow l_6$	−0.25 $h_3 \rightarrow l_2$
26	4.10 / 302	0.1061	+0.37 $h_5 \rightarrow l_0$	+0.25 $h_6 \rightarrow l_0$
27	4.11 / 301	0.0000	−0.57 $h_5 \rightarrow l_1$	−0.21 $h_4 \rightarrow l_0$
28	4.12 / 301	0.0087	+0.44 $h_5 \rightarrow l_0$	+0.24 $h_0 \rightarrow l_5$
29	4.12 / 301	0.0000	−0.37 $h_0 \rightarrow l_4$	−0.30 $h_4 \rightarrow l_5$
30	4.13 / 300	0.0000	+0.36 $h_1 \rightarrow l_6$	−0.36 $h_3 \rightarrow l_2$
31	4.14 / 299	0.1017	−0.39 $h_6 \rightarrow l_0$	+0.24 $h_5 \rightarrow l_0$
32	4.19 / 296	0.0166	−0.45 $h_3 \rightarrow l_3$	+0.29 $h_1 \rightarrow l_8$

Table S4. $S_0 \rightarrow S_n$ transitions of I *in vacuo*. ΔE (eV), wavelength λ (nm), oscillator strengths (f_{osc}) and the two most significant excitations of each transition are reported: h_n = HOMO $-n$ and l_n = LUMO $+n$.

n	ΔE / λ	f_{osc}	excitations	
1	2.13 / 581	0.0008	+0.70 $h_0 \rightarrow l_0$	
2	2.26 / 548	0.0011	+0.68 $h_1 \rightarrow l_0$	
3	2.39 / 518	0.0209	+0.66 $h_2 \rightarrow l_0$	+0.13 $h_1 \rightarrow l_1$
4	2.44 / 507	0.0621	+0.67 $h_3 \rightarrow l_0$	+0.15 $h_0 \rightarrow l_1$
5	2.57 / 481	0.0228	+0.68 $h_0 \rightarrow l_1$	–0.15 $h_3 \rightarrow l_0$
6	2.72 / 455	0.0002	+0.65 $h_1 \rightarrow l_1$	–0.17 $h_2 \rightarrow l_1$
7	2.81 / 441	0.0007	+0.57 $h_2 \rightarrow l_1$	–0.34 $h_3 \rightarrow l_1$
8	2.83 / 437	0.0016	+0.59 $h_3 \rightarrow l_1$	+0.33 $h_2 \rightarrow l_1$
9	3.08 / 402	0.0007	+0.65 $h_0 \rightarrow l_2$	–0.14 $h_0 \rightarrow l_6$
10	3.12 / 397	0.0012	+0.42 $h_0 \rightarrow l_3$	–0.36 $h_0 \rightarrow l_6$
11	3.14 / 395	0.0023	+0.67 $h_4 \rightarrow l_0$	+0.15 $h_3 \rightarrow l_1$
12	3.23 / 383	0.0009	+0.36 $h_0 \rightarrow l_7$	–0.24 $h_0 \rightarrow l_5$
13	3.26 / 379	0.0041	+0.64 $h_1 \rightarrow l_2$	–0.13 $h_0 \rightarrow l_7$
14	3.28 / 377	0.0111	+0.30 $h_1 \rightarrow l_3$	–0.29 $h_1 \rightarrow l_6$
15	3.31 / 374	0.0035	–0.33 $h_2 \rightarrow l_6$	+0.29 $h_2 \rightarrow l_3$
16	3.35 / 370	0.0024	+0.47 $h_3 \rightarrow l_2$	–0.43 $h_2 \rightarrow l_2$
17	3.38 / 366	0.0016	–0.45 $h_2 \rightarrow l_2$	+0.26 $h_0 \rightarrow l_3$
18	3.43 / 361	0.0012	+0.39 $h_3 \rightarrow l_2$	+0.37 $h_0 \rightarrow l_3$
19	3.46 / 357	0.0014	+0.51 $h_5 \rightarrow l_0$	+0.24 $h_4 \rightarrow l_1$
20	3.50 / 354	0.0007	+0.57 $h_4 \rightarrow l_1$	–0.20 $h_5 \rightarrow l_0$
21	3.56 / 348	0.0128	+0.54 $h_1 \rightarrow l_3$	+0.21 $h_3 \rightarrow l_3$
22	3.58 / 345	0.0007	+0.56 $h_6 \rightarrow l_0$	–0.29 $h_5 \rightarrow l_0$
23	3.61 / 343	0.0113	+0.47 $h_3 \rightarrow l_3$	–0.27 $h_2 \rightarrow l_3$
24	3.64 / 340	0.0623	–0.63 $h_0 \rightarrow l_8$	+0.18 $h_3 \rightarrow l_3$

Table S5. $S_0 \rightarrow S_n$ transitions of II *in vacuo*. ΔE (eV), wavelength λ (nm), oscillator strengths (f_{osc}) and the two most significant excitations of each transition are reported: h_n = HOMO $-n$ and l_n = LUMO $+n$.

n	ΔE / λ	f_{osc}	excitations	
1	2.88 / 430	0.0522	+0.69 $h_0 \rightarrow l_0$	
2	2.89 / 429	0.0000	+0.18 $h_1 \rightarrow l_0$	+0.68 $h_0 \rightarrow l_1$
3	2.96 / 418	0.0000	+0.55 $h_1 \rightarrow l_0$	+0.42 $h_2 \rightarrow l_1$
4	2.96 / 418	0.0242	+0.63 $h_2 \rightarrow l_0$	+0.28 $h_1 \rightarrow l_1$
5	2.99 / 415	0.0000	–0.55 $h_2 \rightarrow l_1$	+0.40 $h_1 \rightarrow l_0$
6	2.99 / 414	0.0293	–0.63 $h_1 \rightarrow l_1$	+0.27 $h_2 \rightarrow l_0$
7	3.17 / 391	0.0000	+0.68 $h_3 \rightarrow l_0$	+0.11 $h_2 \rightarrow l_1$
8	3.18 / 389	0.0029	+0.69 $h_3 \rightarrow l_1$	
9	3.26 / 380	0.0004	+0.49 $h_0 \rightarrow l_4$	+0.32 $h_1 \rightarrow l_5$
10	3.27 / 379	0.0000	+0.47 $h_1 \rightarrow l_4$	–0.34 $h_0 \rightarrow l_3$
11	3.41 / 363	0.0003	+0.53 $h_2 \rightarrow l_4$	–0.27 $h_3 \rightarrow l_5$
12	3.42 / 362	0.0000	–0.39 $h_3 \rightarrow l_4$	–0.37 $h_2 \rightarrow l_3$
13	3.76 / 329	0.0095	+0.67 $h_0 \rightarrow l_2$	+0.12 $h_1 \rightarrow l_3$
14	3.80 / 326	0.0040	+0.64 $h_4 \rightarrow l_0$	–0.22 $h_7 \rightarrow l_1$
15	3.81 / 325	0.0000	+0.47 $h_0 \rightarrow l_3$	+0.31 $h_1 \rightarrow l_2$
16	3.81 / 325	0.0000	+0.55 $h_4 \rightarrow l_1$	–0.25 $h_1 \rightarrow l_2$
17	3.83 / 323	0.0000	+0.31 $h_4 \rightarrow l_1$	+0.32 $h_1 \rightarrow l_2$
18	3.83 / 323	0.0037	+0.41 $h_0 \rightarrow l_4$	+0.34 $h_1 \rightarrow l_3$
19	3.88 / 319	0.0084	+0.66 $h_2 \rightarrow l_2$	
20	3.92 / 316	0.0000	–0.45 $h_1 \rightarrow l_2$	+0.32 $h_0 \rightarrow l_5$
21	3.99 / 310	0.0027	+0.44 $h_1 \rightarrow l_3$	+0.44 $h_1 \rightarrow l_5$
22	3.99 / 310	0.0000	+0.50 $h_2 \rightarrow l_3$	+0.37 $h_2 \rightarrow l_5$
23	4.06 / 305	0.0000	+0.54 $h_3 \rightarrow l_2$	+0.27 $h_0 \rightarrow l_6$
24	4.07 / 304	0.0000	+0.50 $h_0 \rightarrow l_6$	–0.24 $h_0 \rightarrow l_5$

Table S6. Significant estimated strenghts of the Ag-Ag donor-acceptor (bond-antibond) interactions in the NBO basis calculated *in vacuo* by the second-order perturbative energy *E(2)* in kcal/mol (NBO program (version 3.1) in Gaussian 09) of I and II. The specification of the orientations of the *p* and *d* atomic orbitals describing the NBOs is privileged with respect to their detailed description to evidence the character of the donor-acceptor interaction. a) Triple-ζ basis set (ECP28MDF + VTZ on Ag), b) double-ζ basis set (LANL2DZ on Ag). The *z*-axis lies in the direction defined by the Ag-Ag atoms.

	donor → acceptor	*E(2)*	donor → acceptor	*E(2)*
a)	$4s \rightarrow 5p_z$	11.48	$4s \rightarrow 5p_z$	8.65
	$5s \rightarrow 5s$	632.22	$5s \rightarrow$ Rydberg($6s$, $7p_z$, $5d_{xy}$)	11.68
	$5s \rightarrow$ Rydberg($6s$, $6p_y$)	37.14	$5s \rightarrow$ Rydberg($6s$, $7p_z$, $5d_{xy}$)	11.22
			$5s \rightarrow$ Rydberg($7s$, $7p_z$, $5d_{z2}$)	23.47
			$5p_x$, $5p_y \rightarrow$ Rydberg($6p_x$, $7p_y$)	89.26
			$5p_x$, $5p_y \rightarrow$ Rydberg($6p_y$, $7p_y$, $5d_{yz}$)	28.58
b)	$5s \rightarrow 5p_z$	93.15	$5s \rightarrow 5p_z$	28.53

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