Real-Time Atomistic Dynamics of Energy Flow in an STM Setup: Revealing the Mechanism of Current-Induced Molecular Emission

Supporting Information

Joanna Jankowska[1,2,*], Oleg V. Prezhdo[1,*]

[1] Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

[2] Institute of Physics, Polish Academy of Sciences, Warsaw, 02-668, Poland

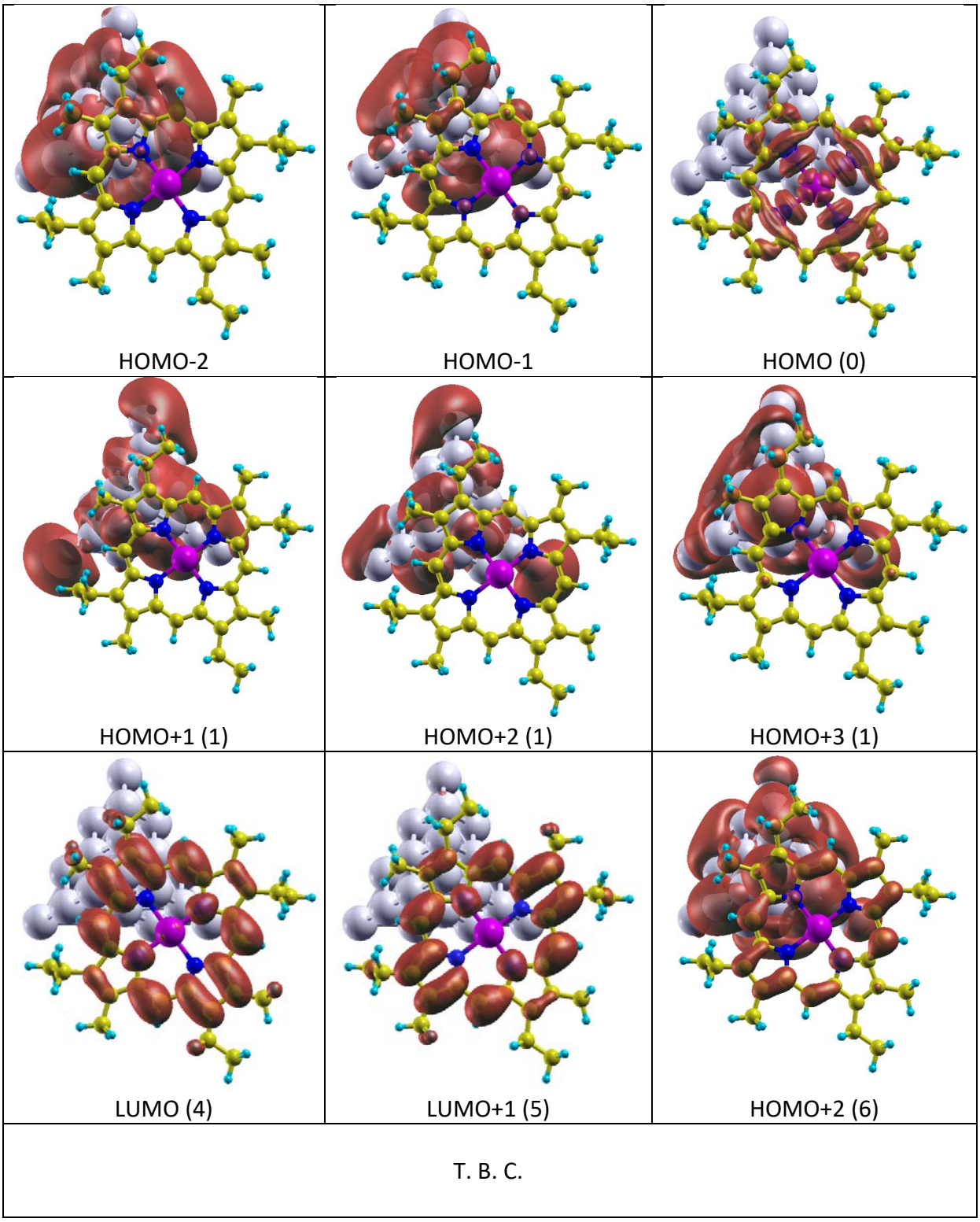
Table S1: Atomic coordinates of the silver tip and Zn(II)-etioporphyrin I system optimized with the PBE functional, with the kinetic energy cutoff for wave function and charge density set to 60 Ry and 800 Ry respectively, and with the Grimme's DFT-D2 dispersion correction included (the tip-molecule distance set to 6 Å).

Atom	X (Å)	Y (Å)	Z (Å)
Ag	7.00	7.00	1.89
Ag	5.62	4.52	2.00
Ag	2.85	4.61	2.07
Ag	4.17	7.04	2.00
Ag	5.55	9.44	2.00
Ag	7.00	11.79	2.07
Ag	8.45	9.44	2.00
Ag	9.83	7.04	2.00
Ag	11.15	4.61	2.07
Ag	8.39	4.52	2.00
Ag	7.00	5.25	4.37
Ag	4.17	5.36	4.38
Ag	5.49	7.88	4.37
Ag	7.00	10.27	4.38
Ag	8.51	7.88	4.37
Ag	9.83	5.36	4.38
Ag	5.51	6.15	6.65
Ag	6.99	8.71	6.65
Ag	8.48	6.14	6.65
Ag	7.00	6.99	8.84
N	8.05	5.75	14.95
C	6.67	5.73	15.03
C	6.17	7.06	15.24

C	7.25	7.92	15.26
C	8.43	7.09	15.05
C	5.88	4.57	14.92
C	6.32	3.26	14.89
N	7.65	2.87	14.90
C	7.64	1.49	14.93
C	6.27	0.99	14.94
C	5.45	2.10	14.92
C	8.77	0.68	14.96
C	10.09	1.14	14.98
C	11.27	0.28	14.99
C	12.37	1.11	14.99
C	11.85	2.48	14.99
N	10.46	2.47	14.99
C	12.64	3.62	14.97
C	12.20	4.94	14.95
C	13.07	6.11	14.96
C	12.25	7.21	14.94
C	10.89	6.71	14.91
N	10.88	5.33	14.92
C	12.63	8.66	14.96
C	14.57	6.06	14.95
C	15.13	5.85	13.53
C	9.76	7.53	14.94
C	13.84	0.84	14.97
C	11.11	-1.22	14.98
C	12.38	-2.09	15.01
C	3.95	2.15	14.91
C	3.38	2.39	13.49
C	5.89	-0.45	14.99
C	4.75	7.47	15.45
C	7.08	9.39	15.53
C	8.28	10.34	15.45
H	14.07	-0.24	14.97
H	14.34	1.29	15.86
H	14.31	1.29	14.08
H	6.37	-0.97	15.84
H	6.20	-0.99	14.07
H	4.80	-0.57	15.09
H	4.04	6.64	15.27
H	4.47	8.32	14.80
H	4.59	7.82	16.50
H	12.13	9.19	15.80

H	12.33	9.18	14.03
H	13.72	8.78	15.08
H	13.73	3.47	14.98
H	8.61	-0.40	14.96
H	4.80	4.72	14.95
H	9.95	8.61	14.96
H	14.92	5.24	15.62
H	14.97	7.00	15.38
H	10.52	-1.50	14.08
H	10.47	-1.50	15.84
H	3.60	2.95	15.59
H	3.55	1.20	15.31
H	6.64	9.48	16.56
H	6.27	9.76	14.86
H	16.24	5.81	13.54
H	14.82	6.68	12.87
H	14.75	4.91	13.09
H	12.10	-3.16	15.03
H	12.99	-1.88	15.91
H	13.01	-1.92	14.12
H	2.28	2.44	13.51
H	3.68	1.57	12.81
H	3.77	3.33	13.07
H	7.94	11.37	15.65
H	8.75	10.32	14.45
H	9.05	10.09	16.21
Zn	9.25	4.11	14.96

Figure S1: Visualization of the selected orbitals of the silver tip and Zn(II)-etioporphyrin I system (top view).



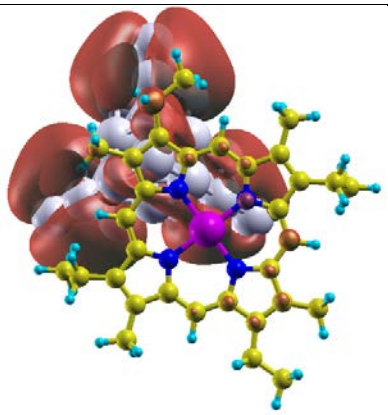
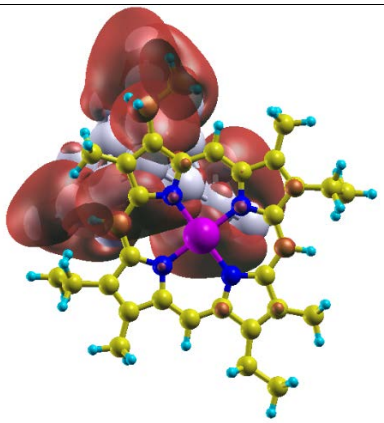
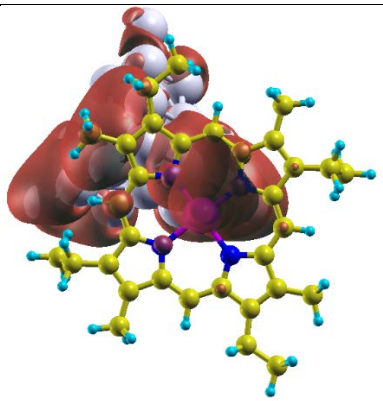
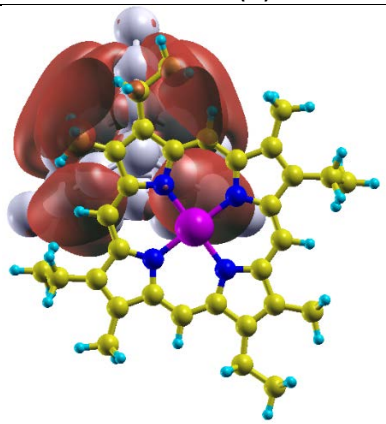
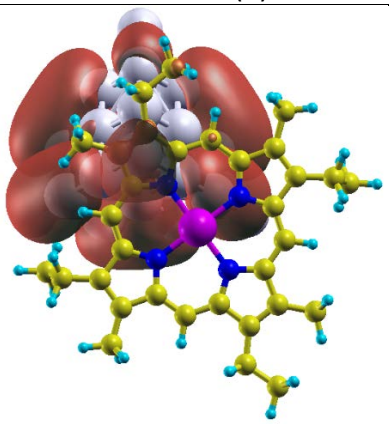
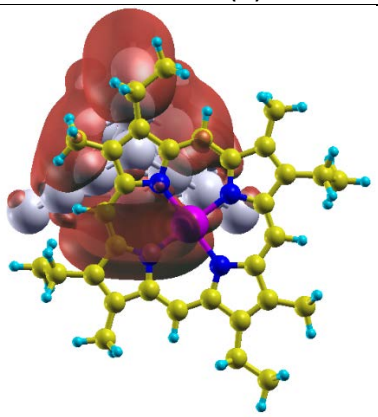
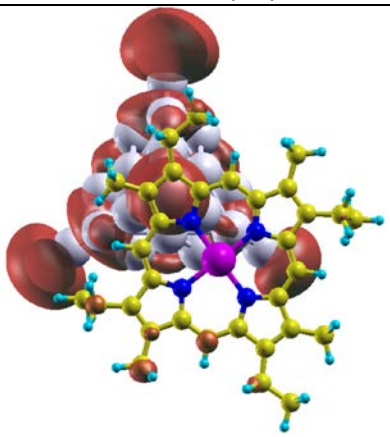
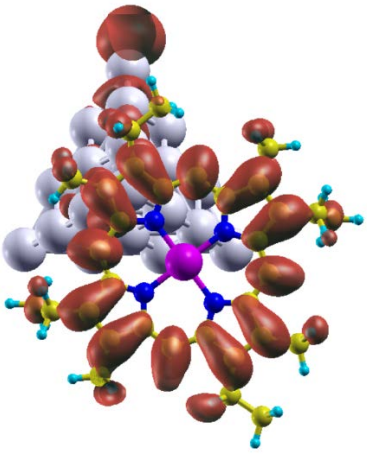
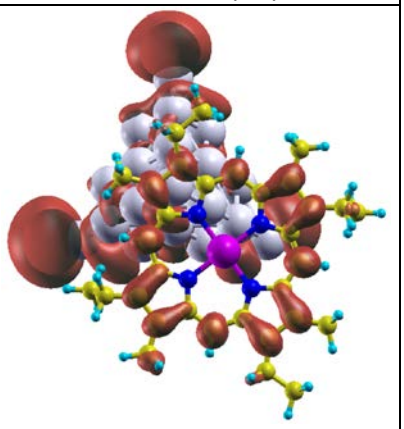
 LUMO+3 (7)	 LUMO+4 (8)	 LUMO+5 (9)
 LUMO+6 (10)	 LUMO+7 (11)	 LUMO+8 (12)
 LUMO+9 (13)	 LUMO+10 (14)	 HOMO+11 (15)

Figure S2: (a) Power spectrum and **(b)** population dynamics for intramolecular electron cooling. For state numbering, please refer to Figure S1.