

# Mechanism of Oxidative Shuttling for [2]Rotaxane in Stoddart-Heath Molecular Switch: Density Functional Theory Study with Continuum-Solvation Model

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## Supporting Information

Table S1. Ionization potentials (IP) and reduction potentials ( $E^0$ ) of TTF and DNP.

DFT	Opt	$E(g)$	ZPE/ $\Delta\Delta G_{0 \rightarrow 298K}$	Opt(sol)	$\Delta G_{solv}$	$E^0(\text{TTF})$	$E^0(\text{DNP})$	IP <sup>a</sup> (TTF)	IP <sup>a</sup> (DNP)	
(a)	B3LYP	6-31G**	6-31G**	-	-	6-31G** S 1.9 Å	0.22 / 1.05	0.88	6.1 <sup>b</sup> (6.3) <sup>c</sup>	6.6 <sup>b</sup> (6.7) <sup>c</sup>
(b)	B3LYP	6-31G**	6-31G**	-	6-31G**	6-31G** S 1.9 Å	0.22 / 1.04	0.89		
(c)	B3LYP	6-31G**	6-31G**	6-31G**	6-31G**	6-31G** S 1.9 Å	0.29 / 1.07	0.89		
(d)	B3LYP	6-31G**	6-311++G**	-	-	6-31G** S 1.9 Å	0.41 / 1.12	1.17	6.3 (6.5)	6.8 (7.1)
(e)	B3LYP	6-31G**	6-311++G**	-	6-31G**	6-31G** S 1.9 Å	0.41 / 1.11	1.18		
(f)	B3LYP	6-31G**	6-311++G**	6-31G**	6-31G**	6-31G** S 1.9 Å	0.48 / 1.14	1.18		
(g)	B3LYP	6-31G**	cc-pVTZ(-f)++	-	-	6-31G** S 1.9 Å	0.38 / 1.07		(6.5)	
(h)	B3LYP	6-31G**	cc-pVTZ(-f)++	6-31G**	-	6-31G** S 1.9 Å	0.44 / 1.10			
(i)	B3LYP	6-31G**	cc-pVTZ(-f)++	6-31G**	6-31G**	6-31G** S 1.9 Å	0.45 / 1.09			
(d')	B3LYP	6-31G**	6-311++G**	-	-	6-31G** S 1.7 Å	0.32 / 0.90	1.18	6.3 (6.5)	6.8 (7.1)
Expt'l							0.3–0.4 / 0.7–0.8 <sup>d</sup>	1.1–1.3 <sup>e</sup>	6.3 (6.7) <sup>f</sup>	(7.4) <sup>e</sup>

<sup>a</sup>From the energy difference between neutral and cationic species. <sup>b</sup>Vertical IP. <sup>c</sup>Adiabatic IP. <sup>d</sup>Ref<sup>1-3</sup>.

<sup>e</sup>1,5-dimethoxynaphthalene, Ref<sup>4</sup>. <sup>f</sup>Ref<sup>3,5</sup>. <sup>g</sup>Estimated (7.38) and measured (7.41) for 1,5-dimethoxynaphthalene, Ref<sup>6</sup>.

Table S2. Master table.

	$s$	$\Delta E$	$\Delta G_{solv}$	$\Delta G_{AN}^0$	q(TTF)	q(DNP)	s(TTF)	s(DNP)	$\Delta\Delta G_{AN}^0$	$E^0$
<sup>1</sup> 2: TTF	0	-1144514.8	-5.6	-1144520.5	0.00 / 0.00	-	-	-	-	-
<sup>2</sup> 2 <sup>+</sup> : TTF <sup>+</sup>	1/2	-1144368.6	-49.4	-1144418.0	1.00 / 1.00	-	1.0	-	-	0.32
<sup>1</sup> 2 <sup>2+</sup> : TTF <sup>2+</sup>	0	-1144115.0	-187.2	-1144302.2	2.00 / 2.00	-	-	-	0.0	0.90
<sup>3</sup> 2 <sup>2+</sup> : TTF <sup>2+</sup>	1	-1144078.3	-185.4	-1144263.7	2.00 / 2.00	-	2.0	-	38.5	-
<sup>1</sup> 3: DNP	0	-435340.9	-6.5	-435347.3	-	0.00 / 0.00	-	-	-	-
<sup>2</sup> 3 <sup>+</sup> : DNP <sup>+</sup>	1/2	-435183.0	-42.2	-435225.2	-	1.00 / 1.00	-	1.0	-	1.18
<sup>1</sup> 4: C(TTF)P	0	-4516518.5	-74.2	-4516592.7	0.16 / 0.32	-	-	-	-	-
<sup>2</sup> 4 <sup>+</sup> : C(TTF)P <sup>+</sup>	1/2	-4516361.5	-117.0	-4516478.5	0.72 / 0.70	-	0.94	-	-	0.83
<sup>1</sup> 4 <sup>2+</sup> : C(TTF)P <sup>2+</sup>	0	-4516119.6	-207.7	-4516327.3	1.52 / 1.28	-	-	-	0.0	2.44
<sup>3</sup> 4 <sup>2+</sup> : C(TTF)P <sup>2+</sup>	1	-4516094.3	-208.5	-4516302.7	1.16 / 0.99	-	1.49	-	24.5	-
<sup>1</sup> 5: C(DNP)P	0	-3807336.3	-71.9	-3807408.2	-	-0.09 / -0.06	-	-	-	-
<sup>2</sup> 5 <sup>+</sup> : C(DNP)P <sup>+</sup>	1/2	-3807167.3	-111.5	-3807278.7	-	0.73 / 0.55	-	0.98	-	1.49
<sup>1</sup> 6b: TTF-DNP	0	-1579098.9	-11.3	-1579110.2	-0.08 / -0.15	0.08 / 0.15	-	-	-	-
<sup>2</sup> 6b <sup>+</sup> : TTF-DNP <sup>+</sup>	1/2	-1578957.8	-48.1	-1579005.9	0.87 / 0.84	0.13 / 0.16	1.00	0.00	-	0.40
<sup>1</sup> 6b <sup>2+</sup> : TTF-DNP <sup>2+</sup>	0	-1578744.2	-140.1	-1578884.3	1.81 / 1.80	0.19 / 0.20	-	-	0.0	1.15
<sup>3</sup> 6b <sup>2+</sup> : TTF-DNP <sup>2+</sup>	1	-1578756.8	-126.4	-1578883.2	0.89 / 0.84	1.11 / 1.16	1.00	1.00	1.1	-
<sup>2</sup> 6b <sup>3+</sup> : TTF-DNP <sup>3+</sup>	1/2	-1578475.3	-289.2	-1578764.5	1.84 / 1.82	1.16 / 1.18	0.00	1.00	-	1.07
<sup>1</sup> 7: C(TTF)P-DNP	0	-4951104.1	-72.2	-4951176.3	0.12 / 0.28	0.01 / 0.02	-	-	-	-
<sup>2</sup> 7 <sup>+</sup> : C(TTF)P-DNP <sup>+</sup>	1/2	-4950955.3	-106.9	-4951062.3	0.61 / 0.60	0.09 / 0.07	0.93	0.02	-	0.83
<sup>1</sup> 7 <sup>2+</sup> : C(TTF)P-DNP <sup>2+</sup>	0	-4950744.0	-177.8	-4950921.9	0.85 / 0.75	0.79 / 0.78	-	-	10.7	-
<sup>3</sup> 7 <sup>2+</sup> : C(TTF)P-DNP <sup>2+</sup>	1	-4950753.7	-178.8	-4950932.5	0.63 / 0.59	1.05 / 1.05	0.95	1.00	0.0	1.50
<sup>1</sup> 8: TTF-C(DNP)P	0	-4951093.0	-75.5	-4951168.4	-0.06 / -0.18	-0.04 / 0.12	-	-	-	-
<sup>2</sup> 8 <sup>+</sup> : TTF-C(DNP)P <sup>+</sup>	1/2	-4950944.3	-113.2	-4951057.5	0.87 / 0.75	0.00 / 0.17	0.98	0.02	-	1.03 (0.69) <sup>a</sup>
<sup>1</sup> 8 <sup>2+</sup> : TTF-C(DNP)P <sup>2+</sup>	0	-4950724.0	-200.3	-4950924.3	1.49 / 1.36	0.31 / 0.40	-	-	2.1	-
<sup>3</sup> 8 <sup>2+</sup> : TTF-C(DNP)P <sup>2+</sup>	1	-4950736.5	-189.8	-4950926.4	0.93 / 0.79	0.79 / 0.75	1.00	0.98	0.0	1.77 (1.56) <sup>a</sup>
<sup>1</sup> 9: C(TTF)P-DNP	0	-4951862.3	-68.3	-4951930.6	-	-	-	-	-	-

<sup>a</sup>Reduction potential with respect to the metastable [TTF-C(DNP)P] in parenthesis.

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