Supporting Information

Spatially Inhomogeneous, Stepwise Phase Transitions in a Thiazyl Diradical: A Structural Mismatch Induced by Lattice Transformation

Rie Suizu,[*,†,‡] *Akito Iwasaki,*[§] *Yoshiaki Shuku,*[§] *Kunio Awaga*[*,‡,#]

[†]Department of Nanomaterials Science, Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[‡] JST-CREST, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

[§] Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

[#] Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

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Table S1. Selected Mean Internal Structural Parameters Related to the Dithiadiazolyl Rings

	150 K	200 K	250 K	280 K	300 K	320 K	340 K	360 K	380 K	400 K
					S-S / Å					
A	2.087	2.087	2.085	2.085	2.078	2.078	2.078	2.0714(8)	2.0718(8)	2.0709(9)
B	2.088	2.087	2.086	2.085	2.085	2.080	2.076			
C	2.082	2.081	2.081	2.077	2.078	2.077	2.075			
D	2.081	2.080	2.078	2.078	2.074	2.074	2.073			
					S-N / Å					
A	1.636	1.632	1.637	1.632	1.632	1.630	1.630	1.629	1.628	1.628
B	1.629	1.627	1.629	1.629	1.631	1.633	1.629			
C	1.637	1.634	1.633	1.632	1.631	1.629	1.627			
D	1.632	1.632	1.634	1.630	1.630	1.624	1.629			
					N-C / Å					
A	1.341	1.338	1.338	1.337	1.343	1.340	1.339	1.337	1.338	1.337
B	1.341	1.338	1.337	1.340	1.338	1.334	1.341			
C	1.341	1.340	1.339	1.338	1.333	1.337	1.340			
D	1.340	1.342	1.337	1.339	1.337	1.343	1.341			
					C-C_{exo} / Å					
A	1.468	1.472	1.466	1.469	1.471	1.474	1.478	1.472	1.472	1.473
B	1.482	1.485	1.480	1.478	1.476	1.478	1.472			
C	1.467	1.467	1.473	1.471	1.472	1.471	1.466			
D	1.479	1.479	1.478	1.473	1.476	1.470	1.460			
					S-S-N / °					
A	94.6	94.4	94.5	94.5	94.7	94.6	94.6	94.6	94.6	94.6
B	94.5	94.5	94.4	94.6	94.5	94.5	94.7			
C	94.6	94.6	94.8	94.6	94.4	94.5	94.6			
D	94.5	94.6	94.6	94.5	94.5	94.7	94.6			
					S-N-C / °					
A	114.2	114.5	114.4	114.5	114.4	114.5	114.6	114.6	114.7	114.7
B	114.6	114.6	114.7	114.4	114.5	114.5	114.5			
C	114.6	114.5	114.6	114.5	114.5	114.7	114.8			
D	114.6	114.5	114.6	114.9	114.9	114.8	115.0			
					N-C-N / °					
A	122.4	122.1	122.1	122.0	121.8	121.8	121.6	121.51(17)	121.34(17)	121.41(18)
B	121.8	122.0	121.8	122.0	122.0	122.1	121.7			
C	121.8	122.0	121.9	121.9	122.0	121.6	121.3			
D	121.7	121.8	121.8	121.1	121.2	119.9	120.9			

Table S2. Torsion angles.

	150 K	200 K	250 K	280 K	300 K	320 K	340 K	360 K	380 K	400 K
					dithiadiazolyl-phenylene / °					
A	18.7	18.2	18.2	18.3	18.3	17.8	17.2	-16.7	-16.5	-16.3
B	-18.6	-18.3	-18.1	-18.0	-18.1	-17.9	-17.4			
C	16.2	16.2	15.9	16.3	16.5	17.1	17.2			
D	-19.5	-19.4	-19.2	-18.6	-17.9	-16.9	-17.1			
					phenylene-phenylene / °					
A	38.0	37.8	37.5	37.8	37.9	37.6	37.4	37.5	37.5	37.5
B	38.5	38.9	38.4	38.1	38.0	37.5	37.2			
C	38.2	38.2	37.8	37.5	37.7	37.8	37.3			
D	38.2	37.8	38.0	37.9	37.7	37.9	38.0			

Table S3. Mean intermolecular S···S bond lengths (Å).

		150 K	200 K	250 K	280 K	300 K	320 K	340 K	360 K	380 K	400 K
						Intracolumnar Contacts					
A	intra-dimer	3.149	3.159	3.179	3.197	3.236	3.280	3.330	3.6202(18)	3.6313(18)	3.6419(18)
	inter-dimer	3.953	3.968	3.974	3.977	3.950	3.923	3.892			
B	intra-dimer	3.145	3.157	3.171	3.175	3.178	3.213	3.276			
	inter-dimer	3.956	3.969	3.981	3.996	4.009	3.991	3.947			
C	intra-dimer	3.210	3.234	3.241	3.256	3.271	3.317	3.387			
	inter-dimer	3.892	3.893	3.912	3.916	3.917	3.885	3.834			
D	intra-dimer	3.215	3.235	3.262	3.317	3.429	3.562	3.559			
	inter-dimer	3.884	3.889	3.889	3.852	3.754	3.637	3.661			
						Intercolumnar Contacts					
A-B	l_1	3.227(2)	3.235(3)	3.247(2)	3.2491(18)	3.2526(16)	3.2575(13)	3.2683(16)	3.3204(10)	3.3270(10)	3.3332(11)
	l_2	3.297(2)	3.307(3)	3.3136(19)	3.3212(18)	3.3355(16)	3.3503(13)	3.3532(16)			
B-C	l_3	3.266(3)	3.275(3)	3.280(3)	3.282(3)	3.283(2)	3.2896(17)	3.304(2)			
	l_4	3.331(3)	3.339(3)	3.346(3)	3.344(3)	3.3396(19)	3.3306(17)	3.332(2)			
C-D	l_5	3.169(3)	3.180(3)	3.192(2)	3.207(2)	3.2329(19)	3.2729(17)	3.277(3)			
	l_6	3.359(3)	3.365(3)	3.373(3)	3.374(3)	3.360(2)	3.3450(17)	3.347(3)			
D-A	l_7	3.222(3)	3.231(3)	3.236(3)	3.234(3)	3.236(3)	3.2360(19)	3.253(3)			
	l_8	3.329(3)	3.336(3)	3.346(3)	3.351(3)	3.354(3)	3.361(2)	3.364(3)			

Table S4. Centroid positions.

		150 K	200 K	250 K	280 K	300 K	320 K	340 K	360 K	380 K	400 K
A	*a*	0.495	0.495	0.495	0.496	0.496	0.497	0.497	0.750	0.750	0.750
	b	0.008	0.007	0.007	0.005	0.003	0.001	0.000	0.250	0.250	0.250
	c	0.502	0.502	0.502	0.501	0.501	0.501	0.501	0.001	0.001	0.000
B	*a*	-0.005	-0.005	-0.005	-0.005	-0.005	-0.005	-0.004	0.000	0.000	0.000
	b	0.120	0.121	0.120	0.121	0.123	0.126	0.125	0.000	0.000	0.000
	c	-0.003	-0.003	-0.003	-0.003	-0.003	-0.002	-0.002	0.251	0.251	0.250
C	*a*	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.250	0.250	0.250
	b	0.259	0.257	0.257	0.255	0.253	0.250	0.250	0.250	0.250	0.250
	c	0.503	0.503	0.503	0.503	0.503	0.502	0.502	0.501	0.501	0.500
D	*a*	0.505	0.505	0.505	0.504	0.503	0.501	0.501	0.500	0.500	0.500
	b	0.371	0.370	0.370	0.371	0.372	0.375	0.375	0.000	0.000	0.000
	c	0.001	0.001	0.001	0.000	0.000	-0.001	-0.001	0.751	0.751	0.750

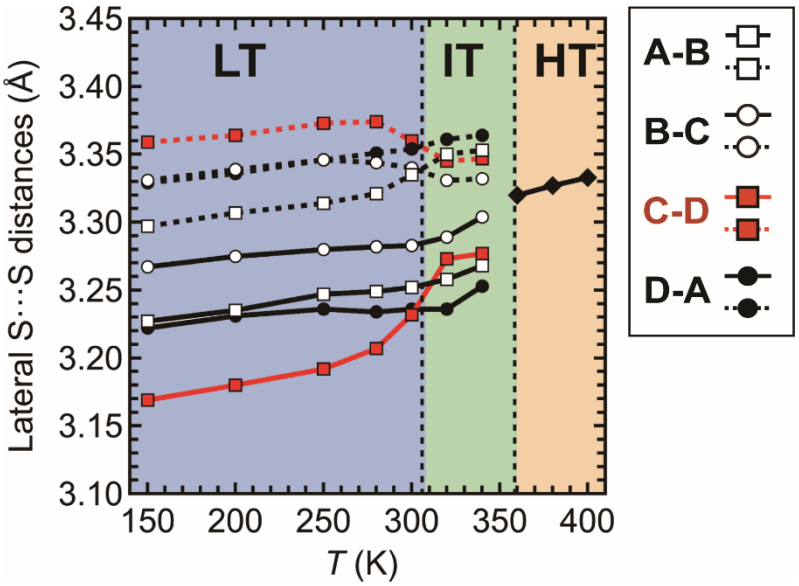

Figure S1. Temperature dependence of the lateral intercolumnar S···S distances.

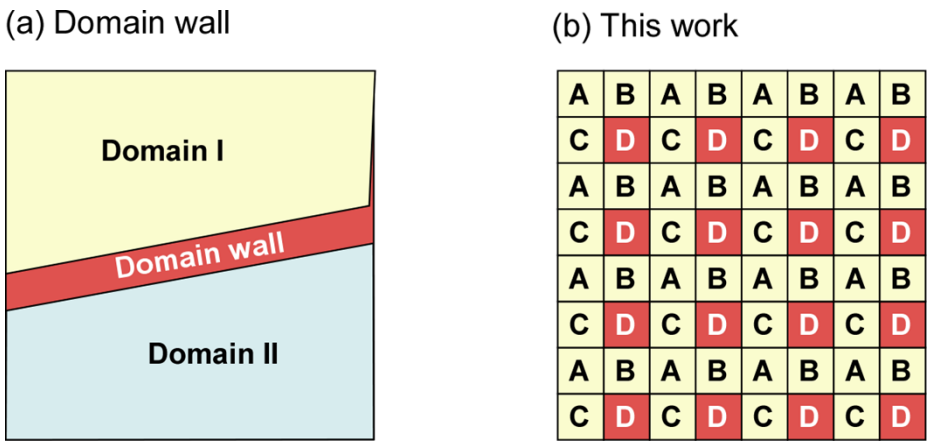

Figure S2. Schematic comparison between the conventional domain walls in low-dimensional molecular crystals (a) and the column **D** in the crystal of **1** (b).

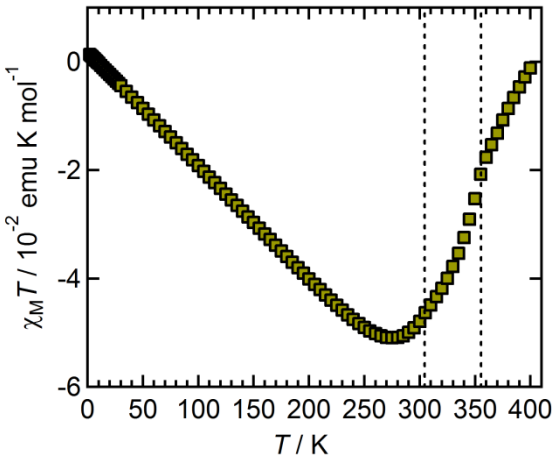

Figure S3. Plot of $\chi_M T$ vs. T.

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