Supplementary Information for

Adsorption-induced stability reversal of photochromic diarylethene on metal surfaces

Tomoko K. Shimizu,[a] Jaehoon Jung,[a] Hiroshi Imada[a] and Yousoo Kim[*a]

[a] Surface and Interface Science Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. Fax: +81 48 467 1945; Tel: +81 48 467 4073; E-mail: ykim@riken.jp

Computation details

In order to support experimental observations on the reversal in thermodynamic stability between the o-DM and c-DM, density functional theory (DFT) calculations were performed for isolated molecules, because more realistic periodic system for single molecule adsorption requires huge size of supercell to separate molecules and thus high computational cost. The PBE0[S1] hybrid density functional was mainly employed to evaluate the relative stabilities between two structural isomers, o-DM and c-DM, for neutral ($Q_{DM} = 0$), anionic (–1) and cationic (+1) states. The optimization of molecular structures and the evaluation of relative energies were carried out using 6-311G(d,p) and 6-311G+(2d,p) basis sets, respectively. The other two hybrid functionals, M06-2X[S2] and CAM-B3LYP[S3], were also utilized to check the validity of PBE0 results. All calculations were performed using Gaussian09 program suite.[S4] Our computational results indicate that the c-DM becomes more stable than the o-DM by about 7 kcal/mol for both cationic and anionic states although at neutral state, the o-DM is more stable than the c-DM by about 12 kcal/mol (see Table 1 in the main article). The other functionals, M06-2X and CAM-B3LYP, also consistently yield the reversal of thermodynamic stability between the two isomers by the change in ionic state (see Table S1).

Table S1. Relative energy (in kcal/mol) between two isomers, o-DM and c-DM, for neutral, cationic and anionic states.

	neutral		anion		cation	
	o-DM	c-DM	o-DM	c-DM	o-DM	c-DM
PBE0	**0.00**	**11.83**	**7.35**	**0.00**	**7.23**	**0.00**
M06-2X	0.00	13.73	4.64	0.00	7.82	0.00
CAM-B3LYP	0.00	15.96	2.46	0.00	5.94	0.00

o-DM   **c-DM**

HOMO   HOMO

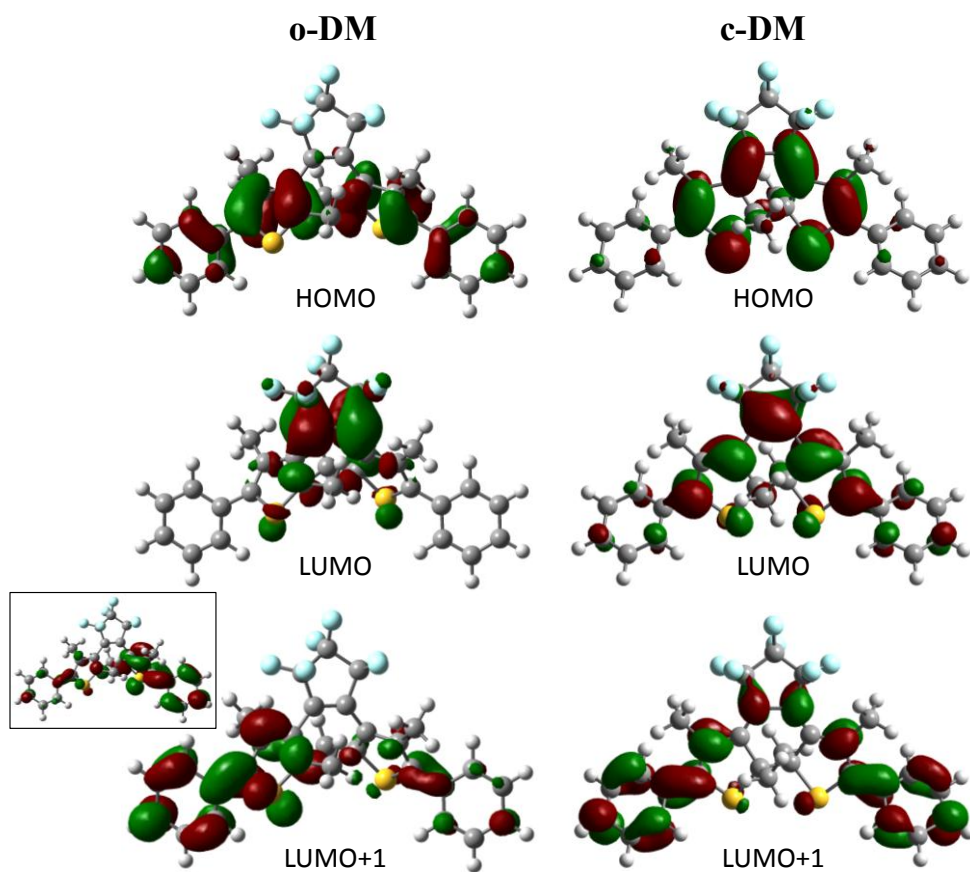LUMO   LUMO

LUMO+1   LUMO+1

Figure S1. Distribution of HOMO, LUMO, and LUMO+1 for neutral o-DM and c-DM. Doubly-delocalized orbital distribution for the LUMO+1 of o-DM is indicated in inset.
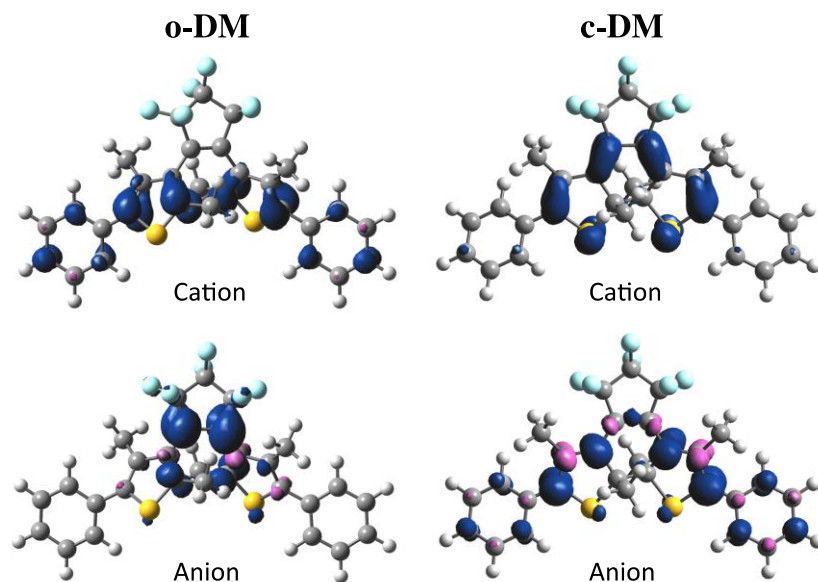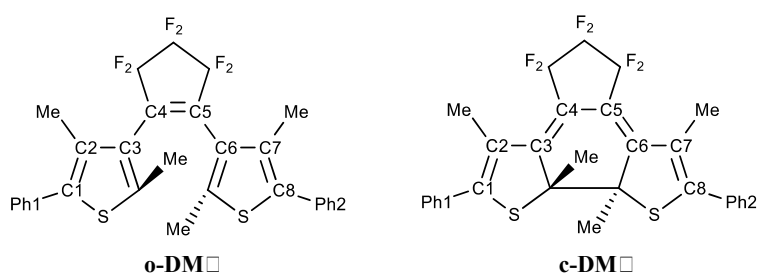
o-DM   **c-DM**

Cation   Cation

Anion   Anion

Figure S2. Spin density distribution of o-DM and c-DM at cationic and anionic states.

The isomerization between the o-DM to c-DM induces significant change in π-conjugated network within a molecule as shown in Fig. S1. The distributions of the frontier molecular orbitals, i.e., highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), display the different π-conjugated network of two isomers; i.e., both the HOMO of the o-DM and the LUMO of c-DM show wider distribution which extends to the terminal Ph-rings. Therefore, we suppose different change in the π-conjugated nature of each isomer at both cationic and anionic states. The spin density distributions of both isomers at cationic and anionic states show close correlation with the HOMO and LUMO, respectively (see Fig. S2).

Table S2. Numerical values of individual bond length and Wiberg bond index (WBI).

o-DM   c-DM

| | Wiberg bond index (WBI) | | | | | | bond length (A) | | | | | |
| | o-DM | | | c-DM | | | o-DM | | | c-DM | | |
	neutral	cation	anion	neutral	cation	anion	neutral	cation	anion	neutral	cation	anion
Ph1-C1	1.061	1.134	1.080	1.062	1.107	1.121	1.467	1.453	1.462	1.468	1.462	1.452
C1-C2	1.536	1.387	1.528	1.567	1.369	1.471	1.374	1.395	1.374	1.368	1.400	1.383
C2-C3	1.198	1.282	1.186	1.152	1.312	1.237	1.440	1.417	1.447	1.443	1.408	1.424
C3-C4	1.023	1.037	1.076	1.553	1.328	1.371	1.467	1.463	1.457	1.361	1.395	1.390
C4-C5	1.727	1.715	1.213	1.114	1.314	1.213	1.352	1.347	1.441	1.458	1.410	1.432
C5-C6	1.027	1.040	1.123	1.533	1.310	1.322	1.468	1.464	1.445	1.364	1.398	1.398
C6-C7	1.194	1.280	1.171	1.174	1.339	1.291	1.441	1.417	1.452	1.437	1.402	1.411
C7-C8	1.541	1.391	1.539	1.552	1.352	1.416	1.373	1.393	1.373	1.369	1.403	1.391
C8-Ph2	1.058	1.129	1.075	1.064	1.112	1.141	1.468	1.454	1.463	1.467	1.460	1.446
STDEV (σ)	0.267	0.216	0.184	0.234	0.100	0.120	0.048	0.040	0.036	0.048	0.026	0.026

To investigate the order of change in π-conjugated network within a molecule, we examine C-C bond lengths (d_{C-C}) and corresponding Wiberg bond indices (WBI)[S5] along carbon chains (C1-C8) connecting two terminal Ph-rings (see Table S2) because highly conjugated system should lead to a small deviation in bond lengths and WBI. Table S2 show the standard deviations (σ) for the d_{C-C} and WBI as well as detailed numerical values of individual bond length and bond index. At both cationic and anionic states, the larger decreases in $\sigma(d_{C-C})$ and $\sigma(\text{WBI})$ for the c-DM than the o-DM clearly indicate the formation of more effective π-conjugated network in the c-DM compared to the o-DM. Therefore, we suggest that this noticeable change in the stability depending on the ionic state can be interpreted using the different influence on the π-conjugated network.

Finally, we performed the calculations to evaluate the changes in barrier height for the isomerization from o-DM to c-DM depending on the ionic state. The geometry of transition state (TS) for neutral molecule at ground state (S_0) was also optimized using spin unrestricted DFT calculations because the transition state at neutral state may have a diradical character. Therefore, in order to get rid of the error due to spin contamination, we employed the approximate spin-correction procedure proposed by Yamaguchi et al.,[S6] in which the contamination of the singlet wavefunction is assumed to be contributed only from the first triplet state (T_1).

$$^1\Psi_{\mathrm{UDFT}} = c_{\mathrm{S}}\ ^1\Phi + c_{\mathrm{T}}\ ^3\Phi$$

The singlet spin-corrected energy ($^1E_{\mathrm{SC}}$) can be written as

$$^1E_{\mathrm{SC}} = {}^1E_{\mathrm{UDFT}} + f_{\mathrm{SC}}\left({}^1E_{\mathrm{UDFT}} - {}^3E_{\mathrm{UDFT}} \right)$$

where $^1E_{\mathrm{UDFT}}$ and $^3E_{\mathrm{UDFT}}$ are singlet and triplet energies calculated at the UPBE0/6-311G+(2d,p)//6-311G(d,p) level, respectively. The fraction of spin contamination is given by

$$f_{SC} = \frac{c_{\mathrm{T}}^2}{1 - c_{\mathrm{S}}^2} \approx \frac{^1\langle S^2 \rangle}{^3\langle S^2 \rangle - {}^1\langle S^2 \rangle}$$

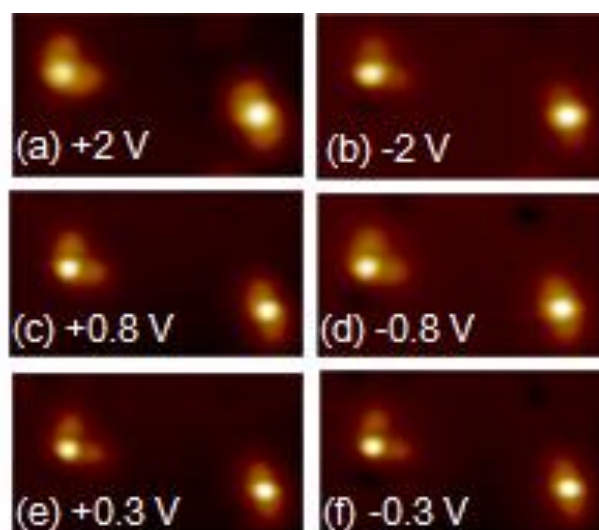where $^\alpha\langle S^2 \rangle$ denotes the spin expectation value for spin state α.

Figure S3. Bias dependent STM images $(7 \times 4 \ nm^2)$ of c-DM (left) and o-DM (right) on Cu(111). Sample bias is indicated in each image. $I_t = 5$ pA for (a) and (b), and 15 pA for others.

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