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# A Theoretical Study on Excited State Double Proton Transfer Reaction of 7-Azaindole Dimer: *Ab Initio* Potential Energy Surface and its Empirical Valence Bond Model

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## Atom indices of a 7-AI monomer



Figure S1: Atom indices of a 7-AI monomer. For a tautomer, the transferring H is labeled as 15.

# **Definition of internal coordinates**

coordinate         type         induces of atoms $r_1$ bond         1         2 $r_2$ bond         2         3 $r_3$ bond         3         4 $r_4$ bond         4         5 $r_5$ bond         6         7 $r_7$ bond         6         7 $r_7$ bond         9         4 $r_10$ bond         9         4 $r_{10}$ bond         9         1 $r_{11}$ bond         5         12 $r_{14}$ bond         5         12 $r_{14}$ bond         6         13 $r_{15}$ bond         7         14 $\theta_{16}$ angle         1         2 $q_{17}$ angle         4         5         12 $r_{14}$ bond         7         14         9 $q_{20}$ angle         3         1         2 $q_{16}$ angle         9         1         2 <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>						
$r_1$ bond         1         2 $r_2$ bond         2         3 $r_3$ bond         3         4 $r_4$ bond         4         5 $r_5$ bond         6         7 $r_7$ bond         7         8 $r_6$ bond         9         4 $r_7$ bond         9         4 $r_10$ bond         9         1 $r_11$ bond         2         10 $r_{11}$ bond         5         12 $r_11$ bond         5         12 $r_{14}$ bond         7         14 $\theta_{16}$ angle         1         2         10 $\theta_{17}$ angle         5         6         13 $\theta_{20}$ angle         4         5         1 $\phi_{21}$ dihedral         9         1         2         1 $\phi_{22}$ dihedral         4         5         6         1 $\phi_{22}$ <td>coordinate</td> <td>type</td> <td></td> <td>induces</td> <td>of atoms</td> <td></td>	coordinate	type		induces	of atoms	
$r_2$ bond       2       3 $r_3$ bond       3       4 $r_4$ bond       4       5 $r_5$ bond       6       7 $r_6$ bond       8       9 $r_7$ bond       9       4 $r_8$ bond       9       1 $r_1$ bond       9       1 $r_1$ bond       2       10 $r_{11}$ bond       2       10 $r_{12}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\phi_{21}$ dihedral       9       1       2       10 $\phi_{22}$ dihedral       9       1       2       11 $\phi_{24}$ dihedral       9       1       2       3 $\phi_{25}$	<i>r</i> 1	bond	1	2		
$r_3$ bond       3       4 $r_4$ bond       4       5 $r_5$ bond       6       7 $r_7$ bond       7       8 $r_8$ bond       9       1 $r_10$ bond       9       1 $r_{10}$ bond       9       1 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       6 $\theta_{20}$ angle       1       2       3       1 $\phi_{22}$ dihedral       9       4       5       1 $\phi_{24}$ dihedral       9       1       2       3       1 $\phi_{24}$ dihedral       5       6       7       <	$r_2$	bond	2	3		
$r_4$ bond       4       5 $r_5$ bond       5       6 $r_6$ bond       7       8 $r_7$ bond       9       4 $r_9$ bond       9       4 $r_{10}$ bond       9       1 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{14}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       10 $\phi_{22}$ dihedral       9       1       2       3       1 $\phi_{24}$ dihedral       4       5       6       1       1 $\phi_{25}$ angle       9	$r_3$	bond	3	4		
r5       bond       5       6         r6       bond       7       8         r7       bond       9       4         r9       bond       9       1         r10       bond       9       1         r11       bond       2       10         r12       bond       3       11         r13       bond       6       13         r14       bond       6       13         r15       bond       7       14 $\theta_{16}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       5       6       14 $\theta_{21}$ dihedral       9       1       2       1 $\theta_{22}$ dihedral       4       5       6       1 $\theta_{24}$ dihedral       9       4       5       1 $\theta_{25}$ angle       1       2       3       4 $\theta_{25}$ angle       7       8       9	r <sub>4</sub>	bond	4	5		
$r_0$ bond $6$ $7$ $r_7$ bond $7$ $8$ $r_8$ bond $9$ $4$ $r_{10}$ bond $9$ $1$ $r_{11}$ bond $2$ $10$ $r_{12}$ bond $3$ $11$ $r_{12}$ bond $5$ $12$ $r_{14}$ bond $6$ $13$ $r_{15}$ bond $7$ $14$ $\theta_{16}$ angle $1$ $2$ $10$ $\theta_{17}$ angle $2$ $3$ $11$ $\theta_{18}$ angle $4$ $5$ $12$ $\theta_{19}$ angle $6$ $7$ $14$ $\phi_{21}$ dihedral $9$ $1$ $2$ $11$ $\phi_{22}$ dihedral $1$ $2$ $3$ $1$ $\phi_{22}$ dihedral $4$ $5$ $6$ $1$ $\phi_{24}$ dihedral $4$ $5$ $6$ $1$ $\phi_{25}$ dihedral	r5	bond	5	6		
$r_0$ bond       7       8 $r_8$ bond       9       4 $r_0$ bond       9       1 $r_{10}$ bond       2       10 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\phi_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       11 $\phi_{22}$ dihedral       9       1       2       11 $\phi_{22}$ dihedral       9       4       5       11 $\phi_{24}$ dihedral       9       1       2       3 $\phi_{24}$ angle       1       2       3       4       9 <tr< td=""><td>r g</td><td>bond</td><td>6</td><td>7</td><td></td><td></td></tr<>	r g	bond	6	7		
$r_9$ bond       9       4 $r_{10}$ bond       9       4 $r_{10}$ bond       9       1 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       10 $\phi_{22}$ dihedral       9       1       2       11 $\phi_{23}$ dihedral       9       4       5       11 $\phi_{25}$ dihedral       4       5       6       1 $\phi_{24}$ dihedral       4       9       1       2       3 $\theta_{25}$ angle       9       1 <t< td=""><td><math>r_0</math></td><td>bond</td><td>7</td><td>8</td><td></td><td></td></t<>	$r_0$	bond	7	8		
$r_8$ bond       9       4 $r_{10}$ bond       9       1 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       5       6       13 $\theta_{20}$ angle       9       1       2       11 $\phi_{22}$ dihedral       9       4       5       11 $\phi_{22}$ dihedral       9       1       2       11 $\phi_{24}$ dihedral       4       5       6       11 $\phi_{25}$ dihedral       5       6       7       14 $\phi_{26}$ angle       9       1       2       3 $\phi_{25}$ dihedral       9	ro	bond	8	9		
ryo       bond       9       1 $r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\phi_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       9       4       5       1 $\phi_{24}$ dihedral       4       5       6       1 $\phi_{25}$ angle       1       2       3       4 $\phi_{26}$ angle       1       2       3       4 $\phi_{25}$ angle       3       4       9       1 $\phi_{31}$ angle       9	ro	bond	9	4		
$r_{11}$ bond       2       10 $r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       9       1       2       1 $\phi_{24}$ dihedral       9       1       2       3       1 $\phi_{24}$ dihedral       5       6       7       14 $\phi_{24}$ dihedral       9       1       2       3       4       9 $\phi_{25}$ dihedral       9       1       2       3       4       9 $\phi_{30}$ angle       7 </td <td>rig</td> <td>bond</td> <td>9</td> <td>1</td> <td></td> <td></td>	rig	bond	9	1		
$r_{12}$ bond       3       11 $r_{13}$ bond       5       12 $r_{14}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       14 $\phi_{22}$ dihedral       1       2       3       11 $\phi_{23}$ dihedral       9       4       5       11 $\phi_{24}$ dihedral       4       5       6       12 $\phi_{24}$ dihedral       5       6       7       14 $\phi_{25}$ dihedral       5       6       7       16 $\phi_{26}$ angle       1       2       3       4       9 $\theta_{30}$ angle       7       8 <t< td=""><td>r 10</td><td>bond</td><td>2</td><td>10</td><td></td><td></td></t<>	r 10	bond	2	10		
$r_{12}$ bond       5       11 $r_{13}$ bond       6       13 $r_{15}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       6       7       14 $\phi_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       9       1       2       1 $\phi_{23}$ dihedral       9       4       5       1 $\phi_{24}$ dihedral       4       5       6       1 $\phi_{25}$ dihedral       5       6       7       1 $\phi_{26}$ angle       9       1       2       3 $\phi_{26}$ angle       1       2       3       4       9 $\theta_{30}$ angle       7       8       9       4       5       6 $\theta_{31}$	r11	bond	23	10		
$r_{13}$ bond       5       12 $r_{14}$ bond       7       14 $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\theta_{21}$ dihedral       9       1       2       1 $\theta_{22}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       9       4       5       14 $\phi_{23}$ dihedral       9       4       5       1 $\phi_{25}$ dihedral       9       4       5       1 $\phi_{26}$ angle       1       2       3       4       9 $\theta_{27}$ angle       1       2       3       4       9 $\theta_{30}$ angle       3       4       9       1       6 $\theta_{31}$ angle       7       8       9       4       5<	7 <sub>12</sub>	bond	5	11		
$r_{14}$ bond       7       14 $\eta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       5       6       13 $\theta_{20}$ angle       6       7       14 $\psi_{21}$ dihedral       9       1       2       14 $\psi_{22}$ dihedral       9       1       2       14 $\psi_{22}$ dihedral       9       4       5       1 $\psi_{24}$ dihedral       4       5       6       7       14 $\psi_{25}$ dihedral       5       6       7       14 $\psi_{26}$ angle       9       1       2       0       11       2       3       4       9       0       12       0       0       13       13       14       14       13       14       14       14       14       14       14       14       14       14       14       14       14       14       14       14       14	7 <sub>13</sub>	bond	5	12		
$r_{15}$ bond $r_{14}$ $\theta_{16}$ angle       1       2       10 $\theta_{17}$ angle       2       3       11 $\theta_{18}$ angle       4       5       12 $\theta_{19}$ angle       6       7       14 $\phi_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       9       1       2       1 $\phi_{23}$ dihedral       9       4       5       1 $\phi_{24}$ dihedral       5       6       7       1. $\phi_{26}$ angle       9       1       2       3 $\phi_{26}$ angle       1       2       3       4 $\phi_{29}$ angle       3       4       9       1 $\phi_{31}$ angle       7       8       9       4       3       4       9 $\phi_{31}$ angle       5       6       7       8       9       4       4       4       4       4       4	$r_{14}$	bond	0	13		
	$r_{15}$	DONU an ala	/	14	10	
	$\Theta_{16}$	angle	1	2	10	
$\theta_{18}$ angle4512 $\theta_{19}$ angle5613 $\theta_{20}$ angle6714 $\phi_{21}$ dihedral9121 $\phi_{22}$ dihedral1231 $\phi_{23}$ dihedral9451 $\phi_{24}$ dihedral4561 $\phi_{25}$ dihedral5671 $\theta_{26}$ angle9123 $\theta_{27}$ angle1234 $\theta_{29}$ angle349 $\theta_{30}$ angle789 $\theta_{31}$ angle789 $\theta_{32}$ angle945 $\theta_{33}$ angle945 $\theta_{34}$ angle456 $\theta_{35}$ angle567 $\theta_{36}$ angle678 $\phi_{37}$ dihedral123 $\phi_{38}$ dihedral123 $\phi_{440}$ dihedral349 $\phi_{441}$ dihedral789 $\phi_{444}$ dihedral789 $\phi_{445}$ dihedral789 $\phi_{446}$ dihedral945 $\phi_{455}$ dihedral945 $\phi_{455}$ dihedral945 $\phi_{46}$	$\theta_{17}$	angle	2	3	11	
$\theta_{19}$ angle5613 $\theta_{20}$ angle6714 $\phi_{21}$ dihedral9121 $\phi_{22}$ dihedral1231 $\phi_{23}$ dihedral9451 $\phi_{24}$ dihedral4561 $\phi_{25}$ dihedral5671 $\theta_{26}$ angle9123 $\theta_{26}$ angle234 $\theta_{27}$ angle123 $\theta_{28}$ angle234 $\theta_{29}$ angle349 $\theta_{31}$ angle789 $\theta_{32}$ angle894 $\theta_{33}$ angle945 $\theta_{44}$ angle4567 $\theta_{36}$ angle678 $\phi_{37}$ dihedral912 $\phi_{38}$ dihedral123 $\phi_{39}$ dihedral234 $\phi_{440}$ dihedral349 $\phi_{441}$ dihedral456 $\phi_{45}$ dihedral789 $\phi_{444}$ dihedral9456 $\phi_{455}$ dihedral678 $\phi_{46}$ dihedral678 $\phi_{46}$ dihedral678 $\phi_{46}$	$\theta_{18}$	angle	4	2	12	
$\theta_{20}$ angle       6       7       14 $\phi_{21}$ dihedral       9       1       2       1 $\phi_{22}$ dihedral       1       2       3       1 $\phi_{23}$ dihedral       9       4       5       1 $\phi_{24}$ dihedral       4       5       6       7       1 $\phi_{25}$ dihedral       5       6       7       1 $\theta_{26}$ angle       9       1       2       3 $\theta_{26}$ angle       2       3       4       9 $\theta_{27}$ angle       1       2       3       4       9 $\theta_{26}$ angle       2       3       4       9       9 $\theta_{30}$ angle       7       8       9       4       6 $\theta_{31}$ angle       6       7       8       9       4       6       6       7       8       9       4       6       6       7       8       9       4       5       6       7       8       9       4       5       6       7       8	$\theta_{19}$	angle	5	6	13	
	$\theta_{20}$	angle	6	7	14	
	<b>\$</b> 21	dihedral	9	1	2	10
	<b>\$</b> 22	dihedral	1	2	3	11
	<b>\$</b> 23	dihedral	9	4	5	12
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<b>\$</b> 24	dihedral	4	5	6	13
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	\$\phi_{25}	dihedral	5	6	7	14
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\theta_{26}$	angle	9	1	2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{27}$	angle	1	2	3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{28}$	angle	2	3	4	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\theta_{29}$	angle	3	4	9	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{30}$	angle	4	9	1	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{31}$	angle	7	8	9	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{32}$	angle	8	9	4	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{33}$	angle	9	4	5	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{34}$	angle	4	5	6	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\theta_{25}$	angle	5	6	7	
	θ36	angle	6	7	8	
	Φ27	dihedral	9	1	2	3
	φ <sub>3</sub> ,	dihedral	1	2	3	4
	φ38 Φ20	dihedral	2	3	4	9
	φ39	dihedral	23	4	0	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	φ40	dihedral	5	- 0	1	2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ψ41 Φ.1-	dihedral	+ 7	9	1	2 1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ψ42	dihadral	/	0	9	4
	Ψ43	dinedrai	0	9	4	5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ψ44		9	4	5	0
$\psi_{46}$ dinedral       5       6       7 $\phi_{47}$ dihedral       6       7       8       9 $\phi_{48}$ dihedral       1       9       4       9 $\phi_{49}$ dihedral       8       9       4       1 $r_{50}$ bond       1 (8)       15 (15)       15 $\theta_{51}$ angle       9 (9)       1 (8)       15 (15) $\phi_{52}$ dihedral       4 (4)       9 (9)       1 (8)       15 (15)	Ψ45	dinedral	4	5	07	/
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Φ46	dinedral	5	6	/	8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	<b>\$</b> 47	dihedral	6	7	8	9
	<b>\$</b> 48	dihedral	1	9	4	5
$\begin{array}{cccccccc} r_{50} & \text{bond} & 1 (8) & 15 (15) \\ \theta_{51} & \text{angle} & 9 (9) & 1 (8) & 15 (15) \\ \phi_{52} & \text{dihedral} & 4 (4) & 9 (9) & 1 (8) & 15 (15) \end{array}$	<b>\$</b> 49	dihedral	8	9	4	3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	r <sub>50</sub>	bond	1 ( 8)	15 (15)		
$\phi_{52}$ dihedral 4 (4) 9 (9) 1 (8) 15 (15	$\theta_{51}$	angle	9 ( 9)	1 ( 8)	15 (15)	
	\$\$52	dihedral	4 ( 4)	9 (9)	1(8)	15 (15)

Table S1: Definition of internal coordinates [ () for monomers of a tautomer. ]

## The internal coordinates using in Eq. (5)

The internal coordinates using in Eq. (5) (natural internal coordinates) is given as follows:

$$q_i = r_i$$
 (for  $i = 1, ..., 15$ ), (S1)

$$q_i = \theta_i$$
 (for  $i = 16, \dots, 20$ ), (S2)

$$q_i = \phi_i$$
 (for  $i = 21, \dots, 25$ ), (S3)

$$q_{26} = 0.6324\theta_{26} - 0.5117\theta_{27} + 0.1954\theta_{28} + 0.1954\theta_{29} - 0.5116\theta_{30}, \tag{S4}$$

$$q_{27} = 0.3717\theta_{27} - 0.6015\theta_{28} + 0.6015\theta_{29} - 0.3717\theta_{30}, \tag{S5}$$

$$q_{28} = 0.5774\theta_{31} - 0.2887\theta_{32} - 0.2887\theta_{33} + 0.5774\theta_{34} - 0.2887\theta_{35} - 0.2887\theta_{36},$$
(S6)

$$q_{29} = 0.5000\theta_{32} - 0.5000\theta_{33} + 0.5000\theta_{35} - 0.5000\theta_{36},\tag{S7}$$

$$q_{30} = 0.4082\theta_{31} - 0.4082\theta_{32} + 0.4082\theta_{33} - 0.4082\theta_{34} + 0.4082\theta_{35} - 0.4082\theta_{36},$$
(S8)

$$q_{31} = 0.6324\phi_{37} - 0.5117\phi_{38} + 0.1954\phi_{39} + 0.1954\phi_{40} - 0.5116\phi_{41}, \tag{S9}$$

$$q_{32} = 0.3717\phi_{38} - 0.6015\phi_{39} + 0.6015\phi_{40} - 0.3717\phi_{41}, \tag{S10}$$

$$q_{33} = 0.5774\phi_{42} - 0.2887\phi_{43} - 0.2887\phi_{44} + 0.5774\phi_{45} - 0.2887\phi_{46} - 0.2887\phi_{47},$$
(S11)

$$q_{34} = 0.5000\phi_{43} - 0.5000\phi_{44} + 0.5000\phi_{46} - 0.5000\phi_{47}, \tag{S12}$$

$$q_{35} = 0.4082\phi_{42} - 0.4082\phi_{43} + 0.4082\phi_{44} - 0.4082\phi_{45} + 0.4082\phi_{46} - 0.4082\phi_{47}, \tag{S13}$$

$$q_{36} = 0.7071\phi_{48} - 0.7071\phi_{49},\tag{S14}$$

where  $\{r_i\}$ ,  $\{\theta_i\}$  and  $\{\phi_i\}$  are given in Table S1.

# The definition of $\vartheta$ in Eq. (10)

The definition of  $\vartheta$  in Eq. (10) is an angle between two planes each of which includes two protons and the averaged position of C and N atoms of each monomer.



Figure S2: Graphical definition of  $\vartheta$  ( $\theta$  in the figure). "H" are the transferring H atoms (H<sub>29</sub> and H<sub>30</sub>), and "×" are the averaged positions of C and N atoms of each monomer, respectively.

# The internal coordinates at the equilibrium geometries in Eq. (5)

coordinates	А	$A^*$	Т	$T^*$
$q_1^{\mathrm{X}}$	2.5925372	2.4518200	2.6275132	2.4308217
$q_2^{\rm X}$	2.5667306	2.7180162	2.5654832	2.7399253
$\hat{q}_3^{\tilde{\mathbf{X}}}$	2.7218150	2.7696040	2.7353528	2.8063599
$q_4^{\rm X}$	2.6708075	2.7061183	2.5859045	2.7161306
$q_5^{\dot{X}}$	2.6135025	2.7064303	2.7208457	2.7266622
$q_6^{X}$	2.6841343	2.6052897	2.5779752	2.5511454
$q_7^{X}$	2.4917979	2.5687652	2.6002479	2.6132843
$q_8^{\rm X}$	2.5383235	2.5426987	2.5467361	2.6155990
$q_9^{\rm X}$	2.6263435	2.5862249	2.7650053	2.5638161
$q_{10}^{\acute{\mathbf{X}}}$	2.5811553	2.7053270	2.4459721	2.6498177
$q_{11}^{X}$	2.0231191	2.0231007	2.0289360	2.0289667
$q_{12}^{\mathbf{X}}$	2.0249011	2.0243302	2.0238963	2.0252201
$q_{13}^{\tilde{X}}$	2.0321786	2.0257161	2.0312925	2.0238338
$q_{14}^{X}$	2.0299443	2.0325190	2.0277068	2.0300379
$q_{15}^{X}$	2.0336426	2.0341529	2.0252684	2.0284492
$q_{16}^{X}$	2.1059131	2.1557256	2.0682843	2.1283642
$q_{17}^{X}$	2.1972201	2.1816701	2.2284846	2.2324353
$q_{18}^{X}$	2.1227640	2.1615093	2.1240036	2.1524406
$q_{19}^{X}$	2.1169384	2.0951695	2.1058832	2.0970655
$q_{20}^{\mathrm{X}}$	2.0861695	2.0634408	2.1483318	2.1217328
$q_{21}^{\mathrm{X}}$	3.1415927	3.1415927	3.1415927	3.1415927
$q_{22}^{\mathrm{X}}$	3.1415927	3.1415927	3.1415927	3.1415927
$q_{23}^{\mathrm{X}}$	3.1415927	3.1415927	3.1415927	3.1415927
$q_{24}^{\mathrm{X}}$	3.1415927	3.1415927	3.1415927	3.1415927
$q_{25}^{\mathrm{X}}$	3.1415927	3.1415927	3.1415927	3.1415927
$q_{26}^{\mathrm{X}}$	-0.0227403	0.0454976	-0.1901739	-0.1421547
$q_{27}^{\mathrm{X}}$	0.0119608	0.0027608	-0.0128891	-0.0153030
$q_{28}^{\mathrm{X}}$	-0.1225686	-0.2819491	0.0009346	-0.1315385
$q_{29}^{\mathrm{X}}$	0.0461145	0.0560220	-0.0058846	-0.0022476
$q_{30}^{\mathrm{X}}$	-0.1192271	-0.1390426	0.0154060	0.0098503
$q_{31}^{\mathrm{X}}$	0.0000000	0.0000000	0.0000000	0.0000000
$q_{32}^{\rm X}$	0.0000000	0.0000000	0.0000000	0.0000000
$q_{33}^{X}$	0.0000000	0.0000000	0.0000000	0.0000000
$q_{34}^{\mathrm{X}}$	0.0000000	0.0000000	0.0000000	0.0000000
$q_{35}^{\rm X}$	0.0000000	0.0000000	0.0000000	0.0000000
$q_{36}^{X}$	0.0000000	0.0000000	0.0000000	0.0000000

Table S2: The internal coordinates at the equilibrium geometries. [unit: a.u. for length, radian for angle]

# Partial charges in Eq. (8)

charge	А	$A^*$	Т	T*
$Q_1^{0,\mathrm{X}}$	-0.169834	-0.082821	-0.581416	-0.490232
$Q_2^{0,\mathrm{X}}$	-0.263313	-0.066338	0.074665	0.074726
$Q_3^{0,\mathrm{X}}$	-0.327666	-0.020124	-0.407244	-0.066384
$Q_4^{0,\mathrm{X}}$	0.095316	0.036474	0.162125	0.081614
$Q_5^{0,\mathrm{X}}$	-0.151021	-0.339202	-0.112857	-0.235512
$Q_6^{0,\mathrm{X}}$	-0.204233	-0.271592	-0.202760	-0.241682
$Q_7^{0,\mathrm{X}}$	0.170251	0.069170	-0.187674	-0.243371
$Q_8^{0,\mathrm{X}}$	-0.478876	-0.637976	-0.068190	-0.137908
$Q_9^{0,\mathrm{X}}$	0.264236	0.263393	0.275304	0.237133
$Q_{10}^{0,{ m X}}$	0.223053	0.180178	0.156244	0.123750
$Q_{11}^{0,X}$	0.193080	0.170111	0.157577	0.123871
$Q_{12}^{0,X}$	0.155419	0.145060	0.148979	0.145596
$Q_{13}^{0,X}$	0.118982	0.134074	0.152760	0.171421
$Q_{14}^{0,X}$	0.086008	0.117481	0.175848	0.193623
$Q_{15}^{0,X}$	0.288597	0.302112	0.256638	0.263355

Table S3: Partial charges [unit:a.u.]

## The dumping function in Eq. (7)

The dumping function used in Eq. (7) is as follows:

$$f(r_{\alpha\beta}) = \begin{cases} \left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right)^4 - 2\left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right)^2 + 2\left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right) & (r_{\alpha\beta} < s_{\alpha\beta}), \\ 1 & (r_{\alpha\beta} \ge s_{\alpha\beta}), \end{cases}$$
(S15)

where

$$s_{\alpha\beta} = A(a_{\alpha}a_{\beta})^{1/6}.$$
 (S16)

Here  $\{a_{\alpha}\}$  denote the "volume" of each atom derived from the atomic polarizability and are given for the atomic species as follows;  $a_{\rm C} = 1.405 \text{ Å}^3$ ,  $a_{\rm H} = 0.514 \text{ Å}^3$ , and  $a_{\rm N} = 1.105 \text{ Å}^3$ . A is a scaling factor and given as A = 2.6.

### Parameters used in the PEF

term	AA*	$TT^*$
$V_0^{\mathrm{X}}$	-378.693877071	-378.666779221
$D_e^{\mathbf{X}}$	$2.556996307 \times 10^{-1}$	$2.408089647 \times 10^{-1}$
$\alpha^{X}$	1.002760889	1.019491804
$r^{X}$	1.927998115	1.934760239
$\alpha_{\theta}^{X}$	$2.414311060 \times 10^{-1}$	$2.777469250  imes 10^{-1}$
$\theta^{X}$	2.176783012	2.057857084
$\alpha_{\phi}^{X}$	$2.113007700 \times 10^{-2}$	$4.205127250 \times 10^{-2}$
$\phi^X$	3.141592654	3.141592654
$V_0^{X^*}$	-378.525263596	-378.568184655
$D_e^{\mathbf{X}^*}$	$2.391871087 \times 10^{-1}$	$2.562908779 \times 10^{-1}$
$\alpha^{X^*}$	1.013914033	1.003143599
$r^{X^*}$	1.940549747	1.926430678
$lpha_{ heta}^{\mathrm{X}^*}$	$2.386010320 \times 10^{-1}$	$2.676720880 \times 10^{-1}$
$\theta^{X^*}$	2.130919718	2.108576850
$\alpha_{\phi}^{X^*}$	$5.529704930 \times 10^{-2}$	$3.437585380  imes 10^{-2}$
φ <sup>'X*</sup>	3.141592654	3.141592654
$V_2^{A^*A} (V_1^{T^*T})$	2.262166652	2.731388624
$\tilde{\zeta_2^{A^*A}}$ ( $\tilde{\zeta_1^{T^*T}}$ )	1.461380588	1.491409338
$\tilde{V}_{2}^{A^{*}A}$ ( $\tilde{V}_{1}^{T^{*}T}$ )	$1.240963675 \times 10^{-1}$	$1.258089837  imes 10^{-1}$
$\tilde{\zeta}_2^{A^*A}$ $(\tilde{\zeta}_1^{T^*T})$	$6.322459320 \times 10^{-1}$	$6.869198610  imes 10^{-1}$
$V_4^{\bar{A}^*A} (V_3^{\bar{T}^*T})$	2.282898550	2.734431873
$\zeta_{4}^{A^{*}A} (\zeta_{3}^{T^{*}T})$	1.461331602	1.491443718
$ ilde{V}_{4}^{A^{*}A}  ( ilde{V}_{3}^{T^{*}T})$	$1.248733091 \times 10^{-1}$	$1.258842582  imes 10^{-1}$
$ ilde{\zeta}_4^{\mathrm{A}^*\mathrm{A}}( ilde{\zeta}_3^{\mathrm{T}^*\mathrm{T}})$	$6.375272414 \times 10^{-1}$	$6.651187377  imes 10^{-1}$
$a_{\Phi_2}^{A^*A} (a_{\Phi_1}^{T^*T})$	$2.480882688 \times 10^{-1}$	$2.313455213 \times 10^{-1}$
$a_{\phi_4}^{\dot{A}^*A} (a_{\phi_3}^{\dot{T}^*T})$	$2.642175920 \times 10^{-1}$	$2.207843240 \times 10^{-1}$
V <sub>corr 0</sub> <sup>X*X</sup>	$-1.667780276 \times 10^{-2}$	$-1.621894161 \times 10^{-2}$
$(a_{\rm corr}^{{\rm X}^*{\rm X}})^{1/6}$	4.377336791	4.618272738
$a_{\vartheta}$	$1.570261956 \times 10^{-1}$	$1.518469875  imes 10^{-1}$
$V^{\rm NN}$	$7.500000000 \times 10^{-5}$	$7.500000000 \times 10^{-5}$
$\zeta^{NN}$	$1.000000000  imes 10^{+1}$	$1.000000000  imes 10^{+1}$
R <sup>NN</sup>	5.00000000	5.00000000
a <sub>mod</sub>	$1.000000000 \times 10^{-1}$	$1.00000000 \times 10^{-1}$

Table S4: Parameters used in the PEF (unit:a.u.).

# The terms in the off-diagonal element in Eq. (14)

The terms in the off-diagonal element, Eq. (14), is as follows.

$$a_1' = 1.362672513 \times 10^{-1},\tag{S17}$$

$$a_2' = 1.047629760 \times 10^{-3} \xi_1^2 - 2.848680071 \times 10^{-2} \xi_1 + 4.827950385 \times 10^{-1}, \tag{S18}$$

$$a'_3 = 1.853914153 \times 10^{-2}, \tag{S19}$$

$$a_1'' = -4.453415570 \times 10^{-2} \xi_1^2 + 3.721369096 \times 10^{-3} \xi_1 - 1.335184827 \times 10^{-1},$$
 (S20)

$$a_2'' = -1.194755309 \times 10^{-1} \xi_1^2 - 1.355779708 \times 10^{-2} \xi_1 + 5.613355470 \times 10^{-1},$$
 (S21)

$$a_3'' = -1.523253963 \times 10^{-2}.$$
(S22)

If  $a_2'' \le 0$ , the second term of Eq. (14) is neglected, *i.e.*,  $a_1'' = 0$ .

#### The force constant matrices in Eq. (5)

The force constant matrices in Eq. (5) are in another file. In the file, the parameters are tabulated as follws.

```
----- force constant matrix for monomer A, a^{A}_{i,j} -----
#
#
            1
                        2
                                   3
#j∖i
                                                4
 1 0.4768785930D+00 0.5564599340D-01 -0.1796669960D-01 0.7318808400D-02
 2 .....
 36 .....
                                           . . . . . . . .
#j∖i
             5
                         6
                                                8
 1 .....
 •
      .
                 .
      .
#j\i
           33
                       34
                                   35
                                              36
 1 .....
 .
      .
                             .
      .
                 .
                             .
 36 .....
                          . . . . . . . . . . . . . . . . . .
#
----- force constant matrix for monomer A*, a^{A*}_{i,j} -----
#
#
#j\i
            1
                        2
                                    3
                                                4
 1 0.6822566280D+00 0.5550027470D-01 0.2299298890D-01 -0.3148648080D-01
    .
                           .
      .
 .
#
 ----- force constant matrix for monomer T, a^{T}_{i,j} -----
#
#
#j\i
             1
                        2
                                    3
                                                4
 1 .....
                   . . . . . . . . . .
#
 ----- force constant matrix for monomer T*, a^{T*}_{i,j} -----
#
#
#j\i
            1
                        2
                                    3
                                                4
 1 .....
                 .
                             .
                                        .
      .
```

# The CRK matrices in Eqs. (7)-(8)

The CRK matrices in Eqs. (7)-(8) are in another file. In the file, the parameters are tabulated as follws.

# #	charge response	e kernel for monome	er A, K^{A}_{i,j}		
#j\i 1 2	1 -0.4149651000D+01	2 0.9245640000D+00	3 0.1956897000D+01	4 -0.1654392000D+01	5 0.3792570000D+00
15					
#j\i 1	6	7	8	9	10
#j\i 1	11	12	13	14	15
15				• •	
#					
# #	charge response	e kernel for monome	er A*, K^{A*}_{i,j	}	
# #j\i 1	1	2	3	4	5
	:				
# #					
# # #	charge response	e kernel for monome	er T, K^{T}_{i,j} ·		
#j\i 1	1	2	3	4	5
•					
# # #	charge response	e kernel for monome			
" # #j\i 1	1	2	3	4	5
•	•	•	•	•	•