Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Suppression of Reversible Photocyclization Reaction Induced Fluorescence Enhancement: A Theoretical Study

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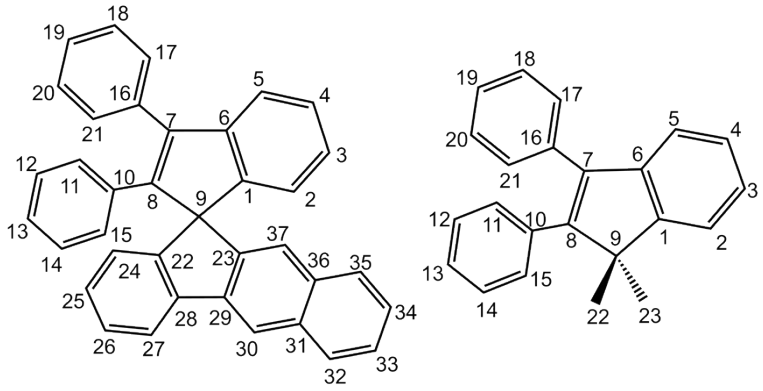

Chart S1. Chemical Structure of SIP-2 and DPI.

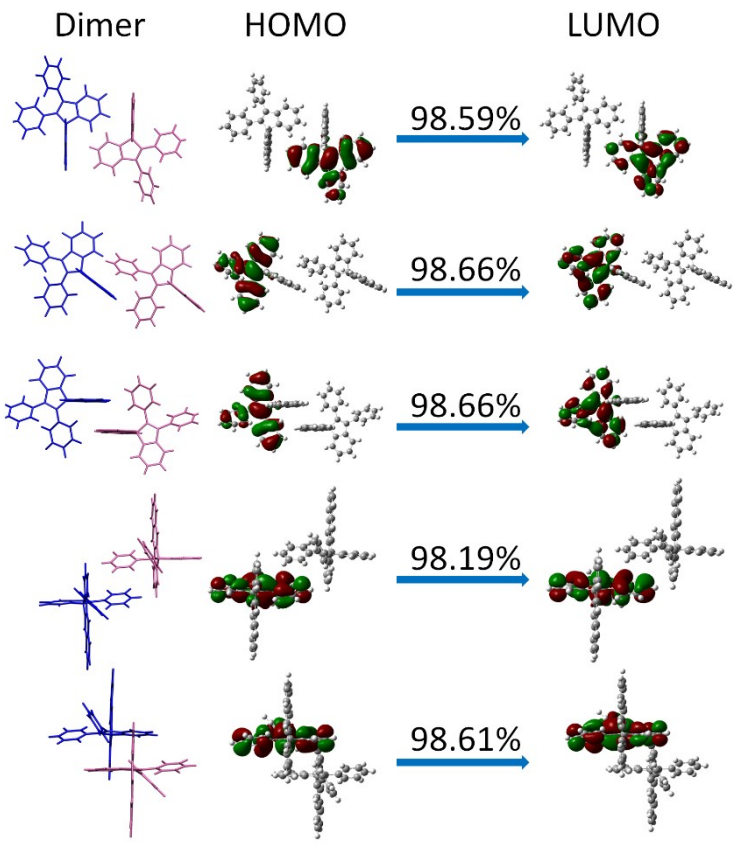

Fig. S1. The HOMO and LUMO orbitals of representative dimers of SIP-2.

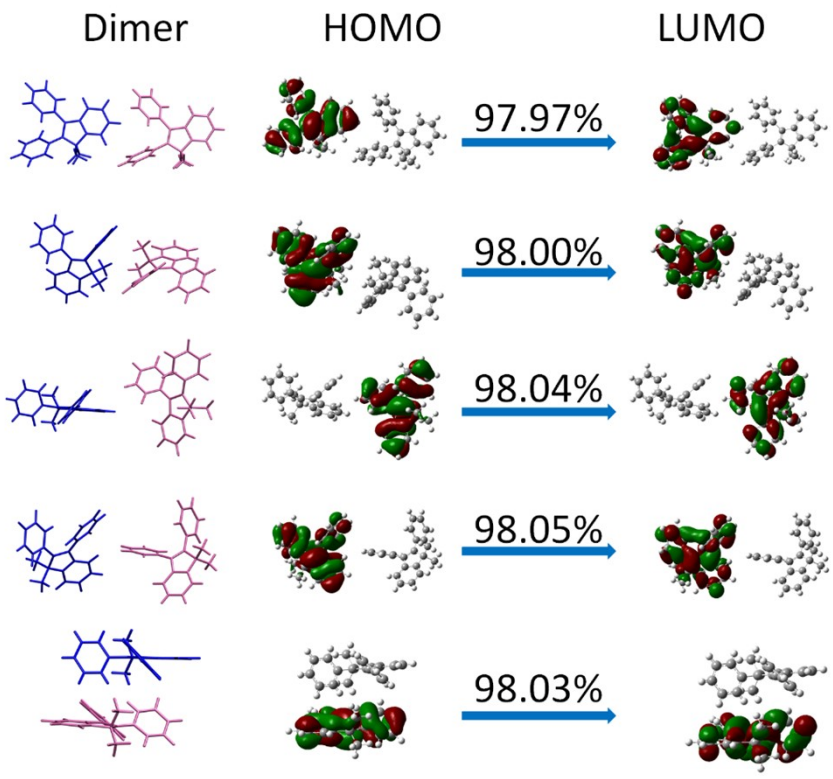

Fig. S2. The HOMO and LUMO orbitals of representative dimers of DPI.

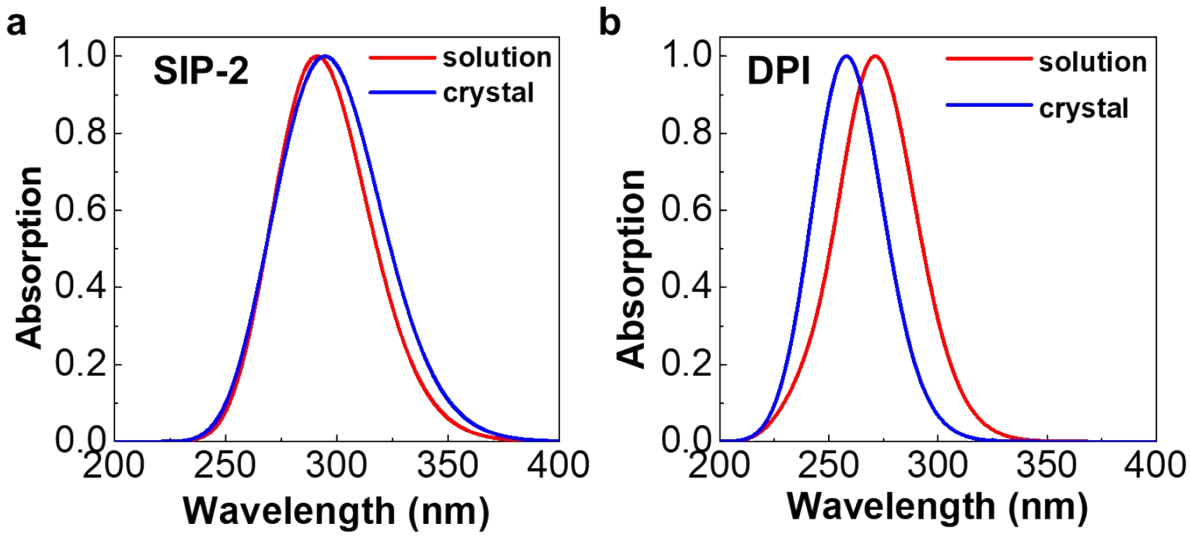

Fig. S3. Calculated absorption spectra of SIP-2 and DPI in solution and crystal state.

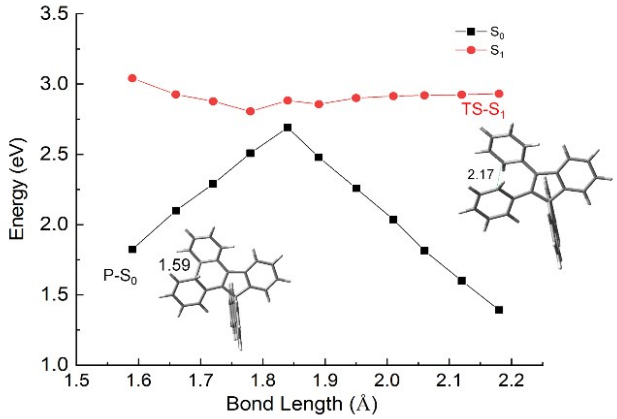

Fig. S4 Energy profiles along the SIP-2-TS -$(S_1/S_0)_x$ reaction coordinate obtained with the TD-M062X approaches.

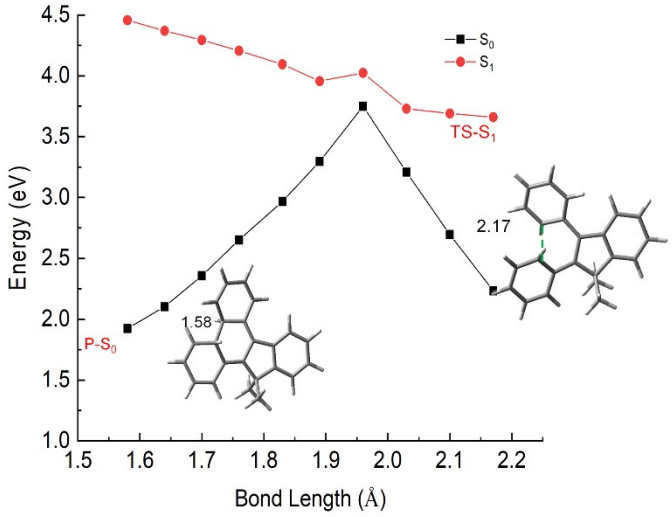

Fig. S5 Energy profiles along the DPI-TS -$(S_1/S_0)_x$ reaction coordinate obtained with the TD-M062X approaches.

Table S1. The calculated absorption and emission wavelength of SIP-2 in THF solution by using PCM model at several different functionals with basis set 6-31G**, respectively.

	Absorption	Emission
Experimental results[1]	3.92 eV/316 nm	2.92 eV/425 nm
B3LYP	3.57 eV/348 nm *f=0.0632*	2.51 eV/493 nm *f=0.4208*
BMK	4.03 eV/308 nm *f=0.3844*	2.65 eV/468 nm *f=0.4697*
BHandHLYP	4.33 eV/286 nm *f=0.4282*	2.69 eV/461 nm *f=0.4913*
M06-2X	**4.16 eV/298 nm *f=0.4075***	**2.68 eV/461 nm *f=0.4542***
M06-HF	3.69 eV/336 nm *f=0.1969*	2.44 eV/508 nm *f=0.4186*
CAM-B3LYP	4.28 eV/289 nm *f=0.3533*	2.68 eV/462 nm *f=0.4767*
ωB97XD	4.29 eV/289 nm *f=0.3949*	2.68 eV/462 nm *f=0.4723*

Table S2. Selected bonds (Å), angles (°) and dihedral angles (°) of DPI and SIP-2 in both aggregate and solution phases at the S_0 (S_1) Minimum.

	DPI						SIP-2					
	Solution			Crystal			Solution			Crystal		
	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$
$C_1\text{-}C_6$	1.48	1.43	0.05	1.48	1.43	0.05	1.48	1.44	0.04	1.48	1.44	0.04
$C_2\text{-}C_9$	1.48	1.41	0.07	1.48	1.41	0.07	1.48	1.41	0.07	1.48	1.42	0.06
$C_1\text{-}C_2$	1.35	1.46	0.11	1.35	1.46	0.11	1.36	1.46	0.10	1.36	1.46	0.10
$C_2\text{-}C_3$	1.52	1.52	0.00	1.53	1.53	0.00	1.53	1.52	0.01	1.53	1.53	0.00
$C_1\text{-}C_5$	1.48	1.43	0.05	1.48	1.43	0.05	1.48	1.43	0.05	1.48	1.43	0.05
$C_6\text{-}C_1\text{-}C_2$	127.0	125.2	1.89	130.0	127.1	2.9	127.4	125.0	2.4	130.0	127.0	3.0
$C_6\text{-}C_1\text{-}C_5$	124.0	126.4	2.4	120.3	123.6	3.3	123.2	126.6	3.4	120.3	123.1	2.8
$C_2\text{-}C_1\text{-}C_5$	109.0	108.0	1.0	108.7	108.3	0.4	109.4	107.9	1.5	109.5	108.3	1.2
$C_7\text{-}C_6\text{-}C_1$	120.9	120.4	0.5	121.1	121.2	0.1	120.6	120.2	0.4	120.6	120.4	0.2
$C_8\text{-}C_6\text{-}C_1$	120.4	122.2	1.8	120.3	121.4	1.1	120.5	122.3	1.8	120.3	121.6	1.3
$C_{10}\text{-}C_9\text{-}C_2$	119.5	121.7	1.2	121.0	119.5	1.5	119.5	122.0	2.5	121.1	123.0	1.9
$C_{15}\text{-}C_9\text{-}C_2$	121.8	122.2	0.4	120.4	123.7	3.3	122.0	121.2	0.8	121.0	120.3	0.7
$C_{11}\text{-}C_9\text{-}C_8$	126.1	124.8	1.3	126.1	123.4	2.7	127.2	126.4	0.8	129.2	128.0	1.2
$C_9\text{-}C_2\text{-}C_3$	122.3	125.1	2.9	122.3	124.3	2.0	122.0	124.0	2.0	120.9	122.1	1.3
$C_1\text{-}C_2\text{-}C_3$	111.3	109.5	1.8	111.6	110.6	1.0	110.5	109.3	1.2	110.0	109.6	0.4
$C_7\text{-}C_6\text{-}C_1\text{-}C_2$	45.6	27.1	18.5	45.4	26.5	18.9	48.0	28.0	20.0	51.3	32.7	18.6
$C_{10}\text{-}C_9\text{-}C_2\text{-}C_1$	60.3	16.0	44.3	73.6	32.8	40.8	41.7	14.4	27.3	29.5	14.7	14.8
$C_{13}\text{-}C_{12}\text{-}C_3\text{-}C_2$							123.8	130.2	6.4	129.4	131.4	2.0

Table S3. Reorganization energies ($\lambda=\lambda_{gs}+\lambda_{es}$) were obtained for SIP-2 and DPI in both solution and crystal states at M06-2X/6-31G(d,p) level by AP method. (Energy unit: meV)

	In solution			In crystal state		
SIP-2	λ_{gs}	λ_{es}	λ	λ_{gs}	λ_{es}	λ
AP	660	810	1470	510	560	1070
NM	680	910	1590	600	630	1230
DPI	λ_{gs}	λ_{es}	λ	λ_{gs}	λ_{es}	λ
AP	720	1110	1830	640	940	1580
NM	946	2126	3072	911	1387	2298

Table S4. Selected internal coordinate (IC) with reorganization energies (λ_i > 1 meV) for SIP-2 in both solution and crystalline states.

In solution		In crystalline state	
ICR	λ_i (meV)	ICR	λ_i (meV)
C7-C8-C10-C11 (D_2)	**115.56**	C7-C8	113.19
C7-C8	111.00	C8-C10	65.10
C9-C8-C10-C11	**109.33**	C8-C7-C16-C21	54.28
C9-C8-C10-C15	96.25	C6-C7	42.55
C8-C10	91.71	C8-C7-C16-C17	34.59
C7-C8-C10-C15	90.48	**C9-C8-C10-C11**	**33.56**
C8-C7-C16-C21	55.57	C6-C7-C16-C21	30.08
C8-C7-C16-C17	37.93	**C7-C8-C10-C11 (D_2)**	**25.89**
C6-C7	37.63	C7-C16	22.76
C6-C7-C16-C21	31.64	C7-C8-C10-C11	20.28
C7-C16	27.22	C6-C7-C16-C17	16.78
C6-C7- C16-C17	20.90	C1-C6	15.34
C10-C11	14.42	C9-C8-C10-C15	14.56
C1-C6	13.29	C13-C14	12.22
C6-C7-C16	12.28	C6-C7-C16	10.74
C10-C15	11.80	C10-C15	10.20
C6-C1-C9-C22	8.38	C5-C6	7.50
C5-C6	7.74	C8-C7-C16	7.18
C8-C9-C22-C27	7.56	C3-C4	5.73
C6-C1-C9-C8	7.23	C6-C1-C9	4.47
C8-C7-C16	6.21	C9-C8-C10	4.16
C13-C14	5.54	C13-C14	4.11
C9-C8-C10	4.58	C5-C6-C7-C8	3.98
C14-C15	4.57	C14-C15	3.64
C2-C1-C9-C22	4.49	C8-C9-C23	3.59
C16-C21	4.38	C4-C5	3.50
C8-C9-C23-C29	4.21	C16-C17	3.29
C3-C4	4.20	C16-C21	3.24
C2-C1-C9-C8	4.04	C8-C9-C22-C24	2.92
C16-C17	3.80	C1-C6- C5	2.77
C6-C1-C9-C23	3.66	C7-C8-C10	2.76
C8-C9-C23-C29	3.37	C8-C9-C22-C28	2.74
C8-C9-C22-C24	3.27	C2-C1-C9-C23	2.59
C1-C6-C5	3.03	C1-C9-C8	2.16
C4-C5	2.97	C6-C1-C9-C22	1.66
C6-C1-C9	2.87	C18-C19	1.54
C6-C7-C8-C9	2.67	C2-C1-C9	1.49
C7-C16-C17	2.62	C17-C16-C21-C20	1.48
C1-C9-C8	2.60	C7-C8-C9-C22	1.27
C7-C8-C9-C22	2.44	C1-C6-C7	1.21
C8-C9	1.80	C7-C16-C17	1.16
C18-C19	1.71	C8-C9	1.08

C7-C8-C10	1.64	C6-C7-C8	1.01
C6-C7-C8	1.51		
C8-C10-C11	1.27		
C10-C8-C9-C22	1.20		
C17-C18	1.19		
C2-C1-C9	1.13		
C17-C16-C21-C20	1.04		

Table S5. Selected IC with reorganization energies (λ_i > 1 meV) for DPI in both solution and crystalline states.

In solution		**In crystalline state**	
ICR	λ_i (meV)	ICR	λ_i (meV)
C7-C8-C10-C11 (D_2)	**418.71**	**C7-C8-C10-C11 (D_2)**	**305.09**
C7-C8-C10-C15	**410.18**	**C7-C8-C10-C15**	**251.79**
C9-C8-C10-C11	**390.39**	**C9-C8-C10-C11**	**196.09**
C9-C8-C10-C15	**382.10**	**C9-C8-C10-C15**	**159.48**
C7-C8	100.28	C7-C8	123.91
C8-C9	99.14	C8-C7-C16-C21	72.41
C10-C8-C9-C23	70.15	C8-C9	54.55
C10-C8-C9-C22	59.88	C8-C7-C16-C17	50.03
C8- C7-C16-C21	58.67	C6-C7-C16-C21	45.11
C7-C8-C9-C23	49.26	C6-C7	43.94
C7-C8-C9-C22	41.68	C7-C16	29.22
C6-C7-C16-C21	39.37	C6-C7-C16-C17	28.18
C7- C8-C16-C17	33.05	C6-C1	11.68
C6-C7	31.77	C10-C8-C9	11.45
C7-C16	29.57	C10-C8-C7	9.82
C6- C7-C16-C17	24.48	C6-C1-H9-C22	9.20
C10-C11	15.01	C5-C6	8.36
C10-C15	14.44	C16-C7-C6	6.84
C9-C8-C10	14.43	C8-C7-C16	6.26
C6- C1-C9-C8	13.76	C8-C7-C16	5.44
C6- C7-C16	13.52	C10-C15	5.43
C1-C6	10.53	C16-C17	5.17
C1-C9-C23	9.43	C8-C10-C15	5.13
C2-C1-C9-C8	8.87	C22-C9-C1-C2	4.89
C8-C7-C16	8.78	C6-C1-C9	4.60
C5-C6	7.48	C3-C4	4.38
C7-C8-C10	6.84	C7-C8-C9-C22	4.21
C13-C14	5.21	C23-C9-C1-C6	3.75
C14-C15	4.64	C4-C35	3.61
C16-C21	4.53	C9-C8-C7-C6	3.12
C16-C17	4.43	C16-C21	2.87
C10-C8-C9-C1	4.31	C8-C10-C11	2.77
C9-C1-C6-C7	3.24	C7-C8-C9-C1	2.59
C3-C4	2.96	C7-C8-C9-C23	2.54
C1-C6-C5	2.45	C1-C6-C5	2.53
C9-C23	2.42	C14-C15	2.43
C4-C5	2.25	C8-C7-C6-C5	2.07
C6- C1-C9	2.02	C10-C8-C9-C23	2.06
C18-C19	1.92	C14-C13	2.06
C7-C16-C17	1.66	C17-C18	1.91
C1-C9-C8	1.55	C8-C9-C1-C6	1.90
C17-C18	1.52	C9-C1-C2	1.80

C17-C16-C21-C20	1.47	C7-C8-C9	1.78
C11-C12	1.39	C8-C9-C1	1.77
C8-C10-C15	1.23	C15-C10-C11-C12	1.63
		C22-C9-C23	1.51
		C12-C11	1.50
		C10-C11	1.43
		C18-C19	1.28
		C23-C9-C1-C2	1.20
		C21-C16-C17-C18	1.16
		C7-C6-C1	1.05

References

1. Z. Zhou, S. Xie, X. Chen, Y. Tu, J. Xiang, J. Wang, Z. He, Z. Zeng and B. Z. Tang, *J. Am. Chem. Soc.*, 2019, **141**, 9803-9807.