Electronic Supplementary Information for:

Excited-state dynamics of dipyrrolyldiketone difluoroboron complexes

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CONTENTS

1. Absorption spectrum of 1 in PMMA

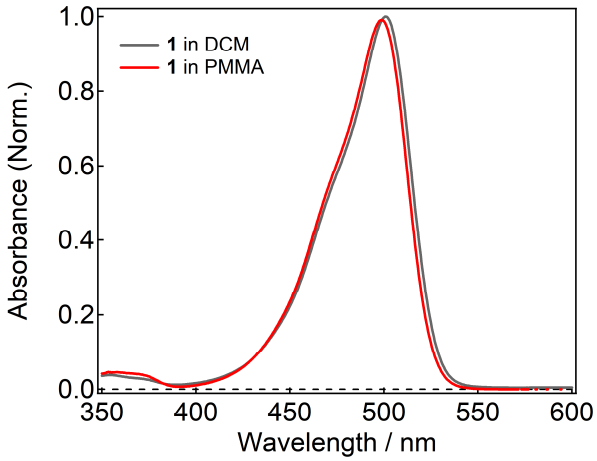

Fig. S1 Absorption spectra of **1** in dichloromethane and PMMA (film).

2. Femtosecond-to-nanosecond transient absorption measurements

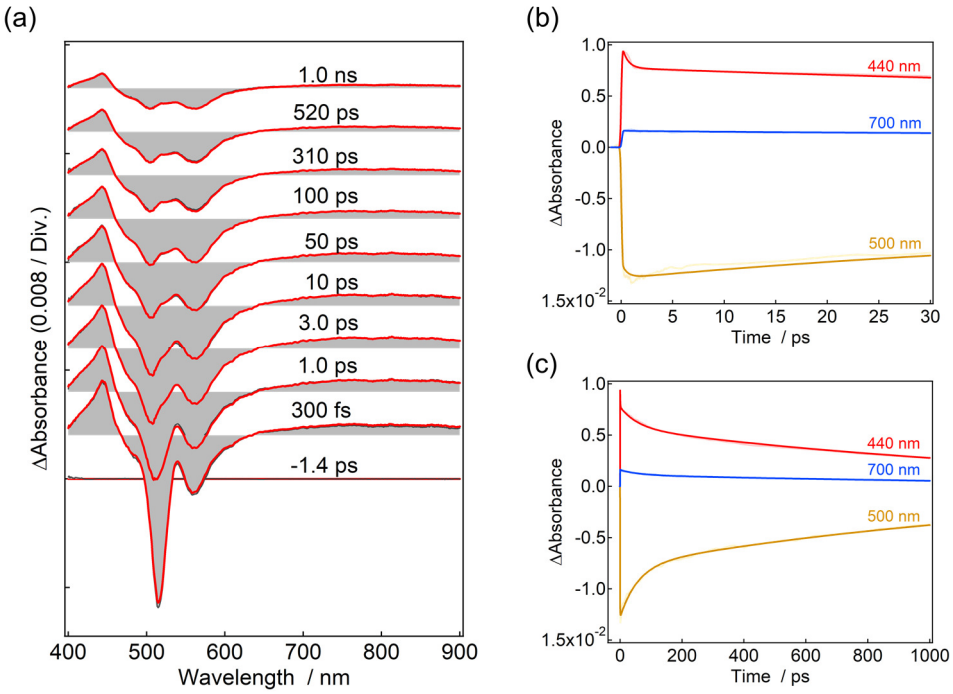

Fig. S2 Time evolutions of femtosecond-to-nanosecond transient absorption spectra of **1** (3.1×10^{-6} M) in dichloromethane excited with a 520-nm femtosecond laser pulse. Thick lines indicate the fitting lines by the SVD global analyses using a three-state sequential kinetic model.

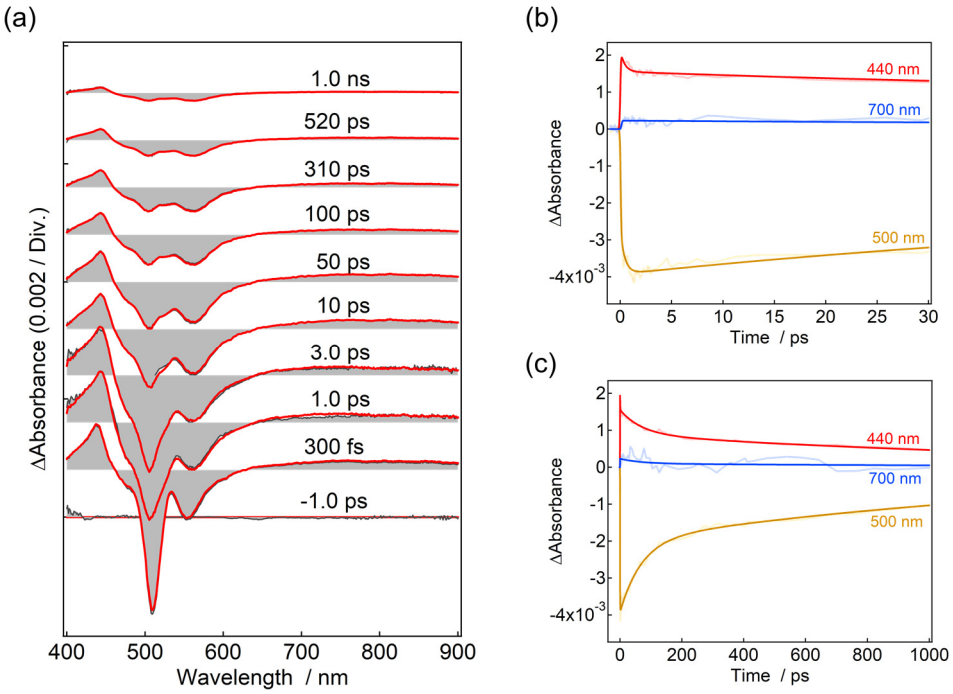

Fig. S3 Time evolutions of femtosecond-to-nanosecond transient absorption spectra of **1** (3.1×10^{-6} M) in dichloromethane excited with a 520-nm femtosecond laser pulse under the weak excitation intensity (10 nJ pulse^{-1}). Thick lines indicate the fitting lines by the SVD global analyses using a three-state sequential kinetic model.

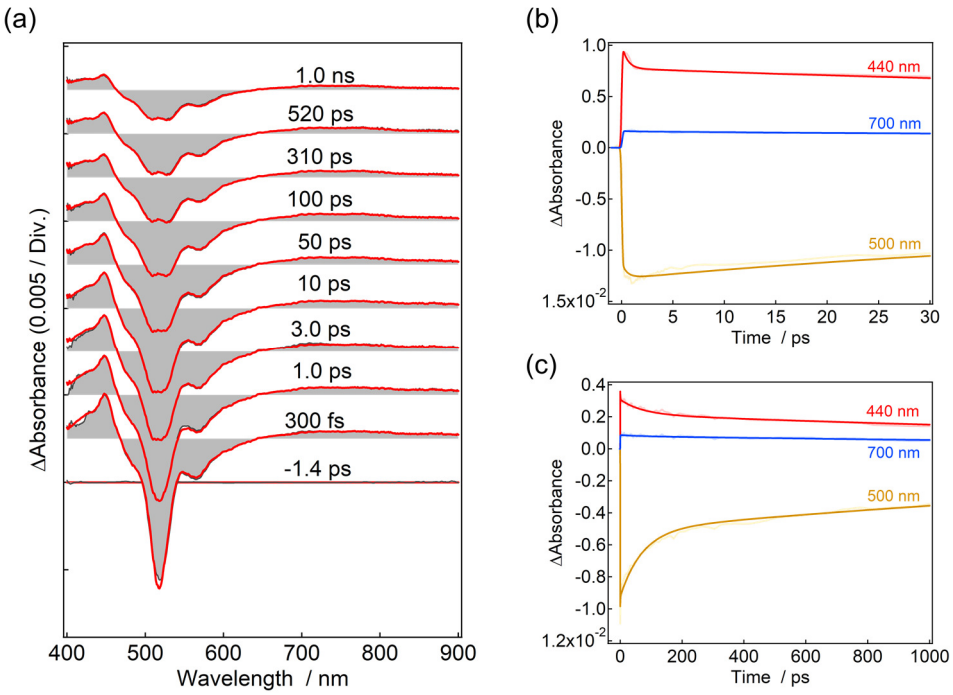

Fig. S4 Time evolutions of femtosecond-to-nanosecond transient absorption spectra of **1**-Cl (2.8×10^{-6} M, **1**:TBACl = 1:1000) in dichloromethane excited with a 520-nm femtosecond laser pulse. Thick lines show the fitting lines by SVD global analyses using a three-state sequential kinetic model.

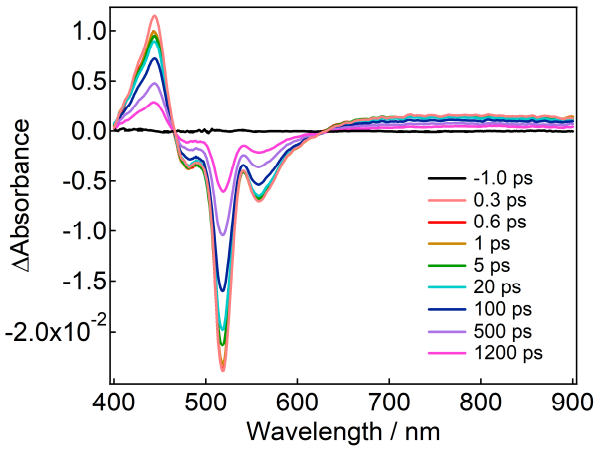

Fig. S5 Time evolutions of femtosecond-to-nanosecond transient absorption spectra of the polymer film of **1** excited with a 520-nm femtosecond laser pulse under the weak excitation intensity (10 nJ $pulse^{-1}$).

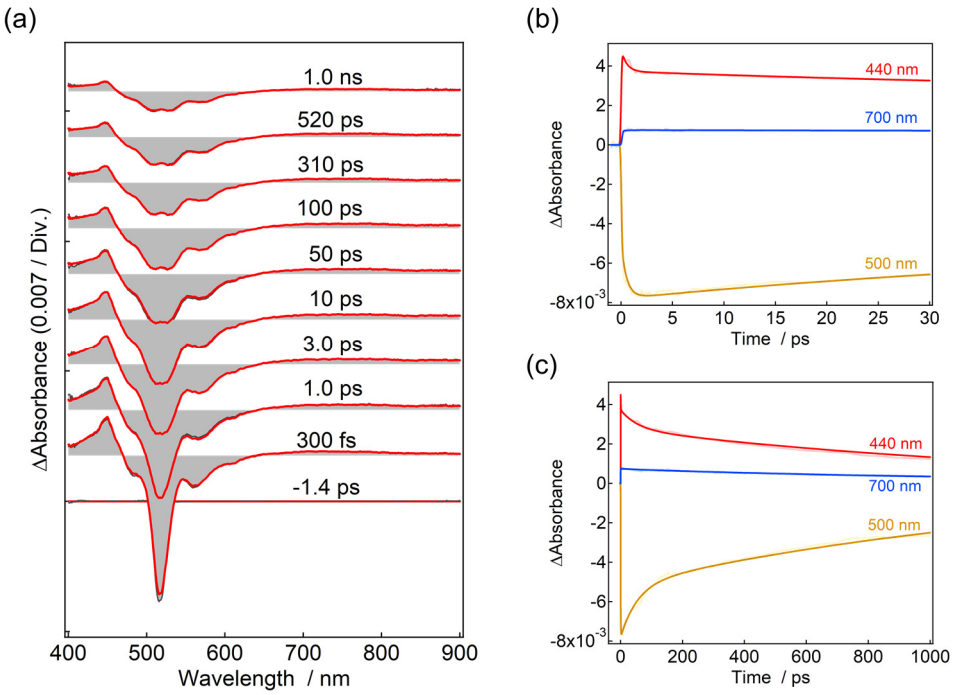

Fig. S6 Time evolutions of femtosecond-to-nanosecond transient absorption spectra of **1**-Br (2.6×10^{-6} M, **1**:TBABr = 1:1000) in dichloromethane excited with a 520-nm femtosecond laser pulse. Thick lines show the fitting lines by the SVD global analyses using a three-state sequential kinetic model.

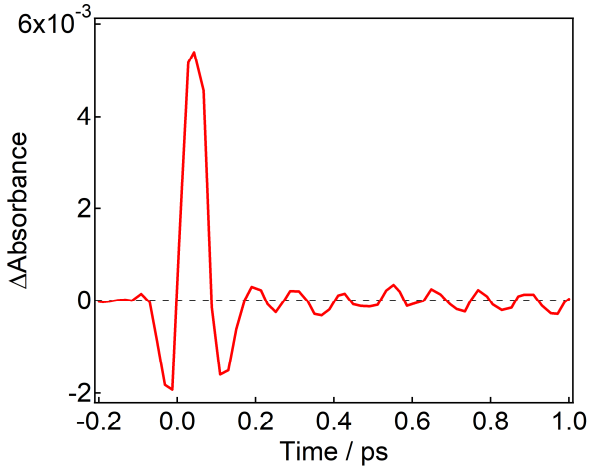

Fig. S7 Transient absorption dynamics of dichloromethane excited with a 520-nm femtosecond laser pulse () probed at 514 nm.

3. Elucidation of the excited-state absorption spectra

To resolve the excited-state absorption spectra from the transient absorption spectra, EAS3 was fitted with the absorption spectrum, emission spectrum and multiple Gaussian functions after converting the axis of the spectra to wavenumbers. The stimulated emission spectra were calculated from the emission spectra using the following relationship:

$$B \propto \int \frac{F(\tilde{\nu})}{\tilde{\nu}^3} \mathrm{d}\tilde{\nu},$$

where B, $\tilde{\nu}$ and $F(\tilde{\nu})$ indicate Einstein coefficient of stimulated emission, wavenumber and fluorescence spectrum as a function of wavenumber, respectively. It should be noted that it was difficult to completely resolve the excited-state absorption spectra from the absorption and emission spectra because their peaks are very close and overlapped. The fitted spectra are converted to wavelength as shown in Fig. S4.

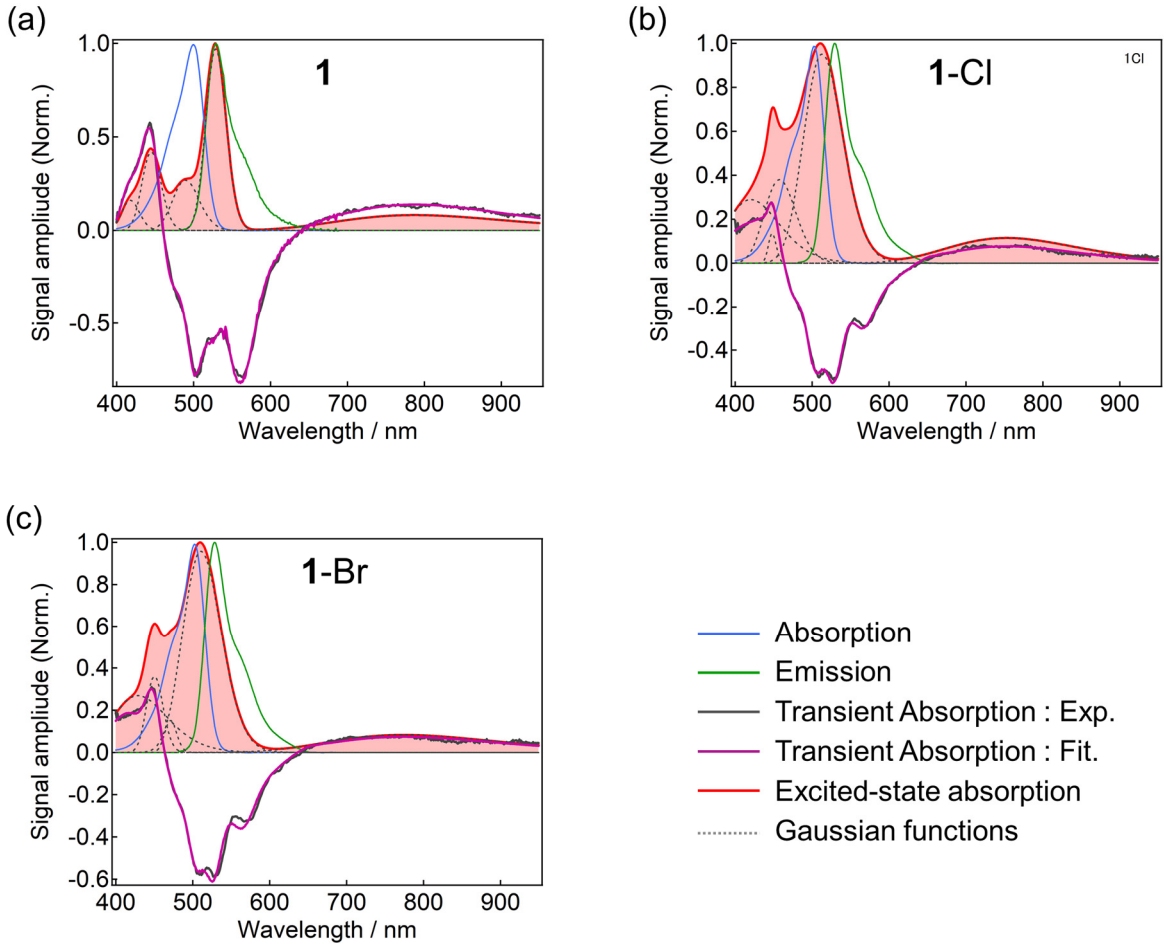

Fig. S8 Transient absorption, fitted excited-state absorption, steady-state absorption, emission spectra of **1**, **1**-Cl and **1**-Br in dichloromethane. Gaussian functions used for fitting are shown as dashed lines.

4. FTIR Spectra

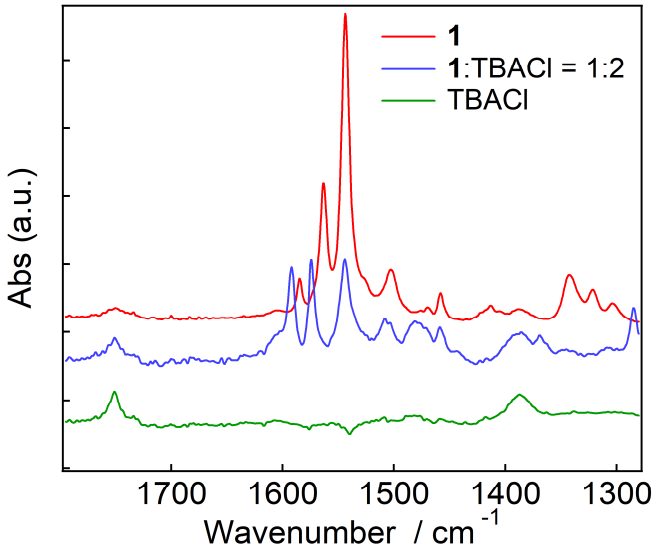

Fig. S9 FTIR spectra of **1** (~1 × 10^{-3} M), **1**-Cl (~1 × 10^{-3} M, **1**:TBACl = 1:2) and TBACl in CD_2Cl_2.

5. DFT calculations

All calculations were carried out using the Gaussian 16 program.[2] The molecular structure was optimized at the B3LYP/6-31+G(d) level of theory, and analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. The TDDFT calculations were performed at the B3LYP/6-31+G(d,p) level of the theory for the optimized structures. The solvent effect (dichloromethane) was considered by using the polarizable continuum model (PCM). The lowest excited state was calculated at B3LYP/6-31+G(d) level of the theory without the solvent effect.

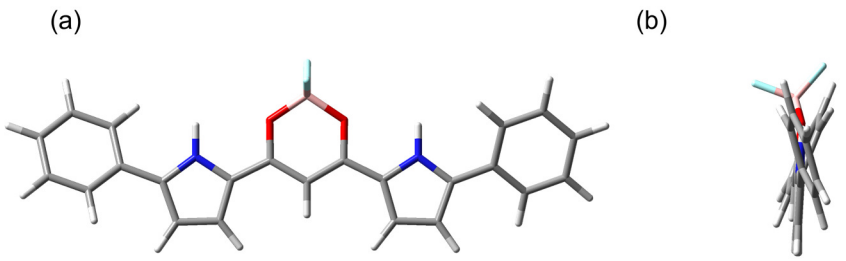

Fig. S10 (a) Front and (b) side views of the optimized structure of the out-out form of **1** calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Table S1. Standard orientation of the optimized geometry of the out-out form of **1** calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	1.2245560	1.1653270	-0.0401230
2	C	1.2055980	-0.1534190	0.0747550
3	C	-0.0005490	-0.8520280	0.1656730
4	C	-1.2055390	-0.1535790	0.0592040
5	O	-1.2233220	1.1651790	-0.0555330
6	B	-0.0007880	1.9817570	0.1652110
7	F	0.0049790	3.0306210	-0.7489500
8	F	-0.0090860	2.4668170	1.4805870
9	C	2.4906020	-0.7842830	0.0694530
10	C	-2.4901980	-0.7847850	0.0384870
11	C	-2.8770330	-2.1322850	0.0883900
12	C	-4.2776030	-2.1701380	0.0539740
13	C	-4.7471920	-0.8462800	-0.0215790
14	N	-3.6487770	-0.0355160	-0.0347660
15	C	-6.1190810	-0.3378420	-0.0905280
16	N	3.6495520	-0.0349970	0.0036100
17	C	4.7472100	-0.8467690	-0.0046510

18	C	4.2771250	-2.1707810	0.0656690
19	C	2.8770300	-2.1321160	0.1133410
20	C	-6.4076880	0.9415790	-0.6042250
21	C	-7.7220780	1.4073510	-0.6575250
22	C	-8.7746650	0.6043650	-0.2065980
23	C	-8.5007840	-0.6711270	0.2997880
24	C	-7.1879050	-1.1372550	0.3605960
25	C	6.1194700	-0.3380110	-0.0611850
26	C	7.1645620	-1.1813940	-0.4872870
27	C	8.4777870	-0.7156270	-0.5427840
28	C	8.7755900	0.6026650	-0.1798480
29	C	7.7467290	1.4496330	0.2445570
30	C	6.4323290	0.9850900	0.3071510
31	H	-0.0011820	-1.9286330	0.2665380
32	H	-2.2103260	-2.9827960	0.1319680
33	H	-4.8961470	-3.0570090	0.0542770
34	H	-3.6504450	0.9763280	-0.0286600
35	H	3.6484190	0.9726120	-0.0883480
36	H	4.8965100	-3.0561140	0.1046830
37	H	2.2108580	-2.9815190	0.1801760
38	H	-5.6107100	1.5718960	-0.9894990
39	H	-7.9234880	2.3961340	-1.0607560
40	H	-9.7976860	0.9678180	-0.2506220
41	H	-9.3106470	-1.3019240	0.6564410
42	H	-6.9873490	-2.1205710	0.7758540
43	H	6.9447610	-2.2006290	-0.7913300
44	H	9.2688900	-1.3812010	-0.8776780
45	H	9.7987990	0.9653340	-0.2257900
46	H	7.9671890	2.4727390	0.5369590
47	H	5.6558670	1.6535760	0.6693810

SCF Done: E(RB3LYP) = -1371.46845781 A.U.

Zero-point correction = 0.356954 (Hartree/Particle)
Thermal correction to Energy = 0.381191
Thermal correction to Enthalpy = 0.382135
Thermal correction to Gibbs Free Energy = 0.298720
Sum of electronic and zero-point Energies = -1371.112442
Sum of electronic and thermal Energies = -1371.088205
Sum of electronic and thermal Enthalpies = -1371.087261
Sum of electronic and thermal Free Energies = -1371.170677

Low frequencies --- -6.1868 -2.1833 0.0002 0.0005 0.0012 1.5789
Low frequencies --- 12.2993 22.1940 26.5776

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.5745 eV 481.58 nm f=1.9563 <S**2>=0.000
104 ->105 0.70540
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1371.40552777
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3512 eV 369.97 nm f=0.0103 <S**2>=0.000
103 ->105 0.69281
104 ->106 0.12669

Excited State 3: Singlet-A 4.0139 eV 308.89 nm f=0.0007 <S**2>=0.000
100 ->105 -0.16145
102 ->105 0.65417
104 ->107 0.11815

Excited State 4: Singlet-A 4.0271 eV 307.87 nm f=0.0015 <S**2>=0.000
99 ->105 -0.10039
101 ->105 0.67455
104 ->108 0.12374

Excited State 5: Singlet-A 4.0628 eV 305.17 nm f=0.0249 <S**2>=0.000
103 ->105 -0.12547
104 ->106 0.68777

Excited State 6: Singlet-A 4.1088 eV 301.75 nm f=0.0116 <S**2>=0.000
98 ->105 0.16152
100 ->105 0.63046
102 ->105 0.18942
104 ->107 -0.14572

Excited State 7: Singlet-A 4.2025 eV 295.02 nm f=0.0205 <S**2>=0.000
99 ->105 0.69093

Excited State 8: Singlet-A 4.3155 eV 287.30 nm f=0.0618 <S**2>=0.000
98 ->105 0.65183
100 ->105 -0.12746
103 ->106 -0.14950

104 ->107 0.16844

Excited State 9: Singlet-A 4.4402 eV 279.23 nm f=0.0346 <S**2>=0.000
100 ->105 0.16115
102 ->105 -0.10988
103 ->106 0.16006
104 ->107 0.62222
104 ->109 0.13312

Excited State 10: Singlet-A 4.5253 eV 273.98 nm f=0.0061 <S**2>=0.000
101 ->105 -0.14876
102 ->106 -0.11215
103 ->109 0.14138
104 ->108 0.64850

Excited State 11: Singlet-A 4.5736 eV 271.09 nm f=0.0049 <S**2>=0.000
101 ->106 -0.11275
102 ->105 -0.11316
103 ->108 0.13848
104 ->107 -0.13148
104 ->109 0.63190

Excited State 12: Singlet-A 4.6817 eV 264.83 nm f=0.2265 <S**2>=0.000
98 ->105 0.14489
100 ->105 -0.14846
103 ->106 0.65106
104 ->107 -0.11665

Excited State 13: Singlet-A 4.7174 eV 262.82 nm f=0.0098 <S**2>=0.000
97 ->105 0.61968
103 ->107 -0.13941
104 ->110 -0.27689

Excited State 14: Singlet-A 4.9197 eV 252.02 nm f=0.0001 <S**2>=0.000
96 ->105 0.68504

Excited State 15: Singlet-A 4.9547 eV 250.23 nm f=0.0596 <S**2>=0.000
97 ->105 0.24200
100 ->106 0.11141

104 ->110 0.56838
104 ->111 -0.25490

Excited State 16: Singlet-A 4.9770 eV 249.12 nm f=0.0102 <S**2>=0.000
104 ->110 0.22224
104 ->111 0.64186

Excited State 17: Singlet-A 5.1463 eV 240.92 nm f=0.0953 <S**2>=0.000
97 ->105 0.15492
102 ->106 -0.10317
103 ->107 0.64033
103 ->109 0.12012
104 ->108 -0.10870

Excited State 18: Singlet-A 5.1978 eV 238.53 nm f=0.0020 <S**2>=0.000
101 ->106 -0.30518
102 ->107 0.15749
103 ->108 0.53925
104 ->109 -0.23698

Excited State 19: Singlet-A 5.2239 eV 237.34 nm f=0.0038 <S**2>=0.000
95 ->105 -0.11061
101 ->107 0.17475
102 ->106 -0.31177
103 ->107 -0.16967
103 ->109 0.48995
104 ->108 -0.19614
104 ->110 0.12739

Excited State 20: Singlet-A 5.2463 eV 236.33 nm f=0.0004 <S**2>=0.000
103 ->111 -0.21264
104 ->112 0.65140

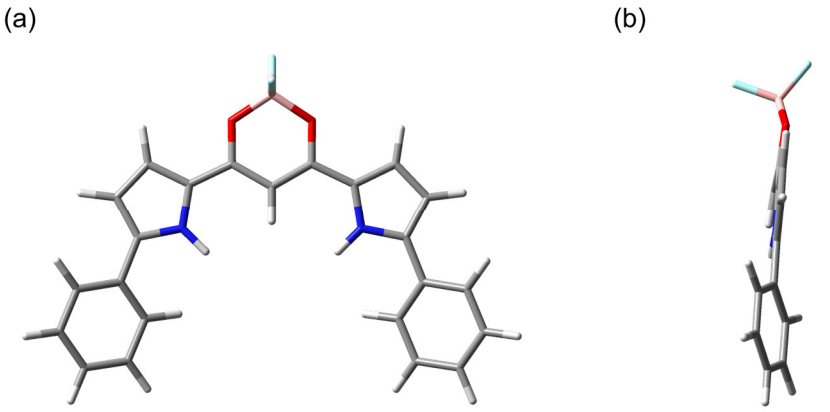

Fig. S11 (a) Front and (b) side views of the optimized structure of the in-in form of **1** calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Table S2. Standard orientation of the optimized geometry of the in-in form of **1** calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	1.2214970	3.2843370	-0.2060640
2	C	1.2110930	1.9722890	-0.0608140
3	C	0.0000000	1.2801430	0.0664730
4	C	-1.2110930	1.9722910	-0.0608040
5	O	-1.2214970	3.2843400	-0.2060510
6	B	0.0000020	4.0896030	0.0498330
7	F	-0.0000010	5.1827240	-0.8087110
8	F	0.0000100	4.5043230	1.3905720
9	C	2.5041110	1.3534550	-0.0779910
10	C	-2.5041110	1.3534580	-0.0779740
11	C	-3.7627060	1.9651460	-0.1505210
12	C	-4.7324610	0.9535400	-0.1267070
13	C	-4.0673290	-0.2805160	-0.0459240
14	N	-2.7263510	-0.0144230	-0.0236890
15	C	-4.6097130	-1.6407980	-0.0032290
16	N	2.7263510	-0.0144260	-0.0236920
17	C	4.0673290	-0.2805190	-0.0459410
18	C	4.7324590	0.9535360	-0.1267530
19	C	3.7627040	1.9651420	-0.1505750
20	C	-3.8484290	-2.7531090	-0.4116350
21	C	-4.3848710	-4.0404960	-0.3597710
22	C	-5.6926180	-4.2422760	0.0929960
23	C	-6.4610280	-3.1437000	0.4941700
24	C	-5.9258760	-1.8566770	0.4499260
25	C	4.6097130	-1.6408000	-0.0032270
26	C	5.9258770	-1.8566730	0.4499250
27	C	6.4610280	-3.1436960	0.4941860
28	C	5.6926160	-4.2422780	0.0930320

29	C	4.3848670	-4.0405030	-0.3597330
30	C	3.8484250	-2.7531160	-0.4116140
31	H	-0.0000010	0.2086750	0.2099570
32	H	-3.9284090	3.0309770	-0.2188730
33	H	-5.8038010	1.0855320	-0.1888880
34	H	-2.0122010	-0.7199150	0.0907870
35	H	2.0122050	-0.7199140	0.0908370
36	H	5.8037990	1.0855260	-0.1889540
37	H	3.9284060	3.0309700	-0.2189550
38	H	-2.8423780	-2.6175820	-0.8002750
39	H	-3.7830940	-4.8852450	-0.6840320
40	H	-6.1097160	-5.2448510	0.1305240
41	H	-7.4771230	-3.2897690	0.8506640
42	H	-6.5247570	-1.0144570	0.7839490
43	H	6.5247600	-1.0144480	0.7839330
44	H	7.4771240	-3.2897610	0.8506770
45	H	6.1097130	-5.2448520	0.1305730
46	H	3.7830880	-4.8852560	-0.6839780
47	H	2.8423730	-2.6175930	-0.8002520

SCF Done: E(RB3LYP) = -1371.45987077 A.U.

Zero-point correction = 0.357018 (Hartree/Particle)
Thermal correction to Energy = 0.381256
Thermal correction to Enthalpy = 0.382201
Thermal correction to Gibbs Free Energy = 0.299257
Sum of electronic and zero-point Energies = -1371.104250
Sum of electronic and thermal Energies = -1371.080012
Sum of electronic and thermal Enthalpies = -1371.079068
Sum of electronic and thermal Free Energies = -1371.162012

Low frequencies --- -3.9705 -0.0007 -0.0005 0.0006 3.2509 4.3577
Low frequencies --- 17.3236 22.2708 26.9211

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.6275 eV 471.88 nm f=1.1751 <S**2>=0.000
104 ->105 0.70477
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1371.39546290
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3435 eV 370.82 nm f=0.3036 <S**2>=0.000
103 ->105 0.69270

104 ->106 0.13069

Excited State 3: Singlet-A 4.0055 eV 309.53 nm f=0.5808 <S**2>=0.000
103 ->105 -0.12735
104 ->106 0.68105

Excited State 4: Singlet-A 4.0607 eV 305.33 nm f=0.0053 <S**2>=0.000
98 ->105 0.10109
102 ->105 0.67961
104 ->109 0.10144

Excited State 5: Singlet-A 4.0640 eV 305.08 nm f=0.0234 <S**2>=0.000
101 ->105 0.67632
104 ->108 0.11543

Excited State 6: Singlet-A 4.1690 eV 297.39 nm f=0.0187 <S**2>=0.000
98 ->105 0.18621
100 ->105 0.64482
103 ->106 0.17098

Excited State 7: Singlet-A 4.2154 eV 294.12 nm f=0.0601 <S**2>=0.000
99 ->105 0.68982

Excited State 8: Singlet-A 4.2308 eV 293.05 nm f=0.0506 <S**2>=0.000
98 ->105 0.62024
100 ->105 -0.11658
103 ->106 -0.17102
104 ->107 0.23902

Excited State 9: Singlet-A 4.4569 eV 278.19 nm f=0.0317 <S**2>=0.000
103 ->106 0.43539
104 ->107 0.52609

Excited State 10: Singlet-A 4.5557 eV 272.15 nm f=0.0038 <S**2>=0.000
101 ->105 -0.14508
102 ->106 0.12912
103 ->109 -0.15593
104 ->108 0.64338

Excited State 11: Singlet-A 4.5699 eV 271.31 nm f=0.0264 <S**2>=0.000

98 ->105	-0.10804
100 ->105	0.17866
101 ->106	0.10555
102 ->105	-0.10258
103 ->106	-0.36090
103 ->108	-0.13294
104 ->107	0.18010
104 ->109	0.49246

Excited State 12: Singlet-A 4.6197 eV 268.38 nm f=0.0175 <S**2>=0.000

98 ->105	0.21589
100 ->105	-0.16840
103 ->106	0.33197
103 ->108	-0.10513
104 ->107	-0.32954
104 ->109	0.40135

Excited State 13: Singlet-A 4.7154 eV 262.93 nm f=0.0120 <S**2>=0.000

97 ->105	0.66444
103 ->107	-0.14715
104 ->111	-0.14765

Excited State 14: Singlet-A 4.7876 eV 258.97 nm f=0.0001 <S**2>=0.000

104 ->110	0.69445

Excited State 15: Singlet-A 4.8735 eV 254.40 nm f=0.0129 <S**2>=0.000

96 ->105	0.69335

Excited State 16: Singlet-A 5.0340 eV 246.29 nm f=0.1155 <S**2>=0.000

95 ->105	-0.17985
97 ->105	0.14386
103 ->107	0.64174

Excited State 17: Singlet-A 5.1105 eV 242.61 nm f=0.0014 <S**2>=0.000

95 ->105	0.51929
102 ->106	-0.14554
103 ->107	0.17990
103 ->109	0.21676

104 ->108 0.12246
104 ->111 -0.30159

Excited State 18: Singlet-A 5.1336 eV 241.52 nm f=0.0000 <S**2>=0.000
101 ->106 -0.31098
102 ->107 -0.14468
103 ->108 0.53921
104 ->109 0.26035

Excited State 19: Singlet-A 5.1371 eV 241.35 nm f=0.0009 <S**2>=0.000
95 ->105 0.40858
97 ->105 0.12344
98 ->106 -0.11650
101 ->107 0.11746
102 ->106 0.22256
103 ->109 -0.36167
104 ->108 -0.17307
104 ->111 0.22302

Excited State 20: Singlet-A 5.1827 eV 239.23 nm f=0.0000 <S**2>=0.000
95 ->105 0.12297
98 ->106 -0.12585
102 ->106 -0.19829
103 ->107 -0.10205
103 ->109 0.30400
104 ->108 0.12288
104 ->111 0.52816

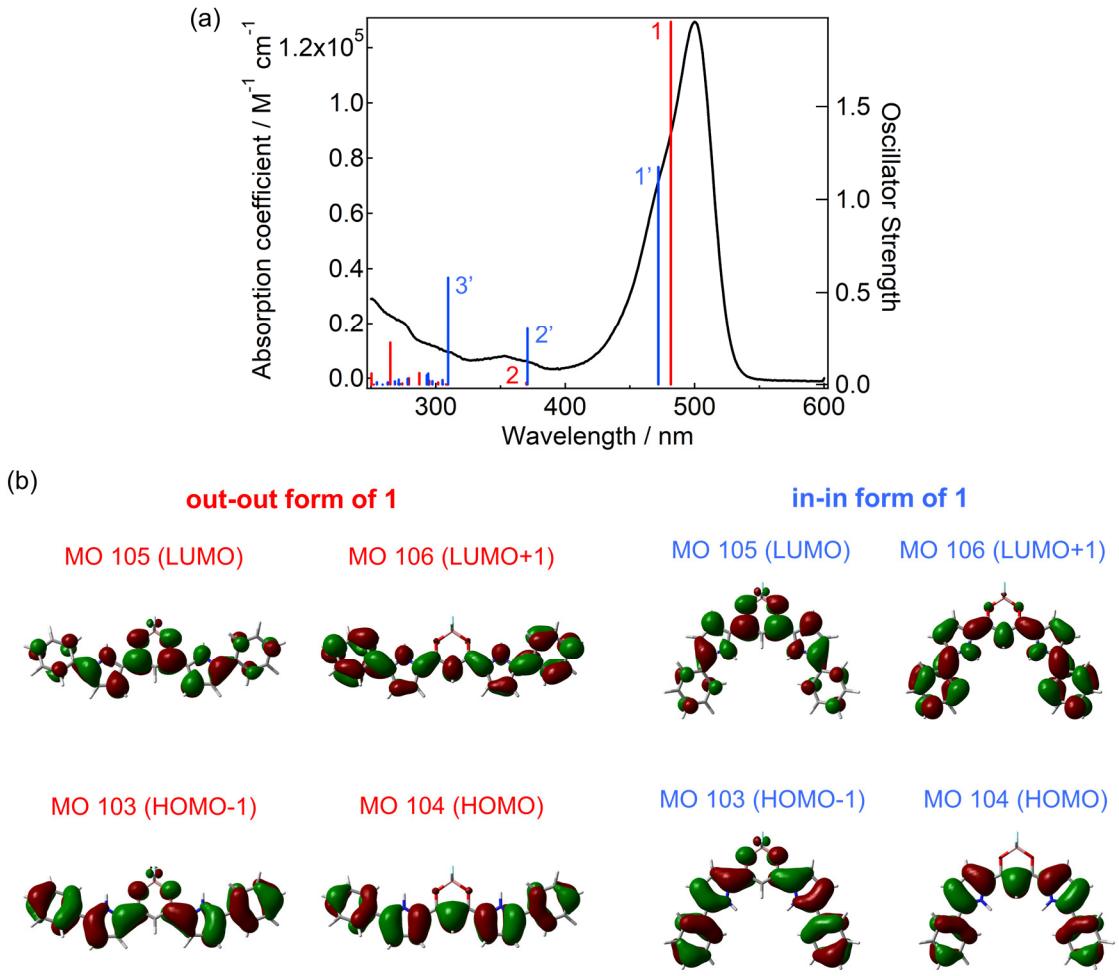

Fig. S12 UV-vis absorption spectrum of **1** in dichloromethane at room temperature. The calculated absorption spectra (the PCM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) (dichloromethane) level of theory) of the out-out and in-in forms of **1** are shown by the red and blue vertical lines, respectively. The electronic transitions and coefficients of the labeled transitions are shown in Tables S3 and S4. The relevant molecular orbitals of the in-in form of **1**.

Table S3. Selected calculated electronic transitions of the out-out form of **1** (the PCM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) (dichloromethane) level of theory).

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1	481.58	0.70540	104 HOMO → 105 LUMO	1.9563
2	369.97	0.69281 0.12669	103 HOMO-1 → 105 LUMO 104 HOMO → 106 LUMO+1	0.0103

Table S4. Selected calculated electronic transitions of the in-in form of **1** (PCM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) (dichloromethane) level of the theory).

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1’	471.88	0.70477	104 HOMO → 105 LUMO	1.1751
2’	370.82	0.69270 0.13069	103 HOMO-1 → 105 LUMO 104 HOMO → 106 LUMO+1	0.3036
3'	309.53	-0.12735 0.68105	103 HOMO-1 → 105 LUMO 104 HOMO-1 → 106 LUMO+1	0.5808

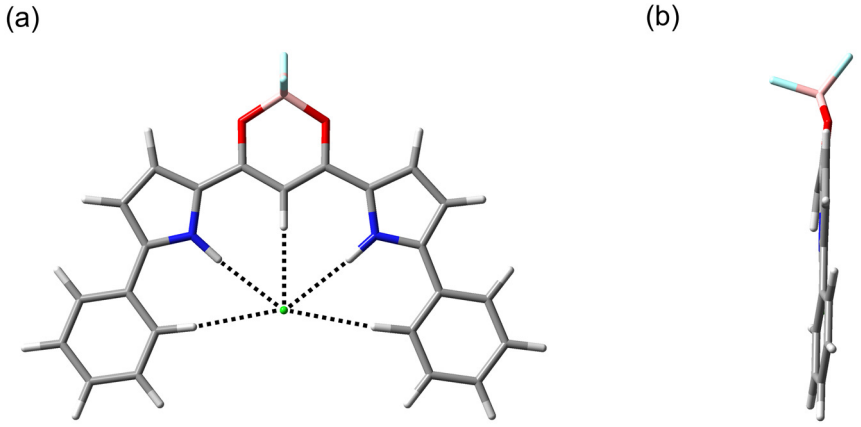

Fig. S13 (a) Front and (b) side views of the optimized structure of **1**-Cl calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Table S5. Standard orientation of the optimized geometry of **1**-Cl calculated at the PCM-B3LYP/6-31+G(d) level of theory (dichloromethane).

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	1.2249580	3.4931630	-0.1766980
2	C	1.2076600	2.1771700	-0.0278800
3	C	0.0000140	1.4900300	0.1092590
4	C	-1.2076380	2.1771730	-0.0278230
5	O	-1.2249390	3.4931680	-0.1766220
6	B	0.0000190	4.2907650	0.0781610
7	F	-0.0000060	5.3909370	-0.7781350
8	F	0.0000620	4.7129420	1.4207250
9	C	2.4885090	1.5341680	-0.0518330
10	C	-2.4884890	1.5341760	-0.0517380
11	C	-3.7592740	2.1229550	-0.1012370
12	C	-4.7034070	1.0900840	-0.0980810
13	C	-4.0091790	-0.1336340	-0.0496210

14	N	-2.6734300	0.1596930	-0.0194740
15	C	-4.5463080	-1.4984090	-0.0248530
16	N	2.6734420	0.1596860	-0.0195190
17	C	4.0091880	-0.1336540	-0.0496920
18	C	4.7034220	1.0900580	-0.0982310
19	C	3.7592960	2.1229360	-0.1013950
20	C	-3.7219820	-2.6247430	0.1685270
21	C	-4.2677920	-3.9095370	0.1927170
22	C	-5.6427270	-4.1022540	0.0272510
23	C	-6.4714770	-2.9913330	-0.1669230
24	C	-5.9310010	-1.7065730	-0.1942500
25	C	4.5463010	-1.4984340	-0.0248740
26	C	5.9310220	-1.7066050	-0.1940380
27	C	6.4714810	-2.9913720	-0.1666740
28	C	5.6426880	-4.1022930	0.0273120
29	C	4.2677280	-3.9095690	0.1925580
30	C	3.7219330	-2.6247690	0.1683250
31	H	0.0000140	0.4166480	0.2429780
32	H	-3.9494810	3.1868710	-0.1242520
33	H	-5.7779130	1.2069360	-0.1150240
34	H	-1.9173830	-0.5308380	-0.0191900
35	H	1.9173900	-0.5308340	-0.0191800
36	H	5.7779260	1.2069060	-0.1152320
37	H	3.9495110	3.1868490	-0.1244620
38	H	-2.6492050	-2.5119070	0.2987400
39	H	-3.6110370	-4.7625120	0.3429910
40	H	-6.0636380	-5.1040290	0.0475880
41	H	-7.5418960	-3.1246800	-0.3010290
42	H	-6.5908610	-0.8596400	-0.3549360
43	H	6.5909230	-0.8596740	-0.3545580
44	H	7.5419230	-3.1247220	-0.3005970
45	H	6.0635860	-5.1040730	0.0476800
46	H	3.6109390	-4.7625430	0.3426890
47	H	2.6491360	-2.5119350	0.2983750
48	Cl	-0.0000350	-2.0214870	0.0230580

SCF Done: E(RB3LYP) = -1831.85301799 A.U.

Zero-point correction = 0.358121 (Hartree/Particle)
Thermal correction to Energy = 0.384269
Thermal correction to Enthalpy = 0.385213
Thermal correction to Gibbs Free Energy = 0.297710
Sum of electronic and zero-point Energies = -1831.496044
Sum of electronic and thermal Energies = -1831.469896
Sum of electronic and thermal Enthalpies = -1831.468952
Sum of electronic and thermal Free Energies = -1831.556455

Low frequencies --- -5.1273 -3.9953 0.0009 0.0015 0.0015 3.9955

Low frequencies --- 23.8617 24.3002 30.1868

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.5521 eV 485.81 nm f=1.0987 <S**2>=0.000

113 ->114 0.70465

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1831.79168378

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3017 eV 375.52 nm f=0.2845 <S**2>=0.000

112 ->114 0.68908

113 ->115 -0.14738

Excited State 3: Singlet-A 3.6437 eV 340.27 nm f=0.0069 <S**2>=0.000

111 ->114 0.70481

Excited State 4: Singlet-A 3.6792 eV 336.99 nm f=0.0005 <S**2>=0.000

110 ->114 0.70476

Excited State 5: Singlet-A 3.7530 eV 330.36 nm f=0.0000 <S**2>=0.000

109 ->114 0.70242

Excited State 6: Singlet-A 3.8974 eV 318.12 nm f=0.5913 <S**2>=0.000

112 ->114 0.14412

113 ->115 0.67742

Excited State 7: Singlet-A 4.0365 eV 307.16 nm f=0.0068 <S**2>=0.000

104 ->114 0.12641

108 ->114 0.67015

113 ->118 -0.10652

Excited State 8: Singlet-A 4.0560 eV 305.68 nm f=0.0491 <S**2>=0.000

105 ->114 0.12529

107 ->114 0.66036

113 ->115 0.10535

113 ->117 -0.14018

Excited State 9: Singlet-A 4.1523 eV 298.59 nm f=0.0164 <S**2>=0.000

106 ->114 0.59958

112 ->115 -0.21819
113 ->116 -0.27778

Excited State 10: Singlet-A 4.2285 eV 293.21 nm f=0.0451 <S**2>=0.000
105 ->114 0.68036
107 ->114 -0.10188
113 ->117 0.10660

Excited State 11: Singlet-A 4.2381 eV 292.55 nm f=0.0154 <S**2>=0.000
104 ->114 0.55734
106 ->114 0.19044
108 ->114 -0.13988
113 ->116 0.33791

Excited State 12: Singlet-A 4.3413 eV 285.59 nm f=0.0442 <S**2>=0.000
104 ->114 -0.27591
112 ->115 -0.41116
113 ->116 0.47092

Excited State 13: Singlet-A 4.4766 eV 276.96 nm f=0.0003 <S**2>=0.000
107 ->114 0.18497
108 ->115 0.10674
112 ->118 -0.12395
113 ->117 0.63642

Excited State 14: Singlet-A 4.4885 eV 276.23 nm f=0.0353 <S**2>=0.000
104 ->114 0.13342
106 ->114 -0.26565
112 ->115 -0.41266
112 ->117 -0.10194
113 ->116 -0.11376
113 ->118 0.44332

Excited State 15: Singlet-A 4.5914 eV 270.04 nm f=0.0273 <S**2>=0.000
104 ->114 -0.27082
106 ->114 0.13294
108 ->114 0.12225
112 ->115 0.31482
113 ->116 0.22451

113 ->118 0.45236

Excited State 16: Singlet-A 4.7923 eV 258.71 nm f=0.0334 <S**2>=0.000
103 ->114 0.58187
112 ->116 0.34985
113 ->119 -0.10722
113 ->120 0.10242

Excited State 17: Singlet-A 4.9243 eV 251.78 nm f=0.0002 <S**2>=0.000
103 ->114 -0.14915
111 ->115 0.66242
112 ->116 0.17641

Excited State 18: Singlet-A 4.9363 eV 251.17 nm f=0.0790 <S**2>=0.000
103 ->114 -0.29456
111 ->115 -0.21501
112 ->116 0.55619
113 ->117 -0.11164
113 ->119 0.11255

Excited State 19: Singlet-A 4.9471 eV 250.62 nm f=0.0080 <S**2>=0.000
102 ->114 0.68603

Excited State 20: Singlet-A 4.9587 eV 250.04 nm f=0.0071 <S**2>=0.000

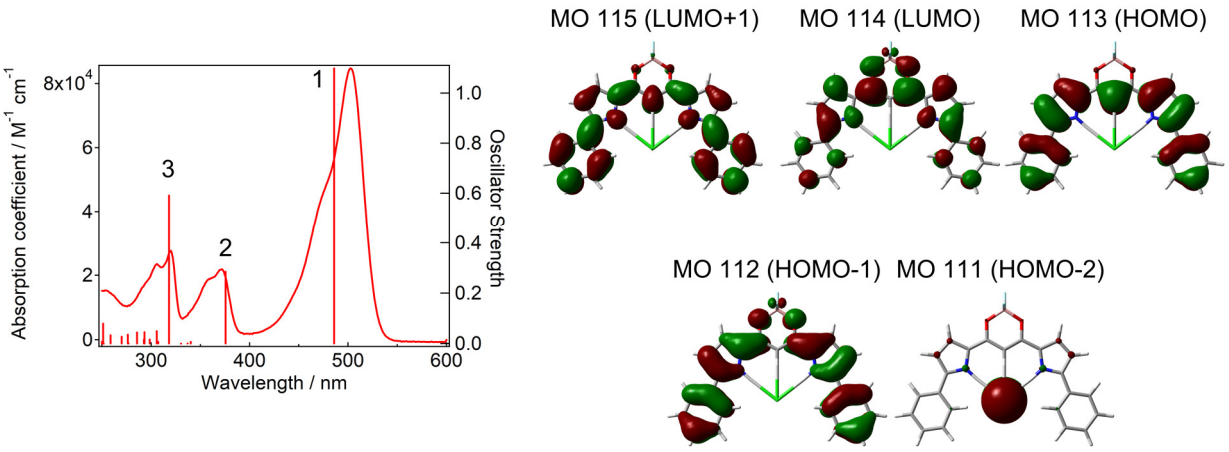

Fig. S14 UV-vis absorption spectrum of **1**-Cl in dichloromethane at room temperature. The calculated absorption spectrum (the PCM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) (dichloromethane) level of theory) is shown by the red vertical lines. The relevant molecular orbitals of **1**-Cl.

Table S6. Selected calculated electronic transition of **1**-Cl at PCM-B3LYP/6-31+G(d,p)// B3LYP/6-31+G(d) (dichloromethane) level of the theory.

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1	485.81	0.70465	113 HOMO → 114 LUMO	1.0987
2	375.52	0.68908	112 HOMO-1 → 114 LUMO	0.2845
		-0.14738	113 HOMO → 115 LUMO+1	
3	318.12	0.14412	112 HOMO-1 → 114 LUMO	0.5913
		0.67742	113 HOMO → 115 LUMO+1	

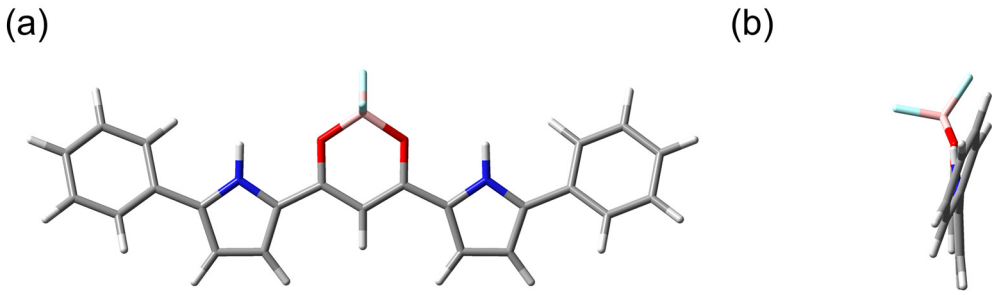

Fig. S15 (a) Front and (b) side views of the optimized structure of the out-out form of **1** at the S_0 state calculated at the B3LYP/6-31+G(d) level of theory.

Table S7. Standard orientation of the optimized geometry of the out-out form of **1** at the S_0 state calculated at the B3LYP/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.5128966	-0.5763154	7.6696996
2	C	-1.0080140	-0.5622248	6.3694300
3	C	0.3024361	-0.1169290	6.1113589
4	C	1.0922078	0.3059564	7.1974045
5	C	0.5877714	0.2831543	8.4966035
6	C	-0.7181647	-0.1547588	8.7394111
7	H	-2.5260860	-0.9271413	7.8472208
8	H	-1.6309402	-0.9285867	5.5571317
9	H	2.0987347	0.6728424	7.0172672
10	H	1.2123832	0.6180976	9.3206550
11	H	-1.1118611	-0.1681202	9.7521325
12	C	0.8472623	-0.0901446	4.7523828
13	C	2.1782896	-0.1310347	4.3072313
14	N	0.0595303	-0.0327566	3.6377923
15	C	2.1681438	-0.0941066	2.9036544
16	H	3.0494314	-0.2137896	4.9425456
17	C	0.8313616	-0.0255178	2.4943081
18	H	-0.9466803	0.0696626	3.6112758
19	H	3.0305745	-0.1273445	2.2517177

20	C	0.2046917	0.0532667	1.2036055
21	C	0.9136703	0.1028792	0.0000000
22	C	0.2046917	0.0532667	-1.2036055
23	H	1.9950331	0.1187192	0.0000000
24	O	-1.1092483	0.0465448	1.2254717
25	O	-1.1092483	0.0465448	-1.2254717
26	B	-1.9169256	0.3865164	0.0000000
27	F	-2.1642653	1.7500844	0.0000000
28	F	-3.0586301	-0.3769832	0.0000000
29	C	0.8313616	-0.0255178	-2.4943081
30	N	0.0595303	-0.0327566	-3.6377923
31	C	2.1681438	-0.0941066	-2.9036544
32	C	0.8472623	-0.0901446	-4.7523828
33	H	-0.9466803	0.0696626	-3.6112758
34	C	2.1782896	-0.1310347	-4.3072313
35	H	3.0305745	-0.1273445	-2.2517177
36	C	0.3024361	-0.1169290	-6.1113589
37	H	3.0494314	-0.2137896	-4.9425456
38	C	-1.0080140	-0.5622248	-6.3694300
39	C	1.0922078	0.3059564	-7.1974045
40	C	-1.5128966	-0.5763154	-7.6696996
41	H	-1.6309402	-0.9285867	-5.5571317
42	C	0.5877714	0.2831543	-8.4966035
43	H	2.0987347	0.6728424	-7.0172672
44	C	-0.7181647	-0.1547588	-8.7394111
45	H	-2.5260860	-0.9271413	-7.8472208
46	H	1.2123832	0.6180976	-9.3206550
47	H	-1.1118611	-0.1681202	-9.7521325

SCF Done: E(RB3LYP) = -1371.44987532 A.U.

Zero-point correction = 0.357484 (Hartree/Particle)
Thermal correction to Energy = 0.381638
Thermal correction to Enthalpy = 0.382583
Thermal correction to Gibbs Free Energy = 0.299712
Sum of electronic and zero-point Energies = -1371.092391
Sum of electronic and thermal Energies = -1371.068237
Sum of electronic and thermal Enthalpies = -1371.067293
Sum of electronic and thermal Free Energies = -1371.150164

Low frequencies --- -3.2359 -1.1836 -0.5710 0.0009 0.0013 0.0026
Low frequencies --- 12.5124 24.9403 27.6184

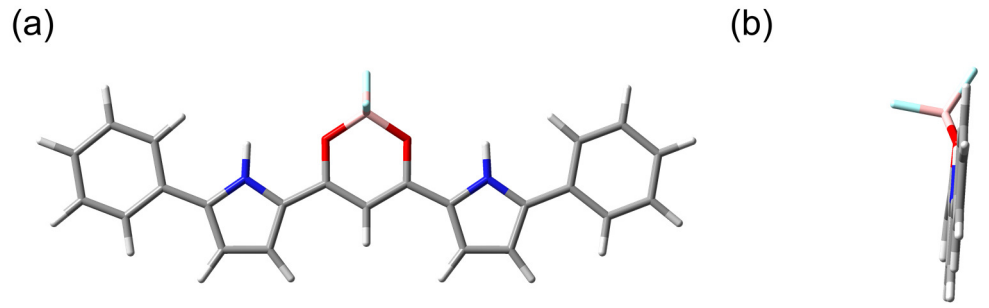

Fig. S16 (a) Front and (b) side views of the optimized structure of the out-out form of **1** at the S_1 state calculated at the B3LYP/6-31+G(d) level of theory.

Table S8. Standard orientation of the optimized geometry of the out-out form of **1** at the S_1 state calculated at the B3LYP/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.5695720	-0.2617888	7.6560021
2	C	-1.0809791	-0.1905135	6.3555887
3	C	0.3115016	-0.0957874	6.1043502
4	C	1.1839151	-0.0758525	7.2228213
5	C	0.6884488	-0.1474559	8.5180942
6	C	-0.6922464	-0.2409939	8.7471319
7	H	-2.6414520	-0.3336350	7.8205396
8	H	-1.7900626	-0.2089731	5.5328107
9	H	2.2557254	-0.0034397	7.0662401
10	H	1.3788023	-0.1302402	9.3574313
11	H	-1.0774901	-0.2965822	9.7615030
12	C	0.8408990	-0.0208379	4.7638852
13	C	2.1786687	0.0750300	4.3097129
14	N	0.0527543	-0.0346904	3.6312257
15	C	2.1726542	0.1167818	2.9160781
16	H	3.0539599	0.1085466	4.9434875
17	C	0.8219531	0.0494262	2.4963039
18	H	-0.9558077	-0.0877998	3.5788723
19	H	3.0339178	0.1873334	2.2659012
20	C	0.1913557	0.0522417	1.2092600
21	C	0.8945269	0.1569890	0.0000000
22	C	0.1913557	0.0522417	-1.2092600
23	H	1.9699875	0.2819015	0.0000000
24	O	-1.1292235	-0.0894065	1.2261005
25	O	-1.1292235	-0.0894065	-1.2261005
26	B	-1.9325467	0.2466089	0.0000000
27	F	-2.1923197	1.6149410	0.0000000
28	F	-3.0765436	-0.5187329	0.0000000
29	C	0.8219531	0.0494262	-2.4963039
30	N	0.0527543	-0.0346904	-3.6312257
31	C	2.1726542	0.1167818	-2.9160781

32	C	0.8408990	-0.0208379	-4.7638852
33	H	-0.9558077	-0.0877998	-3.5788723
34	C	2.1786687	0.0750300	-4.3097129
35	H	3.0339178	0.1873334	-2.2659012
36	C	0.3115016	-0.0957874	-6.1043502
37	H	3.0539599	0.1085466	-4.9434875
38	C	-1.0809791	-0.1905135	-6.3555887
39	C	1.1839151	-0.0758525	-7.2228213
40	C	-1.5695720	-0.2617888	-7.6560021
41	H	-1.7900626	-0.2089731	-5.5328107
42	C	0.6884488	-0.1474559	-8.5180942
43	H	2.2557254	-0.0034397	-7.0662401
44	C	-0.6922464	-0.2409939	-8.7471319
45	H	-2.6414520	-0.3336350	-7.8205396
46	H	1.3788023	-0.1302402	-9.3574313
47	H	-1.0774901	-0.2965822	-9.7615030

SCF Done: E(RB3LYP) = -1371.44684493 A.U.

Zero-point correction = 0.352457 (Hartree/Particle)
Thermal correction to Energy = 0.377269
Thermal correction to Enthalpy = 0.378213
Thermal correction to Gibbs Free Energy = 0.293251
Sum of electronic and zero-point Energies = -1370.997468
Sum of electronic and thermal Energies = -1370.972656
Sum of electronic and thermal Enthalpies = -1370.971711
Sum of electronic and thermal Free Energies = -1371.056673

Low frequencies --- -1.1949 -0.0008 -0.0006 0.0011 1.2210 3.4229

Low frequencies --- 12.2045 17.9252 18.4209

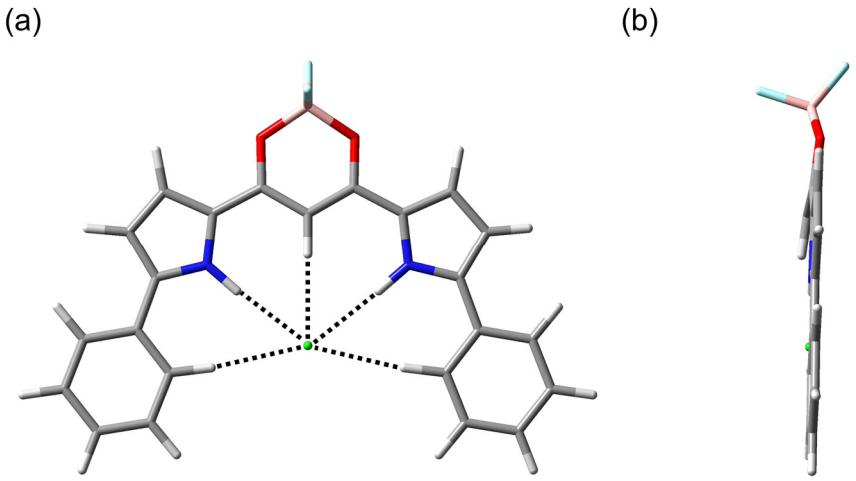

Fig. S17 (a) Front and (b) side views of the optimized structure of **1**-Cl at the S_0 state calculated at the B3LYP/6-31+G(d) level of theory.

Table S9. Standard orientation of the optimized geometry of **1**-Cl at the S_0 state calculated at the B3LYP/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.9353090	0.0540286	4.1189195
2	C	2.6387588	0.0345564	3.6024082
3	C	1.5257677	-0.0261569	4.4649493
4	C	1.7643996	-0.0666275	5.8546420
5	C	3.0612882	-0.0464989	6.3640451
6	C	4.1586333	0.0140460	5.4979692
7	H	4.7739749	0.1006860	3.4284957
8	H	2.5088770	0.0655915	2.5230933
9	H	0.9265622	-0.1134483	6.5441889
10	H	3.2146587	-0.0782777	7.4407130
11	H	5.1715942	0.0296674	5.8937340
12	C	0.1482491	-0.0484253	3.9610473
13	C	-1.0587392	-0.1165285	4.6803565
14	N	-0.1751396	-0.0043772	2.6323392
15	C	-2.1133120	-0.1169528	3.7572259
16	H	-1.1516344	-0.1590638	5.7569452
17	C	-1.5501062	-0.0452059	2.4791733
18	H	0.5001057	0.0226192	1.8558986
19	H	-3.1744937	-0.1566385	3.9592460
20	C	-2.2190599	-0.0127499	1.2034235
21	C	-1.5327816	0.1488814	0.0000000
22	C	-2.2190599	-0.0127499	-1.2034235
23	H	-0.4610970	0.2979195	0.0000000
24	O	-3.5225312	-0.1852512	1.2299873
25	O	-3.5225312	-0.1852512	-1.2299873
26	B	-4.3461203	0.0581276	0.0000000
27	F	-4.7690070	1.3877771	0.0000000

28	F	-5.4090821	-0.8269533	0.0000000
29	C	-1.5501062	-0.0452059	-2.4791733
30	N	-0.1751396	-0.0043772	-2.6323392
31	C	-2.1133120	-0.1169528	-3.7572259
32	C	0.1482491	-0.0484253	-3.9610473
33	H	0.5001057	0.0226192	-1.8558986
34	C	-1.0587392	-0.1165285	-4.6803565
35	H	-3.1744937	-0.1566385	-3.9592460
36	C	1.5257677	-0.0261569	-4.4649493
37	H	-1.1516344	-0.1590638	-5.7569452
38	C	2.6387588	0.0345564	-3.6024082
39	C	1.7643996	-0.0666275	-5.8546420
40	C	3.9353090	0.0540286	-4.1189195
41	H	2.5088770	0.0655915	-2.5230933
42	C	3.0612882	-0.0464989	-6.3640451
43	H	0.9265622	-0.1134483	-6.5441889
44	C	4.1586333	0.0140460	-5.4979692
45	H	4.7739749	0.1006860	-3.4284957
46	H	3.2146587	-0.0782777	-7.4407130
47	H	5.1715942	0.0296674	-5.8937340
48	Cl	1.9276527	0.0936437	0.0000000

SCF Done: E(RB3LYP) = -1831.78792258 A.U.

Zero-point correction = 0.358404 (Hartree/Particle)
Thermal correction to Energy = 0.384385
Thermal correction to Enthalpy = 0.385329
Thermal correction to Gibbs Free Energy = 0.298394
Sum of electronic and zero-point Energies = -1831.429519
Sum of electronic and thermal Energies = -1831.403537
Sum of electronic and thermal Enthalpies = -1831.402593
Sum of electronic and thermal Free Energies = -1831.489529

Low frequencies --- -1.8716 -0.0073 0.0011 0.0021 0.2601 1.1229

Low frequencies --- 19.5214 25.5903 26.9275

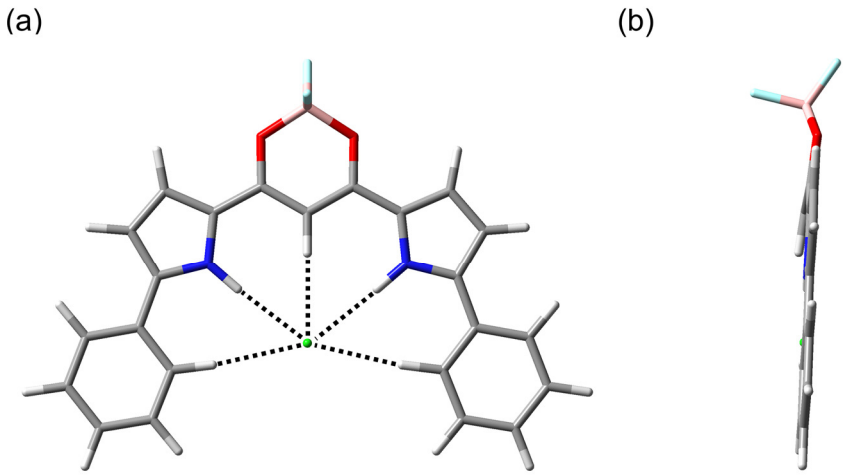

Fig. S18 (a) Front and (b) side views of the optimized structure of **1**-Cl at the S_1 state calculated at the B3LYP/6-31+G(d) level of theory.

Table S10. Standard orientation of the optimized geometry of **1**-Cl at the S_1 state calculated at the B3LYP/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.9297902	0.0849031	4.1056864
2	C	2.6368413	0.0537484	3.5900031
3	C	1.5162740	-0.0249752	4.4582351
4	C	1.7641633	-0.0710349	5.8559664
5	C	3.0590580	-0.0386237	6.3574992
6	C	4.1573164	0.0399183	5.4866508
7	H	4.7676854	0.1446764	3.4150699
8	H	2.5039065	0.0884453	2.5109719
9	H	0.9295488	-0.1326236	6.5481586
10	H	3.2176702	-0.0749399	7.4332944
11	H	5.1706312	0.0650670	5.8805348
12	C	0.1606325	-0.0584023	3.9595099
13	C	-1.0604744	-0.1317575	4.6831838
14	N	-0.1726194	-0.0215426	2.6236370
15	C	-2.1102038	-0.1414513	3.7727300
16	H	-1.1471826	-0.1691025	5.7606321
17	C	-1.5483050	-0.0686027	2.4747380
18	H	0.4998652	0.0020444	1.8448662
19	H	-3.1712776	-0.1852248	3.9730591
20	C	-2.2266815	-0.0515511	1.2129291
21	C	-1.5366459	0.0816962	0.0000000
22	C	-2.2266815	-0.0515511	-1.2129291
23	H	-0.4647970	0.2341413	0.0000000
24	O	-3.5451363	-0.2161784	1.2328849
25	O	-3.5451363	-0.2161784	-1.2328849
26	B	-4.3380059	0.0951857	0.0000000

27	F	-4.6528460	1.4610525	0.0000000
28	F	-5.4768395	-0.6949782	0.0000000
29	C	-1.5483050	-0.0686027	-2.4747380
30	N	-0.1726194	-0.0215426	-2.6236370
31	C	-2.1102038	-0.1414513	-3.7727300
32	C	0.1606325	-0.0584023	-3.9595099
33	H	0.4998652	0.0020444	-1.8448662
34	C	-1.0604744	-0.1317575	-4.6831838
35	H	-3.1712776	-0.1852248	-3.9730591
36	C	1.5162740	-0.0249752	-4.4582351
37	H	-1.1471826	-0.1691025	-5.7606321
38	C	2.6368413	0.0537484	-3.5900031
39	C	1.7641633	-0.0710349	-5.8559664
40	C	3.9297902	0.0849031	-4.1056864
41	H	2.5039065	0.0884453	-2.5109719
42	C	3.0590580	-0.0386237	-6.3574992
43	H	0.9295488	-0.1326236	-6.5481586
44	C	4.1573164	0.0399183	-5.4866508
45	H	4.7676854	0.1446764	-3.4150699
46	H	3.2176702	-0.0749399	-7.4332944
47	H	5.1706312	0.0650670	-5.8805348
48	Cl	1.9292999	0.0636941	0.0000000

SCF Done: E(RB3LYP) = -1831.78541893 A.U.

Zero-point correction = 0.353492 (Hartree/Particle)
Thermal correction to Energy = 0.379990
Thermal correction to Enthalpy = 0.380934
Thermal correction to Gibbs Free Energy = 0.293543
Sum of electronic and zero-point Energies = -1831.335427
Sum of electronic and thermal Energies = -1831.308929
Sum of electronic and thermal Enthalpies = -1831.307985
Sum of electronic and thermal Free Energies = -1831.395377

Low frequencies --- -1.8208 -0.8531 -0.0015 -0.0012 -0.0008 0.8974

Low frequencies --- 22.1224 26.1524 34.1798

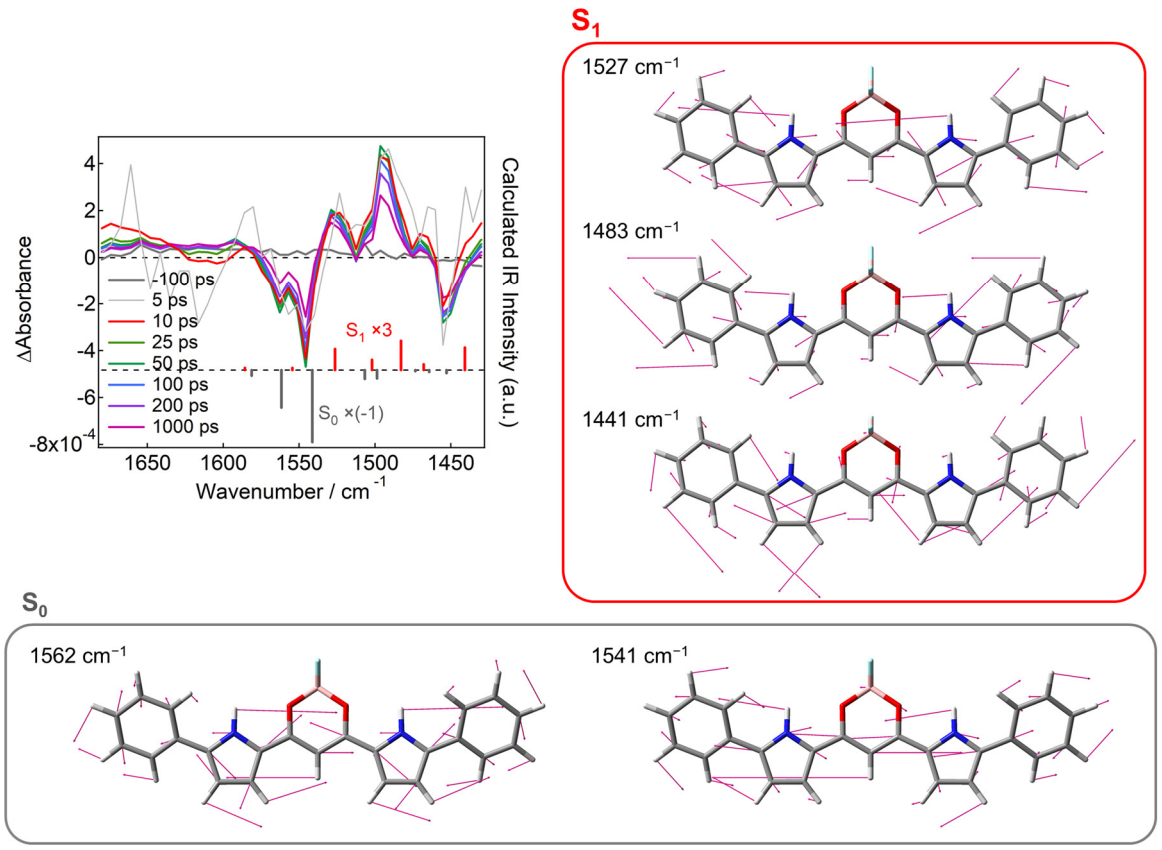

Fig. S19 Time-resolved IR spectra of the out-out form of **1** in deuterated dichloromethane at room temperature. Relevant vibrational modes of the out-out form of **1** at the S_0 and S_1 states calculated at the B3LYP/6-31+G(d) level of theory.

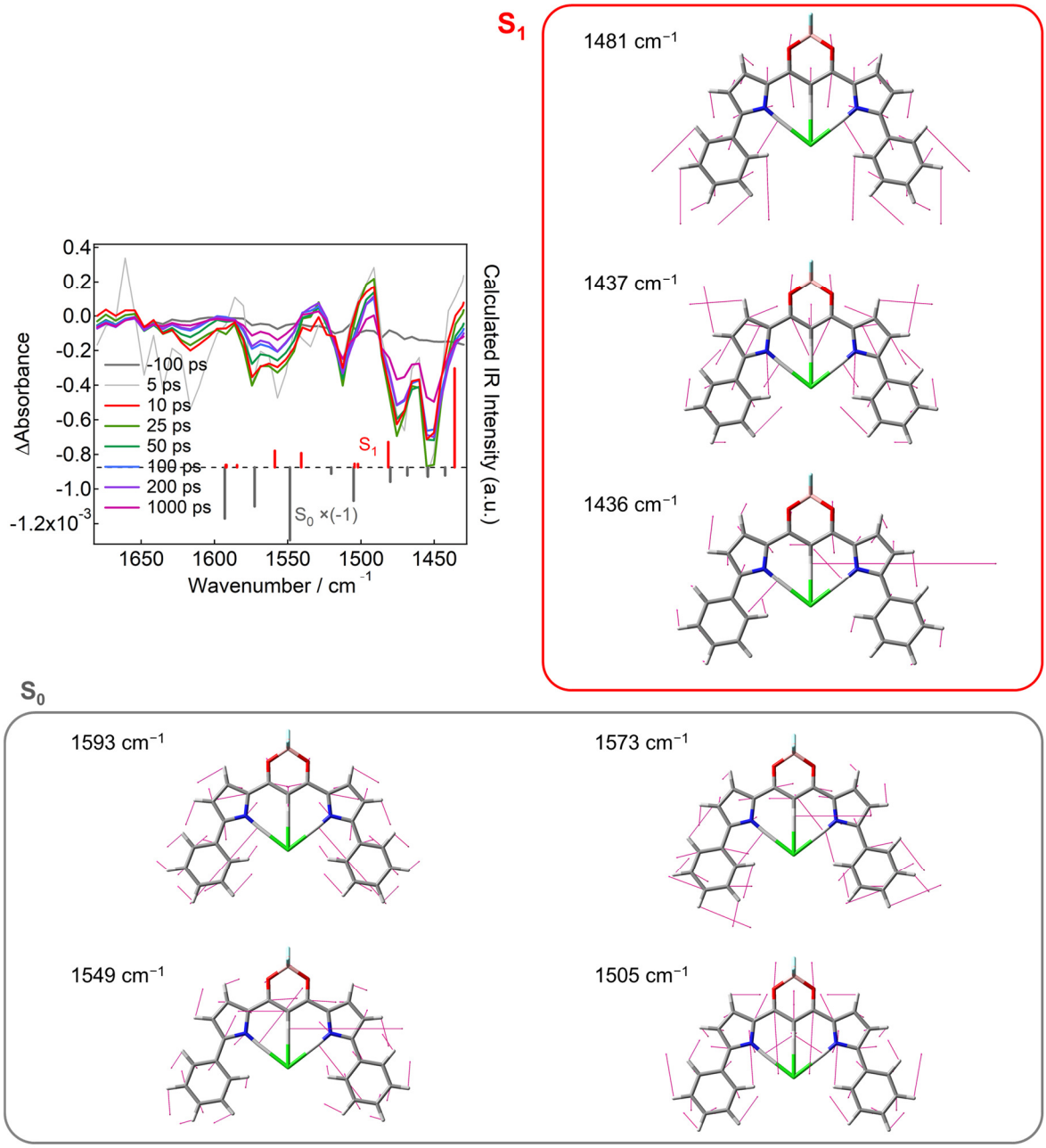

Fig. S20 Time-resolved IR spectra of **1**-Cl in deuterated dichloromethane at room temperature. Relevant vibrational modes of **1**-Cl at the S_0 and S_1 states calculated at the B3LYP/6-31+G(d) level of theory.