Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

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X-ray Crystallography

The single crystals of **1** and $\mathbf{1}^{\cdot+}\cdot[SbF_6]^-$ were obtained by the solvent diffusion method (**1**: benzene/*n*-hexane, $\mathbf{1}^{\cdot+}\cdot[SbF_6]^-$: acetone/ *n*-hexane). Data collections were performed on a Rigaku Saturn70 diffractometer with Mo-Kα radiation (λ = 0.71075 Å) at –130˚C. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. All the calculations were performed by using CrystalStructure crystallographic software package,[S1] except for refinement, which was performed by using SHELXL-97.[S2]

[S1] CrystalStructure 4.0, Crystal Structure Analysis Package, Rigaku Corporation (2000–2011). Tokyo196-8666, Japan

[S2] G. M. Sheldrick, Acta Cryst. A 2008, 64, 112.

Table S1: X-ray crystallographic data for **1**.

empirical formula	$2(C_{60}H_{52}N_6)\ C_6H_6$
formula weight	1786.21
T [˚C]	–130
λ [Å]	0.71075
crystal system	monoclinic
space group	P 2_1/n (#14)
Z	8
a [Å]	14.2255(16)
b [Å]	29.980(4)
c [Å]	22.944(3)
α [˚]	90.0000
β [˚]	92.5721(18)
γ [˚]	90.0000
V [Å^3]	9775(2)
ρ_{calcd} [g cm^{-3}]	1.115
μ (CuKα)[cm^{-1}]	0.717
collected data	79941
unique data / R_{int}	22367/0.0971
no. of parameters	1288
goodness-of-fit[a]	1.072
$R1$ ($I > 2\sigma$), $wR2$ (all reflections)[b]	0.1153, 0.3164
residual density [e Å^{-3}]	1.26/-0.45

[a] GOF = $\left\{\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]/(n-p)\right\}^{1/2}$, where n and p denote the number of data and parameters.

[b] $R1 = \sum(\|F_0\| - \|F_c\|)/\sum\|F_0\|$ and $wR2 = \left\{\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]/\sum\left[w\left(F_0^2\right)^2\right]\right\}^{1/2}$ where $w = 1/\left[\sigma^2\left(F_0^2\right) + (a\cdot P)^2 + b\cdot P\right]$ and $P = \left[\left(\mathrm{Max};0,F_0^2\right) + 2\cdot F_c^2\right]/3$.

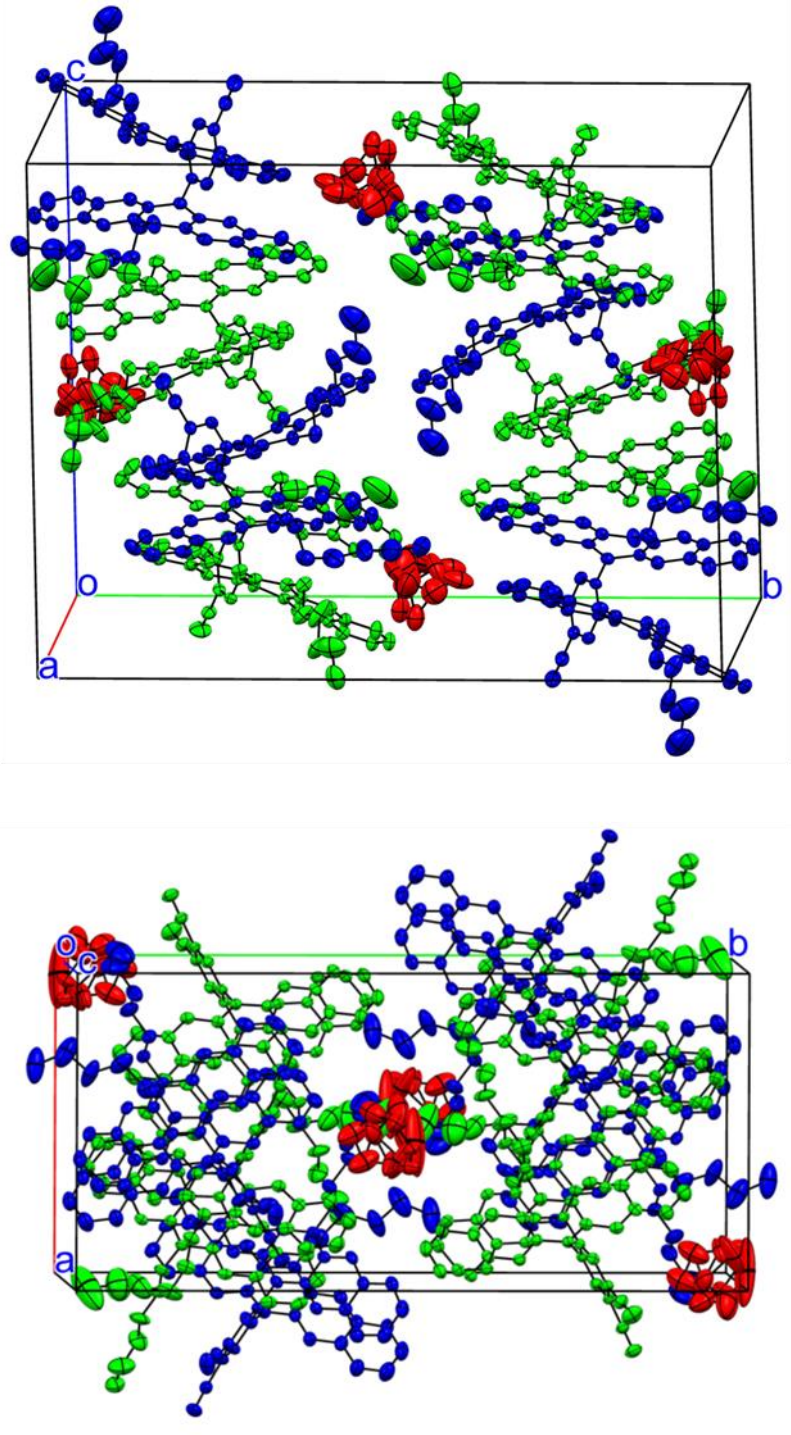

Figure S1. (a) Packing structure of **1**. Solvent molecules (benzene) were shown in red colour. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

Table S2: X-ray crystallographic data for $\mathbf{1}^{\cdot+}\cdot[SbF_6]^-$.

empirical formula	$C_{60}H_{52}N_6\cdot SbF_6\cdot C_3H_6O$
formula weight	1150.93
T [˚C]	–130
λ [Å]	0.71075
crystal system	monoclinic
space group	P21/n (#14)
Z	4
a [Å]	15.927(3)
b [Å]	13.626(2)
c [Å]	25.437(4)
α [˚]	90.0000
β [˚]	106.335(2)
γ [˚]	90.0000
V [Å^3]	5297.5(14)
ρ_{calcd} [g cm^{-3}]	1.443
μ (CuKα)[cm^{-1}]	5.912
collected data	42411
unique data / R_{int}	12100/ 0.0425
no. of parameters	712
goodness-of-fit[a]	1.074
$R1$ ($I > 2\sigma$), $wR2$ (all reflections)[b]	0.0603, 0.1568
residual density [e Å^{-3}]	1.33/-0.93

[a] GOF = $\left\{\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]/(n-p)\right\}^{1/2}$, where n and p denote the number of data and parameters.

[b] $R1 = \sum(\|F_0\| - \|F_c\|)/\sum\|F_0\|$ and $wR2 = \left\{\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]/\sum\left[w\left(F_0^2\right)^2\right]\right\}^{1/2}$ where $w = 1/\left[\sigma^2\left(F_0^2\right) + (a\cdot P)^2 + b\cdot P\right]$ and $P = \left[\left(\text{Max}; 0, F_0^2\right) + 2\cdot F_c^2\right]/3$.

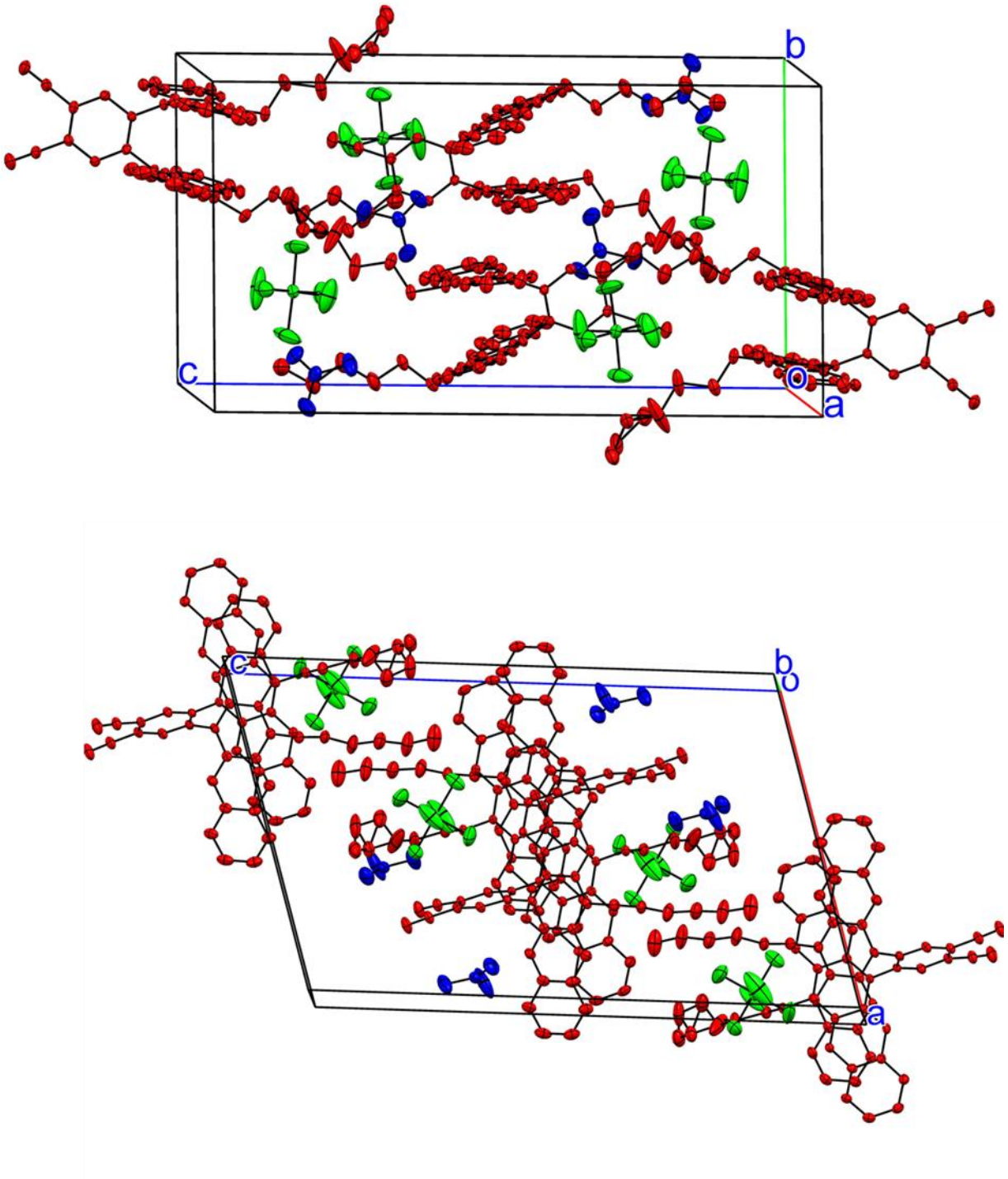

Figure S2. (a) Packing structure of $\mathbf{1}^{\cdot+}\cdot[SbF_6]^-$. Solvent molecules (chloroform) were shown in blue colour. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

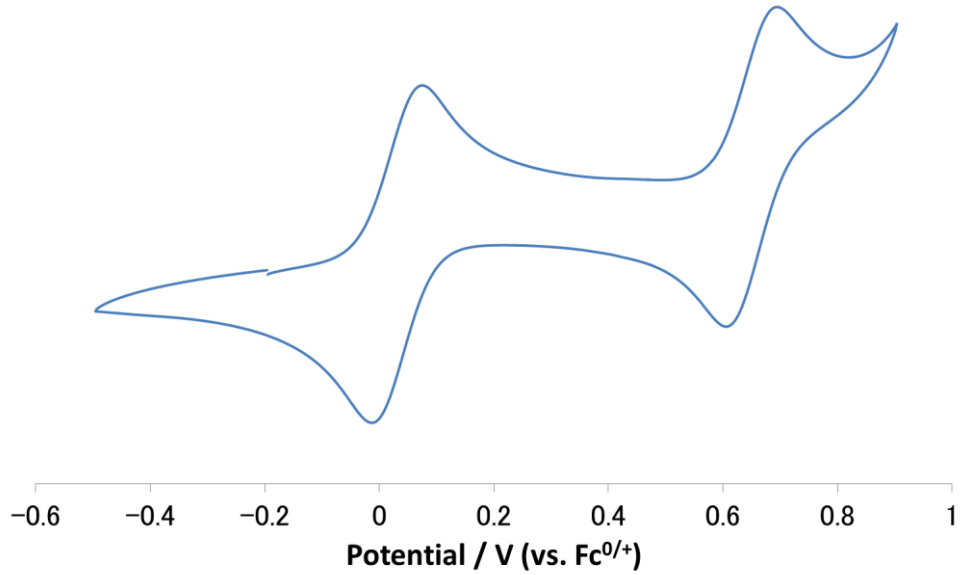

Figure S3. Cyclic voltammogram of **3** measured in CH_2Cl_2 containing 0.1 M *n*-Bu_4NBF_4 at 298 K (scan rate 100 m V s^{-1}).

Table S3. Oxidation potentials of **3** (V vs. $Fc^{0/+}$) in CH_2Cl_2 containing 0.1 M *n*-Bu_4NBF_4 at 298 K.

	E_1	E_2
3	0.006	0.622

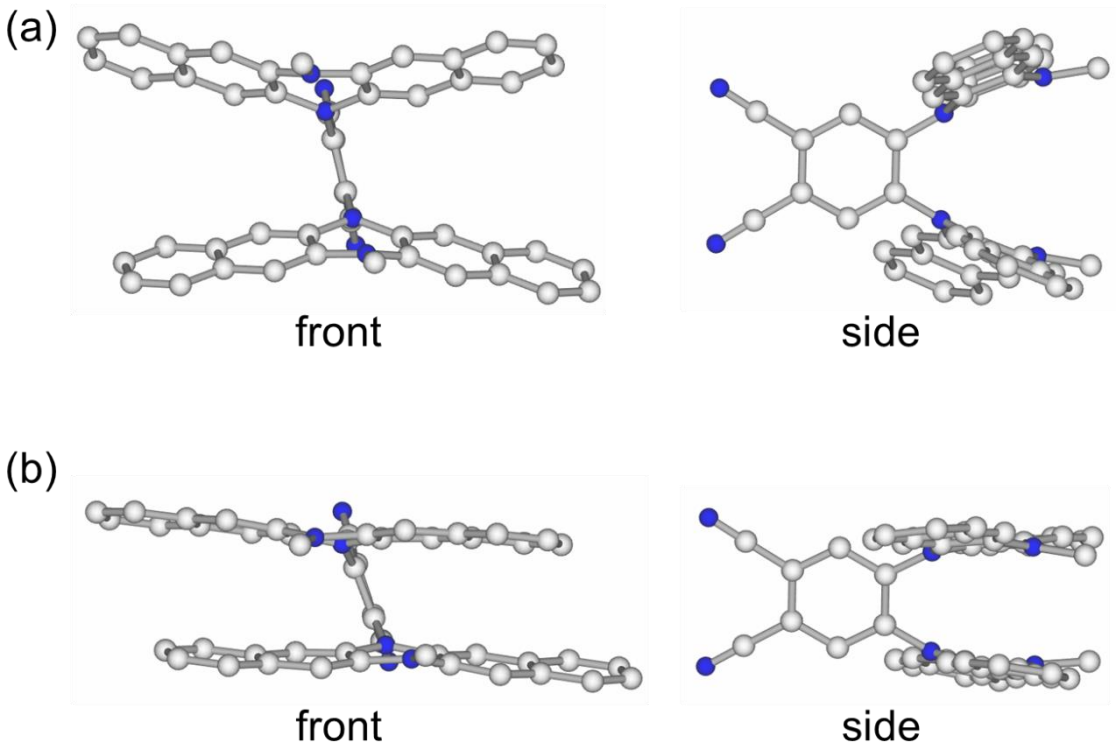

Figure S4. Optimized structure of **1'** at the (a) B3LYP/6-31G* and (b) M06-2X/6-31G* level of theory.

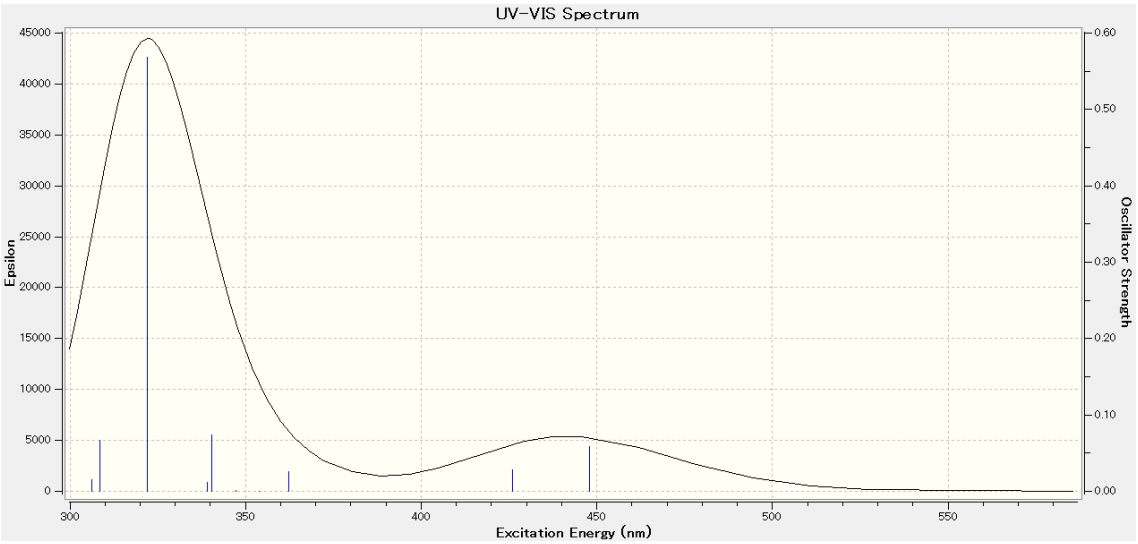

Figure S5. The simulated absorption spectrum of **1'** based on the TD-DFT calculations at the M06-2X/6-31G* level.

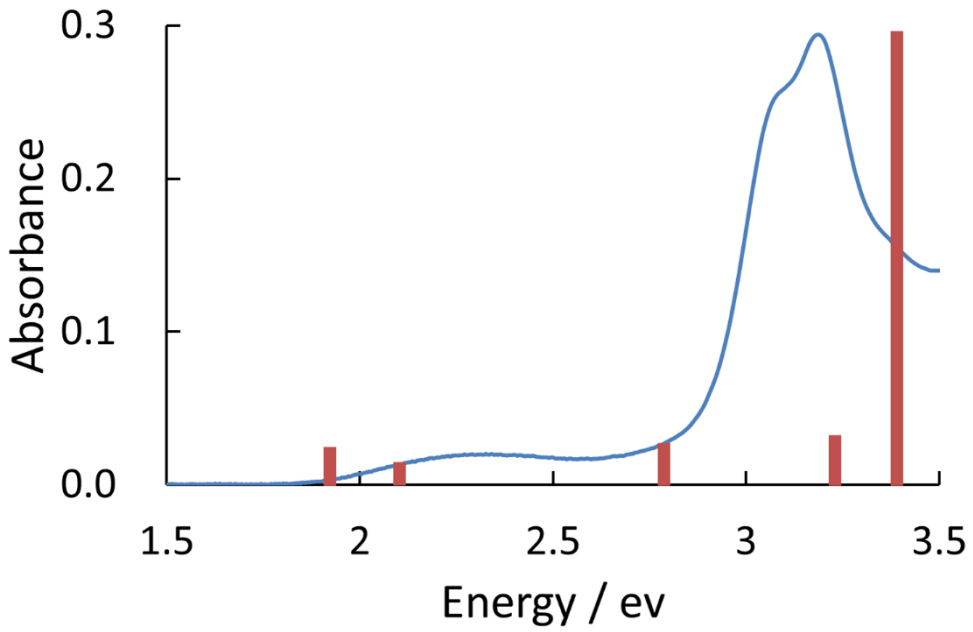

Figure S6. The electronic transitions of **1'** based on the TD-DFT calculations with the B3LYP/6-31G* level at the optimized geometry with the M06-2X/6-31G* level. The red bars represent the TD-DFT-calculated energy transitions and their relative oscillator strength. The blue line represents the UV-Vis-NIR absorption spectrum of **1'** in CH_2Cl_2.

Table S4. TD-DFT-calculated excitations of **1'** with the oscillator strength (*f*) value larger than 0.015 (B3LYP/6-31G*//M06-2X/6-31G*).

	$h\nu$ (eV, cm^{-1}, nm)	*f*	Assignment
Excitation 1	1.928, 15548, 643	0.0357	HOMO → LUMO [≈100%]
Excitation 2	2.104, 16968, 589	0.0167	(HO-1)MO → LUMO [97%]
Excitation 3	2.788, 22484, 445	0.0387	(HO-1)MO → (LU+1)MO [95%]
Excitation 4	3.235, 26089, 383	0.0439	(HO-1)MO → (LU+2)MO [67%]
			HOMO → (LU+3)MO [25%]
Excitation 5	3.395, 27379, 365	0.4727	HOMO → (LU+3)MO [67%]
			(HO-1)MO → (LU+2)MO [19%]

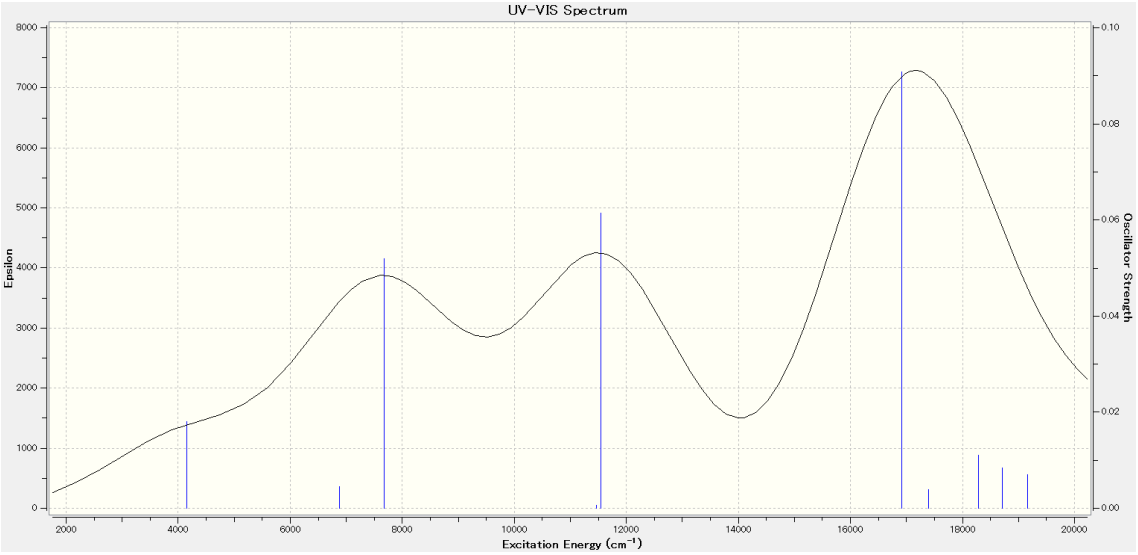

Figure S7. The simulated absorption spectrum of **1'**$^{\bullet+}$ based on the TD-DFT calculations at the UB3LYP/6-31G* level at the optimized geometry with the UM06-2X/6-31G* level.

Table S5. TD-DFT-calculated excitations of **1'**$^{\bullet+}$ at the UB3LYP/6-31G* level at the optimized geometry with the UM06-2X/6-31G* level.

	$h\nu$ (eV, cm^{-1}, nm)	f	Assignment
Excitation 1	0.515,4154, 2407	0.0181	β-HOMO → β-LUMO [93%]
Excitation 2	0.853, 6882, 1453	0.0045	β-(HO-2)MO → β-LUMO [≈100%]
Excitation 3	0.951, 7669, 1304	0.0519	β-(HO-1)MO → β-LUMO [91%]
Excitation 4	1.432, 11550, 866	0.0614	β-(HO-3)MO → β-LUMO [96%]
Excitation 5	2.097, 16911, 591	0.0908	β-(HO-5)MO → β-LUMO [95%]

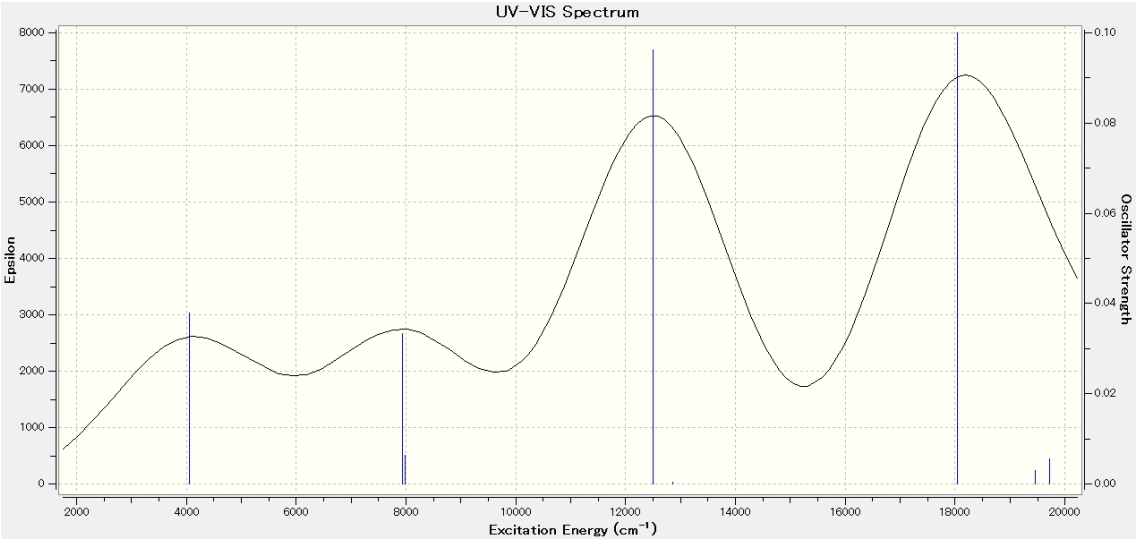

Figure S8. The simulated absorption spectrum of **1'**$^{\cdot+}$ based on the TD-DFT calculations with the BLYP-based hybrid functional with 35% exact exchange and the SVP basis at the optimized geometry with the UM06-2X/6-31G* level.

Table S6. TD-DFT-calculated excitations of **1'**$^{\cdot+}$ at the BLYP-based hybrid functional with 35% exact exchange and the SVP basis at the optimized geometry with the UM06-2X/6-31G* level.

	$h\nu$ (eV, cm^{-1}, nm)	f	Assignment
Excitation 1	0.503, 4055, 2466	0.0380	β-HOMO → β-LUMO [97%]
Excitation 2	0.984, 7931, 1261	0.0334	β-(HO-2)MO → β-LUMO [95%]
Excitation 3	0.990, 7981, 1253	0.0063	β-(HO-1)MO → β-LUMO [97%]
Excitation 4	1.550, 12502, 800	0.0962	β-(HO-3)MO → β-LUMO [93%]
Excitation 5	2.236, 18035, 554	0.1000	β-(HO-5)MO → β-LUMO [95%]

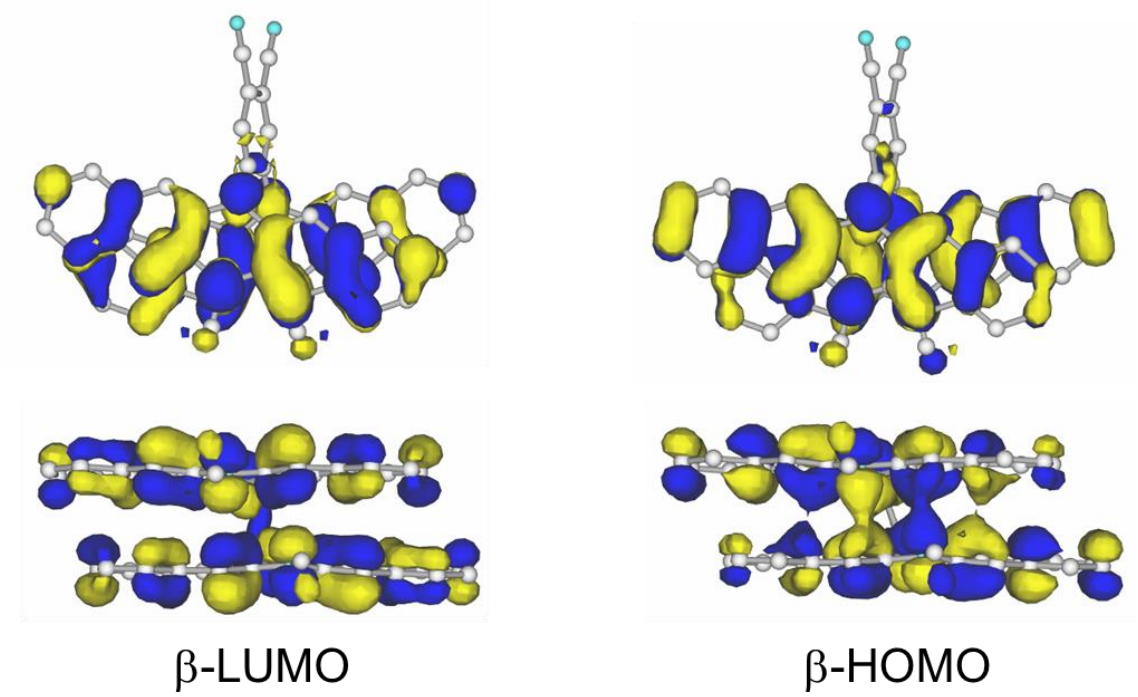

Figure S9. Singly occupied MOs of **1'**$^{\cdot+}$ associated with the lowest energy transition calculated at the BLYP-based hybrid functional with 35% exact exchange and the SVP basis at the optimized geometry with the UM06-2X/6-31G* level.

Initial geometry of the structure optimization of **1'** (B3LYP/6-31G*)

N	0.797700	0.413054	-1.225404	H	6.649132	-1.736637	-2.026220
C	2.194362	0.146853	-1.313747	H	8.337036	-0.059974	-1.350415
C	-0.152830	-0.448122	-1.837442	C	6.874003	1.422021	-0.754996
C	0.285125	-1.743422	-2.280705	H	5.217068	2.689723	-0.257975
C	2.604121	-1.154081	-1.776253	H	7.622373	2.148726	-0.461467
N	1.621234	-2.112959	-2.062189	C	-4.666756	-1.419005	-3.405440
C	-1.459216	-0.065453	-2.032827	H	-4.106637	0.401539	-2.422093
C	3.952570	-1.426172	-1.900355	H	-5.704457	-1.130260	-3.522935
C	4.953462	-0.489803	-1.529100	C	-4.234881	-2.683441	-3.872839
H	4.274484	-2.380336	-2.294357	H	-2.588073	-4.043288	-4.068393
C	6.340235	-0.770932	-1.640155	H	-4.944760	-3.347207	-4.352672
C	4.543631	0.781721	-1.024139	C	-2.010104	-3.524305	2.189360
C	3.153062	1.062869	-0.940479	C	0.357568	1.622475	-0.611613
C	5.532798	1.723818	-0.638766	C	-0.357558	1.623135	0.610538
H	2.855412	2.031227	-0.564119	C	0.665385	2.844464	-1.219406
C	-2.415019	-0.929528	-2.631688	C	-0.665171	2.845804	1.217101
H	-1.783208	0.914205	-1.710387	N	-0.797806	0.414387	1.225526
C	-1.981579	-2.212648	-3.088731	H	-1.173577	2.839501	2.171859
C	-3.775301	-0.560203	-2.797400	C	-0.332614	4.067152	0.622943
C	-0.619905	-2.575875	-2.908810	C	0.332941	4.066472	-0.626532
C	-2.921302	-3.072867	-3.715309	C	-0.659231	5.290679	1.272425
H	-0.295244	-3.532083	-3.296015	C	0.659722	5.289292	-1.277256
C	7.280555	0.164544	-1.261608	C	0.152726	-0.446496	1.837990

C	-2.194472	0.148199	1.314165
C	-2.604033	-1.152871	1.776481
C	-0.285004	-1.741978	2.280899
N	-1.620987	-2.111718	2.061988
C	-3.153311	1.064200	0.941236
C	1.458884	-0.063384	2.034007
C	2.414745	-0.927286	2.633028
H	1.782634	0.916469	1.711899
C	1.981571	-2.210700	3.089521
C	0.620072	-2.574329	2.909066
C	2.921376	-3.070785	3.716164
H	0.295591	-3.530752	3.295894
C	-4.543845	0.782863	1.025014
H	-2.855832	2.032641	0.564950
C	-5.533165	1.724901	0.639886
C	-4.953470	-0.488787	1.529832
C	-3.952428	-1.425119	1.900781
H	-4.274173	-2.379414	2.294612
C	4.234757	-2.680948	3.874304
H	2.588364	-4.041437	4.068815
H	4.944692	-3.344622	4.354182
C	4.666366	-1.416211	3.407474
C	3.774837	-0.557543	2.799360
H	5.703923	-1.127145	3.525446
H	4.105969	0.404424	2.424452
C	-6.874322	1.422935	0.756239
H	-5.217589	2.690886	0.259175
H	-7.622808	2.149594	0.462895
C	-7.280669	0.165343	1.262729
C	-6.340199	-0.770085	1.641020
H	-8.337114	-0.059306	1.351637
H	-6.648941	-1.735883	2.026975
C	2.010576	-3.525470	-2.189800
H	1.173922	2.837102	-2.174087
H	1.164136	-4.151038	-1.897958
H	2.316581	-3.787926	-3.211237
H	2.836836	-3.726316	-1.503847
H	-1.163629	-4.149679	1.897184
H	-2.315829	-3.787054	3.210809
H	-2.836481	-3.725103	1.503541
N	0.933046	6.284357	-1.819683
N	-0.932357	6.286415	1.813720

Optimized geometry of **1'** (B3LYP/6-31G*)

N	0.639641	0.364608	-1.286486	H	6.232669	-2.188088	-2.540648
C	2.000271	0.024802	-1.498862	H	8.087784	-0.632053	-2.037674
C	-0.381633	-0.349768	-1.959273	C	6.786983	0.962077	-1.352210
C	-0.078350	-1.676562	-2.413370	H	5.272144	2.352606	-0.740493
C	2.276741	-1.303711	-1.973294	H	7.607425	1.639758	-1.132718
N	1.198579	-2.185780	-2.139107	C	-4.923714	-0.788026	-3.676612
C	-1.633617	0.179928	-2.179886	H	-4.186236	0.957160	-2.670885
C	3.585414	-1.679297	-2.203926	H	-5.917117	-0.375593	-3.829520
C	4.677385	-0.813229	-1.929674	C	-4.625527	-2.090410	-4.138721
H	3.805133	-2.663174	-2.602792	H	-3.138604	-3.629081	-4.298286
C	6.025270	-1.195233	-2.147752	H	-5.391182	-2.670116	-4.647207
C	4.402661	0.489508	-1.416355	C	-1.457471	-3.598019	2.331626
C	3.048511	0.875288	-1.221392	C	0.304473	1.584725	-0.639496
C	5.484695	1.360061	-1.131696	C	-0.304730	1.585685	0.637100
H	2.860383	1.867909	-0.829730	C	0.572495	2.804193	-1.269162
C	-2.658216	-0.566683	-2.822516	C	-0.572928	2.806136	1.264809
H	-1.862394	1.187671	-1.851630	N	-0.639743	0.366563	1.286000
C	-2.358069	-1.884372	-3.283681	H	-1.008672	2.802056	2.257707
C	-3.958562	-0.042949	-3.031819	C	-0.288209	4.027370	0.642800
C	-1.050520	-2.400514	-3.074424	C	0.287596	4.026387	-0.649116
C	-3.369443	-2.626551	-3.944709	C	-0.578885	5.252437	1.325571
H	-0.825735	-3.388951	-3.459447	C	0.578084	5.250403	-1.333839
C	7.059219	-0.326715	-1.865828	C	0.381665	-0.346820	1.959638

C	-2.000316	0.026926	1.499038
C	-2.276571	-1.300996	1.975255
C	0.078605	-1.673078	2.415417
N	-1.198292	-2.182785	2.141871
C	-3.048686	0.876945	1.220644
C	1.633561	0.183371	2.179558
C	2.658314	-0.562287	2.823046
H	1.862139	1.190760	1.850069
C	2.358410	-1.879471	3.285818
C	1.050932	-2.396082	3.077275
C	3.369947	-2.620684	3.947680
H	0.826329	-3.384086	3.463511
C	-4.402759	0.491310	1.416435
H	-2.860738	1.869058	0.827610
C	-5.484930	1.361393	1.130855
C	-4.677260	-0.810752	1.931585
C	-3.585155	-1.676373	2.206720
H	-3.804698	-2.659743	2.606931
C	4.625949	-2.084098	4.140984
H	3.139293	-3.622827	4.302475
H	5.391728	-2.663065	4.650125
C	4.923892	-0.782219	3.677297
C	3.958584	-0.038082	3.031653
H	5.917234	-0.369435	3.829652
H	4.186077	0.961627	2.669499
C	-6.787133	0.963611	1.352233
H	-5.272550	2.353419	0.738245
H	-7.607682	1.640929	1.132019
C	-7.059145	-0.324501	1.867677
C	-6.025061	-1.192557	2.150523
H	-8.087645	-0.629676	2.040201
H	-6.232287	-2.184892	2.544824
C	1.457909	-3.601246	-2.326923
H	1.008247	2.798574	-2.262049
H	0.576221	-4.167943	-2.018937
H	1.697951	-3.863148	-3.368580
H	2.294233	-3.897533	-1.689649
H	-0.575823	-4.165055	2.024138
H	-1.697197	-3.858571	3.373695
H	-2.293949	-3.895201	1.694975
N	0.824486	6.230049	-1.909712
N	-0.825446	6.232963	1.899875

Initial geometry of the structure optimization of **1'** (M06-2X/6-31G*)

N	0.639641	0.364608	-1.286486	H	6.232669	-2.188088	-2.540648
C	2.000271	0.024802	-1.498862	H	8.087784	-0.632053	-2.037674
C	-0.381633	-0.349768	-1.959273	C	6.786983	0.962077	-1.352210
C	-0.078350	-1.676562	-2.413370	H	5.272144	2.352606	-0.740493
C	2.276741	-1.303711	-1.973294	H	7.607425	1.639758	-1.132718
N	1.198579	-2.185780	-2.139107	C	-4.923714	-0.788026	-3.676612
C	-1.633617	0.179928	-2.179886	H	-4.186236	0.957160	-2.670885
C	3.585414	-1.679297	-2.203926	H	-5.917117	-0.375593	-3.829520
C	4.677385	-0.813229	-1.929674	C	-4.625527	-2.090410	-4.138721
H	3.805133	-2.663174	-2.602792	H	-3.138604	-3.629081	-4.298286
C	6.025270	-1.195233	-2.147752	H	-5.391182	-2.670116	-4.647207
C	4.402661	0.489508	-1.416355	C	-1.457471	-3.598019	2.331626
C	3.048511	0.875288	-1.221392	C	0.304473	1.584725	-0.639496
C	5.484695	1.360061	-1.131696	C	-0.304730	1.585685	0.637100
H	2.860383	1.867909	-0.829730	C	0.572495	2.804193	-1.269162
C	-2.658216	-0.566683	-2.822516	C	-0.572928	2.806136	1.264809
H	-1.862394	1.187671	-1.851630	N	-0.639743	0.366563	1.286000
C	-2.358069	-1.884372	-3.283681	H	-1.008672	2.802056	2.257707
C	-3.958562	-0.042949	-3.031819	C	-0.288209	4.027370	0.642800
C	-1.050520	-2.400514	-3.074424	C	0.287596	4.026387	-0.649116
C	-3.369443	-2.626551	-3.944709	C	-0.578885	5.252437	1.325571
H	-0.825735	-3.388951	-3.459447	C	0.578084	5.250403	-1.333839
C	7.059219	-0.326715	-1.865828	C	0.381665	-0.346820	1.959638

C	-2.000316	0.026926	1.499038
C	-2.276571	-1.300996	1.975255
C	0.078605	-1.673078	2.415417
N	-1.198292	-2.182785	2.141871
C	-3.048686	0.876945	1.220644
C	1.633561	0.183371	2.179558
C	2.658314	-0.562287	2.823046
H	1.862139	1.190760	1.850069
C	2.358410	-1.879471	3.285818
C	1.050932	-2.396082	3.077275
C	3.369947	-2.620684	3.947680
H	0.826329	-3.384086	3.463511
C	-4.402759	0.491310	1.416435
H	-2.860738	1.869058	0.827610
C	-5.484930	1.361393	1.130855
C	-4.677260	-0.810752	1.931585
C	-3.585155	-1.676373	2.206720
H	-3.804698	-2.659743	2.606931
C	4.625949	-2.084098	4.140984
H	3.139293	-3.622827	4.302475
H	5.391728	-2.663065	4.650125
C	4.923892	-0.782219	3.677297
C	3.958584	-0.038082	3.031653
H	5.917234	-0.369435	3.829652
H	4.186077	0.961627	2.669499
C	-6.787133	0.963611	1.352233
H	-5.272550	2.353419	0.738245
H	-7.607682	1.640929	1.132019
C	-7.059145	-0.324501	1.867677
C	-6.025061	-1.192557	2.150523
H	-8.087645	-0.629676	2.040201
H	-6.232287	-2.184892	2.544824
C	1.457909	-3.601246	-2.326923
H	1.008247	2.798574	-2.262049
H	0.576221	-4.167943	-2.018937
H	1.697951	-3.863148	-3.368580
H	2.294233	-3.897533	-1.689649
H	-0.575823	-4.165055	2.024138
H	-1.697197	-3.858571	3.373695
H	-2.293949	-3.895201	1.694975
N	0.824486	6.230049	-1.909712
N	-0.825446	6.232963	1.899875

Optimized geometry of **1'** (M06-2X/6-31G*)

N	0.814908	0.570462	-1.181032	H	6.550477	-1.937654	-1.116390
C	2.194369	0.250441	-1.177963	H	8.288296	-0.230962	-0.700080
C	-0.152147	-0.382378	-1.560477	C	6.883375	1.415673	-0.604013
C	0.232492	-1.762082	-1.633154	H	5.280741	2.836055	-0.565661
C	2.556091	-1.137934	-1.281291	H	7.652033	2.159721	-0.420584
N	1.544104	-2.099099	-1.308290	C	-4.784800	-1.587450	-2.360521
C	-1.447313	-0.015474	-1.812138	H	-4.103041	0.422699	-2.074296
C	3.886409	-1.486748	-1.275236	H	-5.831500	-1.305481	-2.416360
C	4.913367	-0.528210	-1.078635	C	-4.413895	-2.946676	-2.462195
H	4.178843	-2.524101	-1.388139	H	-2.804471	-4.362599	-2.441266
C	6.279357	-0.891433	-0.998814	H	-5.177776	-3.702393	-2.618032
C	4.552936	0.831508	-0.922415	C	-1.885512	-3.489191	1.094499
C	3.178923	1.187541	-0.994017	C	0.375936	1.781048	-0.600781
C	5.564507	1.793265	-0.684955	C	-0.375961	1.780916	0.600998
H	2.930003	2.233320	-0.860581	C	0.692948	2.996446	-1.203078
C	-2.458910	-0.980611	-2.058127	C	-0.693107	2.996184	1.203478
H	-1.732387	1.031537	-1.759637	N	-0.814863	0.570219	1.181088
C	-2.084517	-2.345318	-2.144669	H	-1.213645	2.990312	2.155462
C	-3.823604	-0.623849	-2.170898	C	-0.343849	4.210495	0.612502
C	-0.718348	-2.698764	-1.969587	C	0.343573	4.210627	-0.611904
C	-3.092392	-3.316330	-2.365235	C	-0.689484	5.443455	1.264802
H	-0.444041	-3.742373	-2.079221	C	0.689064	5.443728	-1.264012
C	7.243914	0.058665	-0.763437	C	0.152202	-0.382641	1.560452

C	-2.194317	0.250154	1.177830
C	-2.556049	-1.138218	1.281167
C	-0.232456	-1.762338	1.633207
N	-1.544073	-2.099383	1.308390
C	-3.178841	1.187265	0.993826
C	1.447387	-0.015747	1.812039
C	2.458984	-0.980868	2.058067
H	1.732472	1.031256	1.759454
C	2.084555	-2.345548	2.144811
C	0.718377	-2.698984	1.969773
C	3.092404	-3.316564	2.365487
H	0.444079	-3.742580	2.079553
C	-4.552854	0.831260	0.922115
H	-2.929896	2.233053	0.860485
C	-5.564385	1.793023	0.684515
C	-4.913311	-0.528450	1.078329
C	-3.886381	-1.487003	1.275020
H	-4.178874	-2.524328	1.387999
C	4.413925	-2.946939	2.462324
H	2.804447	-4.362812	2.441687
H	5.177793	-3.702655	2.618224
C	4.784867	-1.587741	2.360401
C	3.823696	-0.624132	2.170690
H	5.831579	-1.305806	2.416183
H	4.103168	0.422391	2.073921
C	-6.883245	1.415436	0.603399
H	-5.280596	2.835811	0.565254
H	-7.651876	2.159482	0.419840
C	-7.243812	0.058436	0.762830
C	-6.279296	-0.891660	0.998377
H	-8.288188	-0.231187	0.699336
H	-6.550448	-1.937871	1.115968
C	1.885578	-3.488907	-1.094503
H	1.213453	2.990784	-2.155079
H	1.030879	-3.993605	-0.638855
H	2.157598	-4.006313	-2.024472
H	2.713823	-3.544953	-0.385542
H	-1.030708	-3.993907	0.639073
H	-2.157793	-4.006595	2.024387
H	-2.713554	-3.545231	0.385297
N	0.977725	6.425394	-1.803213
N	-0.978261	6.425007	1.804149

Initial geometry of the structure optimization of **1'**$^{\cdot+}$ (M06-2X/6-31G*)

N	0.814908	0.570462	-1.181032	H	6.550477	-1.937654	-1.116390
C	2.194369	0.250441	-1.177963	H	8.288296	-0.230962	-0.700080
C	-0.152147	-0.382378	-1.560477	C	6.883375	1.415673	-0.604013
C	0.232492	-1.762082	-1.633154	H	5.280741	2.836055	-0.565661
C	2.556091	-1.137934	-1.281291	H	7.652033	2.159721	-0.420584
N	1.544104	-2.099099	-1.308290	C	-4.784800	-1.587450	-2.360521
C	-1.447313	-0.015474	-1.812138	H	-4.103041	0.422699	-2.074296
C	3.886409	-1.486748	-1.275236	H	-5.831500	-1.305481	-2.416360
C	4.913367	-0.528210	-1.078635	C	-4.413895	-2.946676	-2.462195
H	4.178843	-2.524101	-1.388139	H	-2.804471	-4.362599	-2.441266
C	6.279357	-0.891433	-0.998814	H	-5.177776	-3.702393	-2.618032
C	4.552936	0.831508	-0.922415	C	-1.885512	-3.489191	1.094499
C	3.178923	1.187541	-0.994017	C	0.375936	1.781048	-0.600781
C	5.564507	1.793265	-0.684955	C	-0.375961	1.780916	0.600998
H	2.930003	2.233320	-0.860581	C	0.692948	2.996446	-1.203078
C	-2.458910	-0.980611	-2.058127	C	-0.693107	2.996184	1.203478
H	-1.732387	1.031537	-1.759637	N	-0.814863	0.570219	1.181088
C	-2.084517	-2.345318	-2.144669	H	-1.213645	2.990312	2.155462
C	-3.823604	-0.623849	-2.170898	C	-0.343849	4.210495	0.612502
C	-0.718348	-2.698764	-1.969587	C	0.343573	4.210627	-0.611904
C	-3.092392	-3.316330	-2.365235	C	-0.689484	5.443455	1.264802
H	-0.444041	-3.742373	-2.079221	C	0.689064	5.443728	-1.264012
C	7.243914	0.058665	-0.763437	C	0.152202	-0.382641	1.560452

C	-2.194317	0.250154	1.177830
C	-2.556049	-1.138218	1.281167
C	-0.232456	-1.762338	1.633207
N	-1.544073	-2.099383	1.308390
C	-3.178841	1.187265	0.993826
C	1.447387	-0.015747	1.812039
C	2.458984	-0.980868	2.058067
H	1.732472	1.031256	1.759454
C	2.084555	-2.345548	2.144811
C	0.718377	-2.698984	1.969773
C	3.092404	-3.316564	2.365487
H	0.444079	-3.742580	2.079553
C	-4.552854	0.831260	0.922115
H	-2.929896	2.233053	0.860485
C	-5.564385	1.793023	0.684515
C	-4.913311	-0.528450	1.078329
C	-3.886381	-1.487003	1.275020
H	-4.178874	-2.524328	1.387999
C	4.413925	-2.946939	2.462324
H	2.804447	-4.362812	2.441687
H	5.177793	-3.702655	2.618224
C	4.784867	-1.587741	2.360401
C	3.823696	-0.624132	2.170690
H	5.831579	-1.305806	2.416183
H	4.103168	0.422391	2.073921
C	-6.883245	1.415436	0.603399
H	-5.280596	2.835811	0.565254
H	-7.651876	2.159482	0.419840
C	-7.243812	0.058436	0.762830
C	-6.279296	-0.891660	0.998377
H	-8.288188	-0.231187	0.699336
H	-6.550448	-1.937871	1.115968
C	1.885578	-3.488907	-1.094503
H	1.213453	2.990784	-2.155079
H	1.030879	-3.993605	-0.638855
H	2.157598	-4.006313	-2.024472
H	2.713823	-3.544953	-0.385542
H	-1.030708	-3.993907	0.639073
H	-2.157793	-4.006595	2.024387
H	-2.713554	-3.545231	0.385297
N	0.977725	6.425394	-1.803213
N	-0.978261	6.425007	1.804149

Optimized geometry of **1'**$^{\cdot+}$ (M06-2X/6-31G*)

N	0.691058	0.583559	-1.233290	H	6.266287	-2.247726	-1.149533
C	2.040531	0.186977	-1.247405	H	8.099874	-0.623340	-0.815444
C	-0.332217	-0.311565	-1.570537	C	6.785651	1.101138	-0.764097
C	-0.036721	-1.719161	-1.604448	H	5.274748	2.617044	-0.766894
C	2.322782	-1.220462	-1.316960	H	7.598274	1.805228	-0.617648
N	1.261031	-2.127345	-1.350015	C	-5.047470	-1.234098	-2.231270
C	-1.609654	0.131111	-1.808927	H	-4.228891	0.740111	-2.118262
C	3.637906	-1.648257	-1.289268	H	-6.071984	-0.886931	-2.317089
C	4.709554	-0.742793	-1.145540	C	-4.777744	-2.626848	-2.226654
H	3.879453	-2.700222	-1.376550	H	-3.275885	-4.149673	-2.139215
C	6.056648	-1.184680	-1.065230	H	-5.597879	-3.331070	-2.322045
C	4.424362	0.645091	-1.038377	C	-1.577638	-3.546331	1.252347
C	3.077369	1.076223	-1.105764	C	0.322218	1.815548	-0.630437
C	5.493008	1.555500	-0.846198	C	-0.322215	1.815590	0.630524
H	2.881454	2.138178	-1.015668	C	0.596164	3.022532	-1.259896
C	-2.685868	-0.769431	-1.980812	C	-0.596049	3.022608	1.259967
H	-1.817606	1.196876	-1.803880	N	-0.691082	0.583638	1.233421
C	-2.408515	-2.167202	-1.986816	H	-1.043644	3.019302	2.248913
C	-4.023594	-0.326890	-2.122207	C	-0.294958	4.237238	0.636092
C	-1.077071	-2.606853	-1.844078	C	0.295159	4.237200	-0.636052
C	-3.489869	-3.083668	-2.119397	C	-0.595040	5.470835	1.309084
H	-0.890399	-3.670368	-1.933833	C	0.595343	5.470759	-1.309069
C	7.071598	-0.282364	-0.876628	C	0.332182	-0.311505	1.570636

C	-2.040568	0.187095	1.247556
C	-2.322853	-1.220335	1.317134
C	0.036645	-1.719086	1.604615
N	-1.261129	-2.127244	1.350224
C	-3.077385	1.076354	1.105819
C	1.609646	0.131155	1.808928
C	2.685843	-0.769399	1.980822
H	1.817620	1.196914	1.803840
C	2.408452	-2.167159	1.986896
C	1.076990	-2.606786	1.844230
C	3.489784	-3.083647	2.119493
H	0.890307	-3.670292	1.934042
C	-4.424375	0.645243	1.038281
H	-2.881447	2.138302	1.015703
C	-5.492982	1.555659	0.845911
C	-4.709599	-0.742634	1.145428
C	-3.637983	-1.648106	1.289320
H	-3.879561	-2.700063	1.376592
C	4.777671	-2.626856	2.226714
H	3.275771	-4.149646	2.139340
H	5.597788	-3.331096	2.322121
C	5.047433	-1.234112	2.231290
C	4.023582	-0.326884	2.122189
H	6.071955	-0.886967	2.317104
H	4.228907	0.740112	2.118190
C	-6.785615	1.101308	0.763598
H	-5.274697	2.617199	0.766627
H	-7.598209	1.805401	0.617003
C	-7.071593	-0.282192	0.876102
C	-6.056682	-1.184512	1.064895
H	-8.099861	-0.623161	0.814738
H	-6.266341	-2.247557	1.149166
C	1.577491	-3.546441	-1.252125
H	1.043780	3.019169	-2.248832
H	0.698201	-4.095334	-0.925441
H	1.920146	-3.944560	-2.213694
H	2.353752	-3.682207	-0.497980
H	-0.698390	-4.095261	0.925616
H	-1.920273	-3.944437	2.213928
H	-2.353934	-3.682067	0.498231
N	0.847010	6.450754	-1.868421
N	-0.846630	6.450855	1.868427

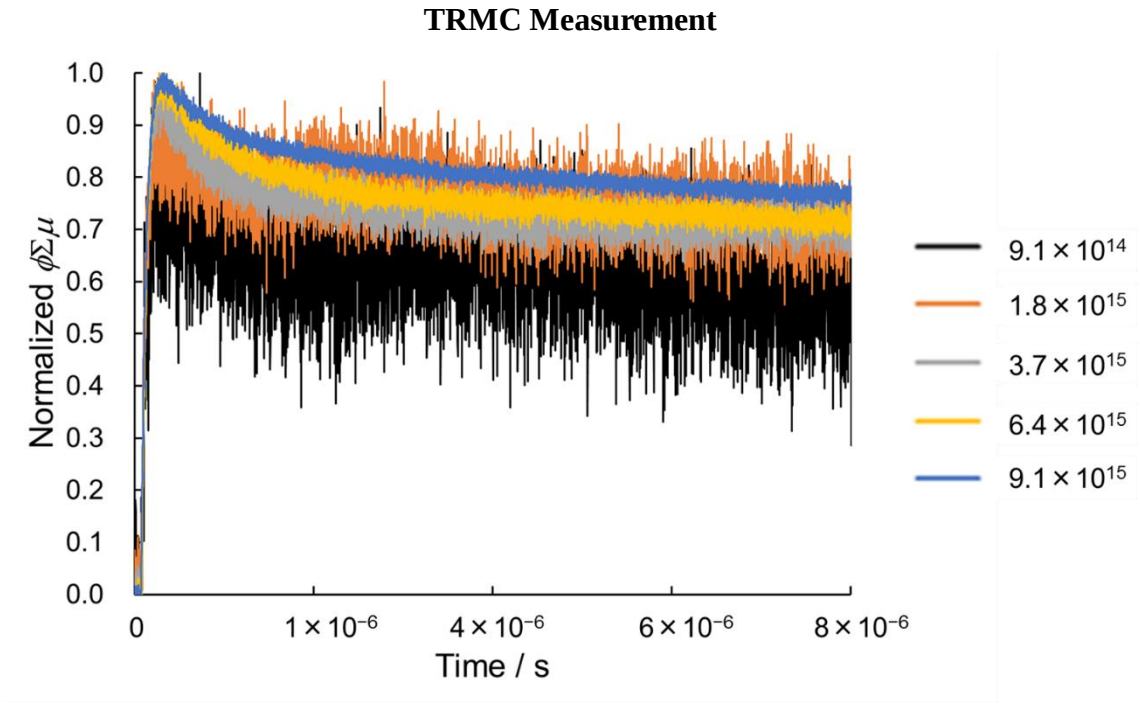

Figure S10. $\phi\Sigma\mu$ transients of $\mathbf{1}^{\cdot+}\cdot[SbF_6]^-$ irradiated with different laser intensities.