Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Systematic Radical Species Control by Electron Push–Pull Substitution in the Perylene-based D–π–A Compounds

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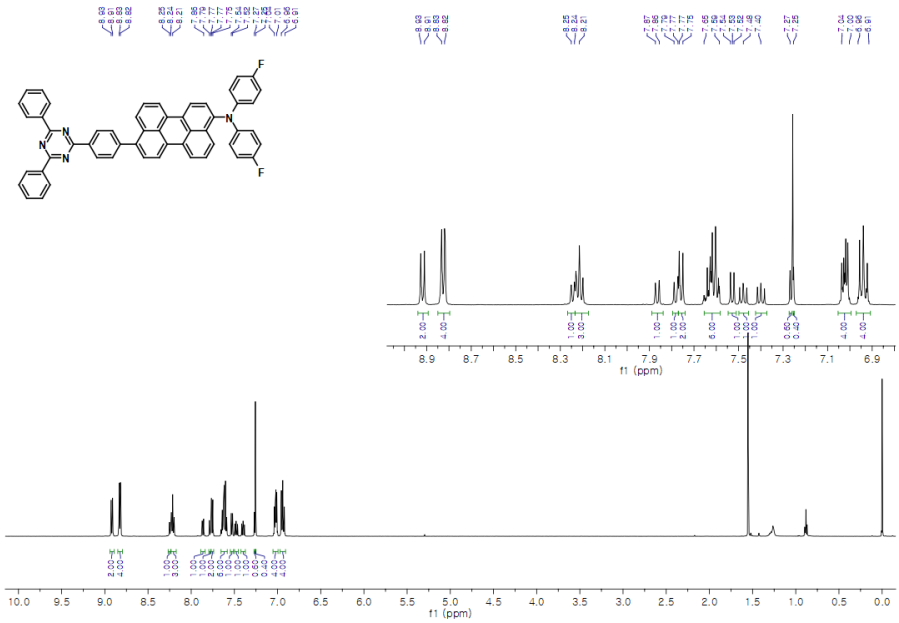


Figure S1. ^{1}H-NMR spectrum of **3a** in $CDCl_3$ (500MHz, 293K)

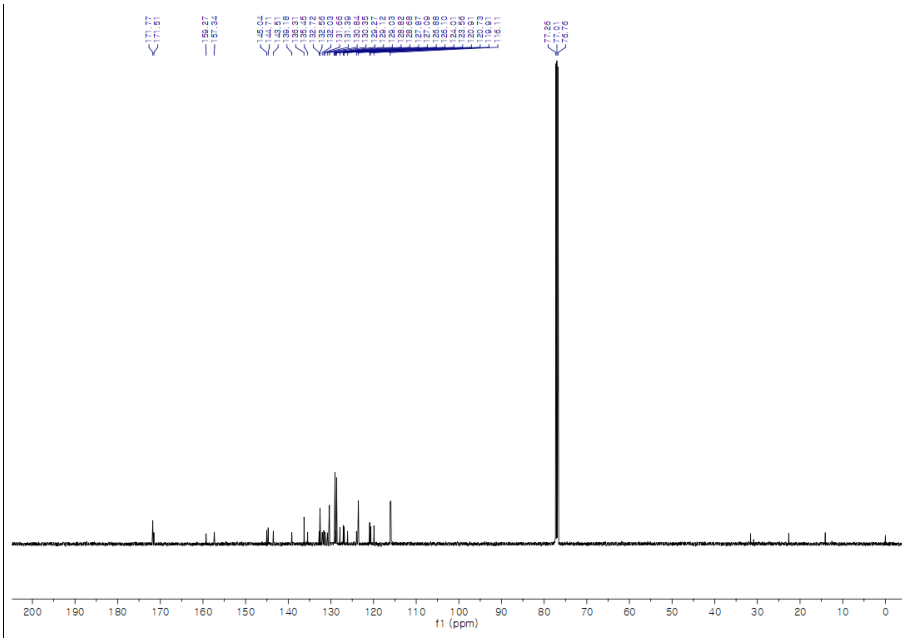


Figure S2. $^{13}C\{^{1}H\}$-NMR spectrum of **3a** in $CDCl_3$ (125MHz, 293K)

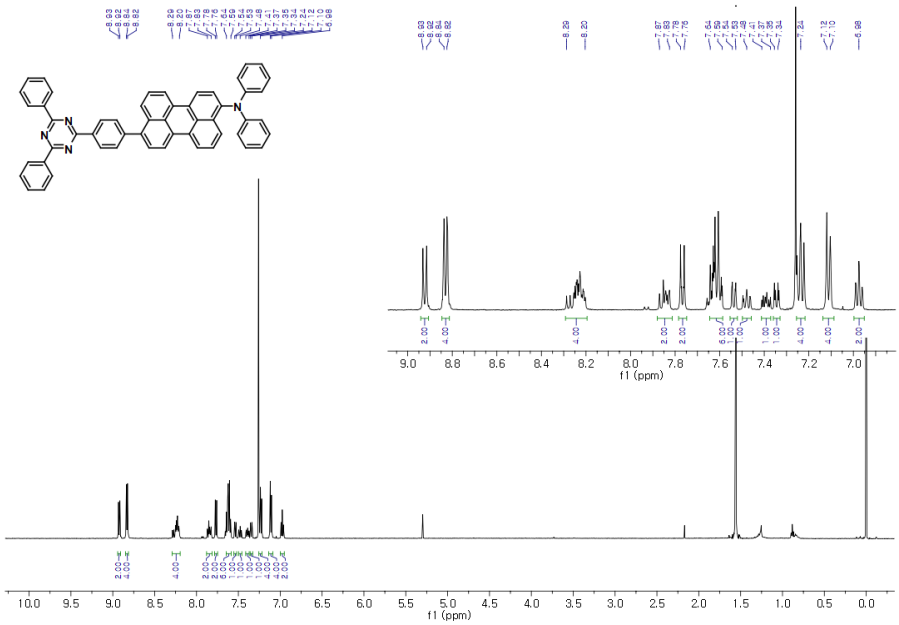


Figure S3. ^{1}H-NMR spectrum of **3b** in $CDCl_3$ (500MHz, 293K)

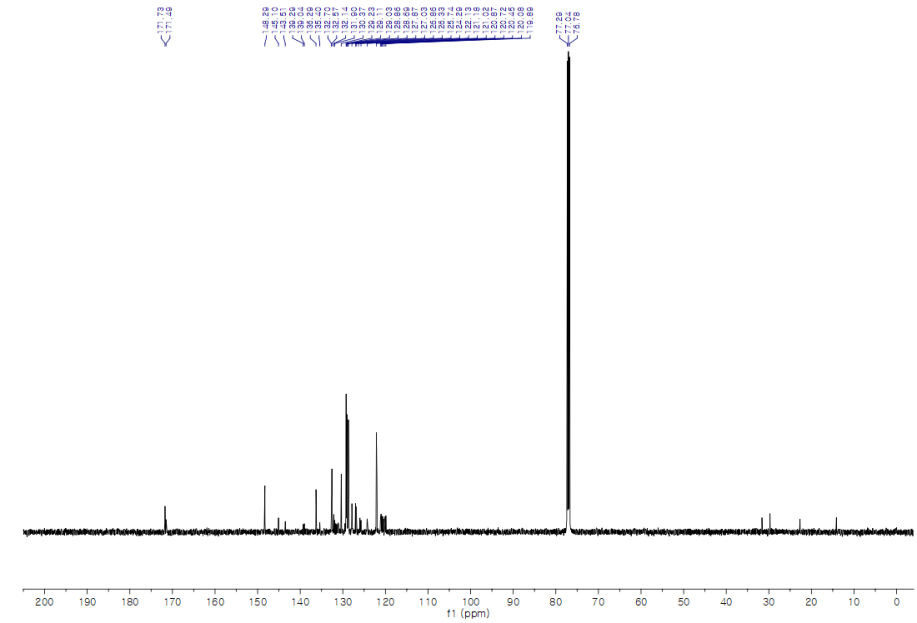


Figure S4. $^{13}C\{^{1}H\}$-NMR spectrum of **3b** in $CDCl_3$ (125MHz, 293K)

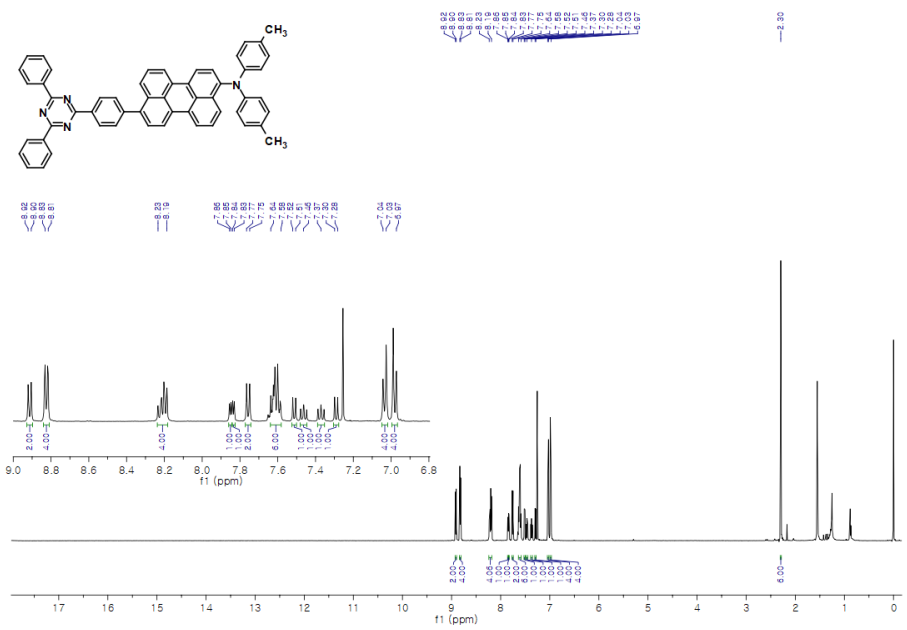


Figure S5. ^{1}H-NMR spectrum of **3c** in $CDCl_3$ (500MHz, 293K)

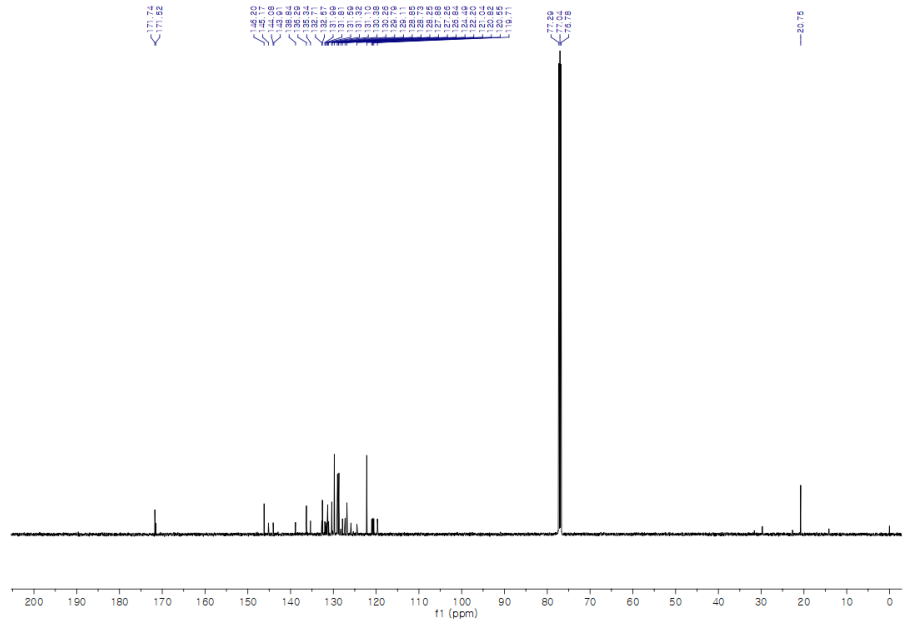


Figure S6. $^{13}C\{^{1}H\}$-NMR spectrum of **3c** in $CDCl_3$ (125MHz, 293K)

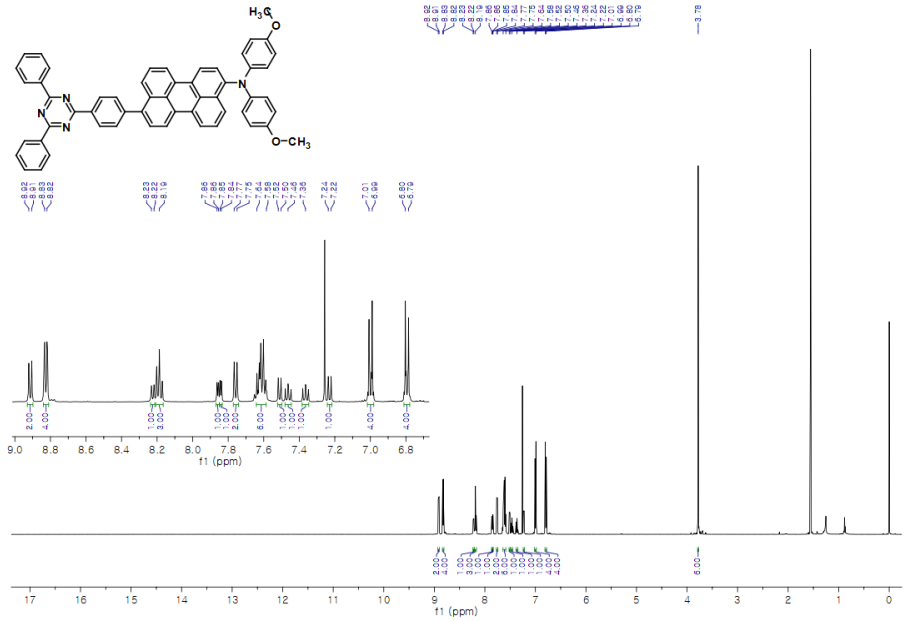


Figure S7. ^{1}H-NMR spectrum of **3d** in $CDCl_3$ (500MHz, 293K)

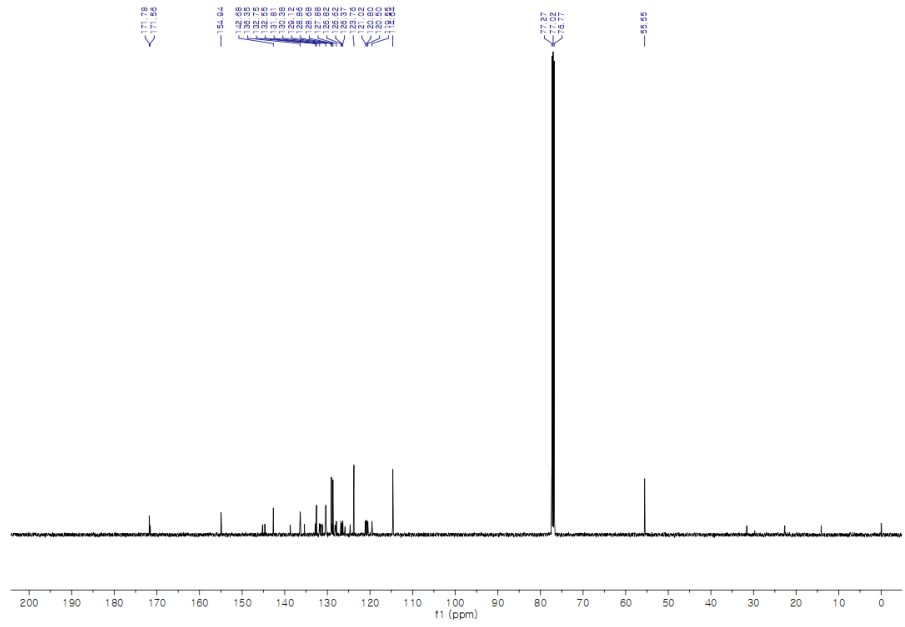
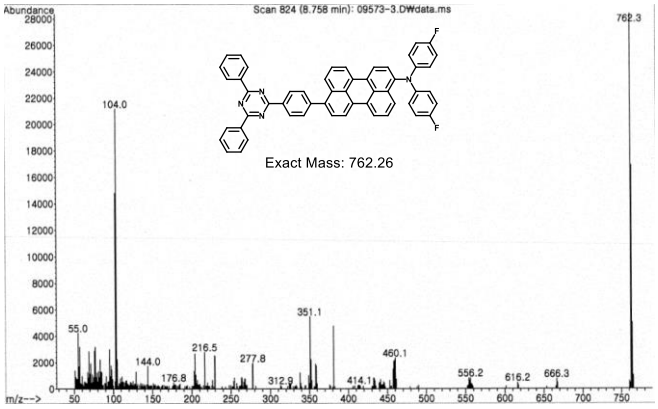


Figure S8. $^{13}C\{^{1}H\}$-NMR spectrum of **3d** in $CDCl_3$ (125MHz, 293K)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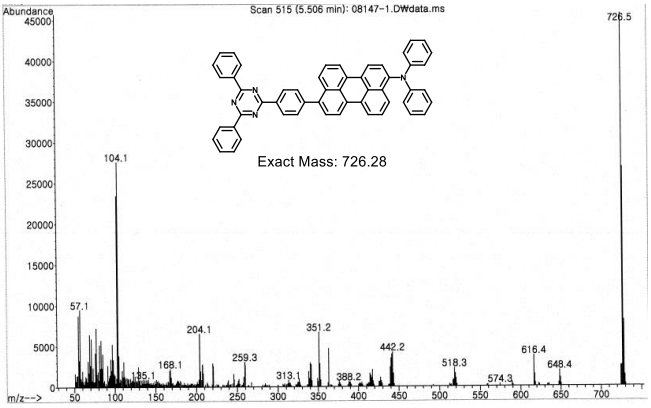
312.9
414.1
556.2
616.2
666.3
m/z-->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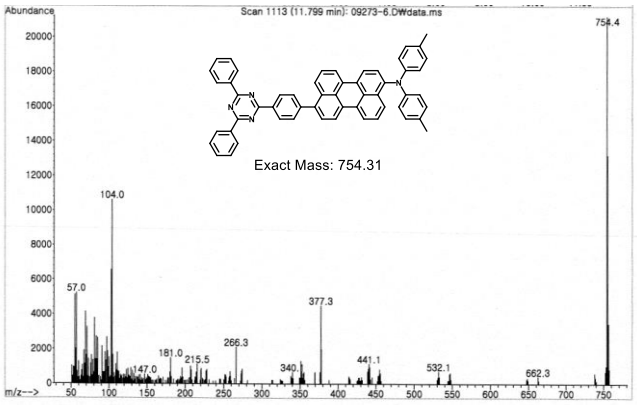
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m/z-->

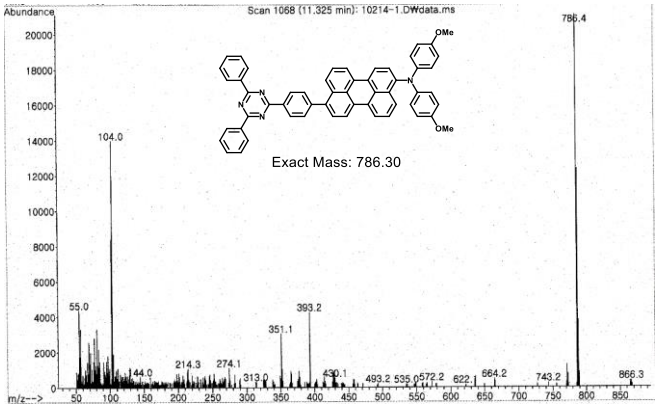

Figure S9. GC-MS data of **3a–3d**

(A)

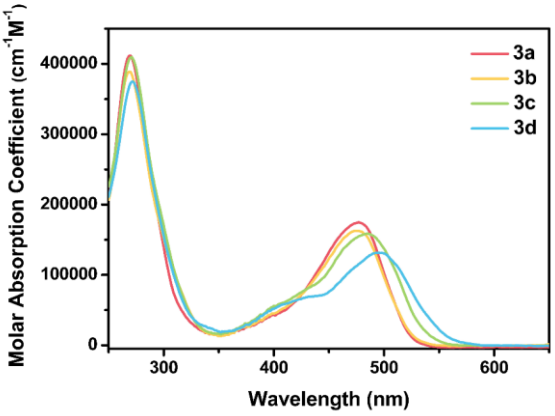

Figure S10(A). UV-vis absorption spectra of **3a–3d** in DCM solution at 1 μM.

(B)

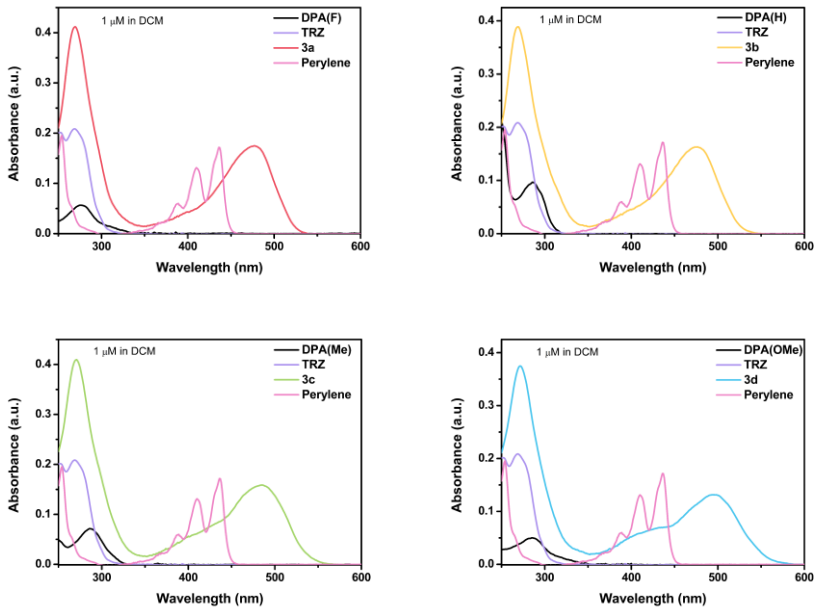

Figure S10(B). UV-vis absorption spectra in DCM solution of *N,N*-bis(4′-(*R*)-phenyl)amino (R: F, H, Me, OMe) (DPA(R)), Triazine (TRZ), **3a–3d**, and Perylene.

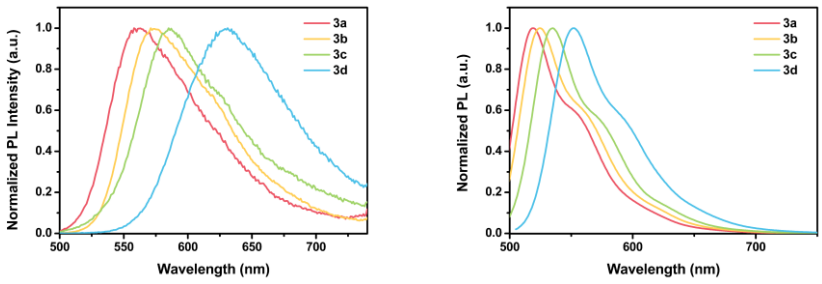

Figure S11. (Left): Emission spectra of **3a–3d** in film state. (Right): Emission spectra of **3a–3d** in *n*-Hexane solution.

Table S1. Spectroscopic parameters of **3a–3d** in various solvents

compounds	Solvents	λ_{max} abs (nm)	λ_{max} em (nm)	Stokes shift (cm^{-1})
3a	*n*-Hexane	477	519	1696
	Cyclohexane	478	521	1727
	Toluene	481	536	2133
	THF	478	556	2935
	DCM	477	559	3075
	ACN	472	581	3975
3b	*n*-Hexane	477	524	1880
	Cyclohexane	477	527	1989
	Toluene	481	542	2340
	THF	475	564	3322
	DCM	474	570	3553
	ACN	470	588	4270
3c	*n*-Hexane	487	535	1842
	Cyclohexane	490	538	1821
	Toluene	490	554	2358
	THF	486	579	3305
	DCM	485	590	3669
	ACN	475	622	4975
3d	*n*-Hexane	496	552	2045
	Cyclohexane	496	555	2143
	Toluene	499	585	2946
	THF	495	628	4278
	DCM	494	632	4420
	ACN	489	675	5635

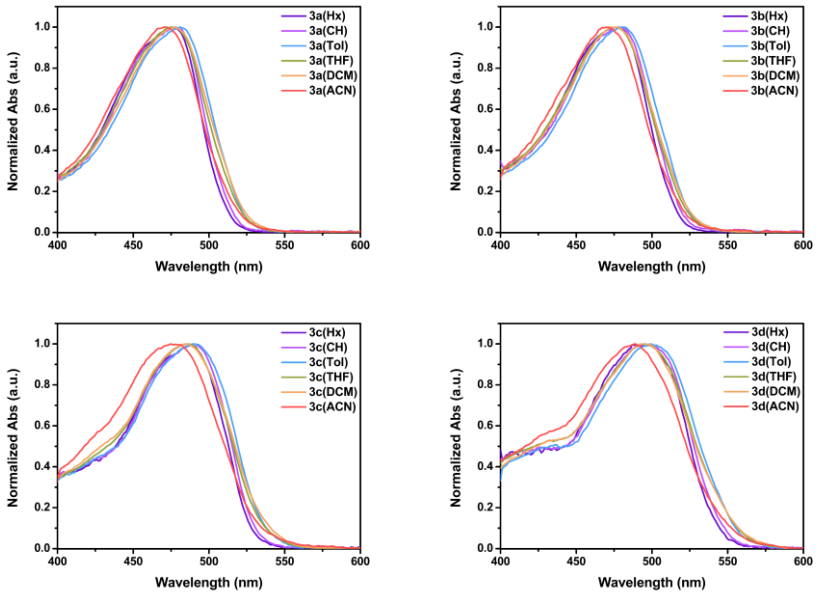

Figure S12. UV-vis absorption spectra of **3a–3d** in *n*-Hexane, Cyclohexane, Toluene, THF, DCM, and ACN at room temperature

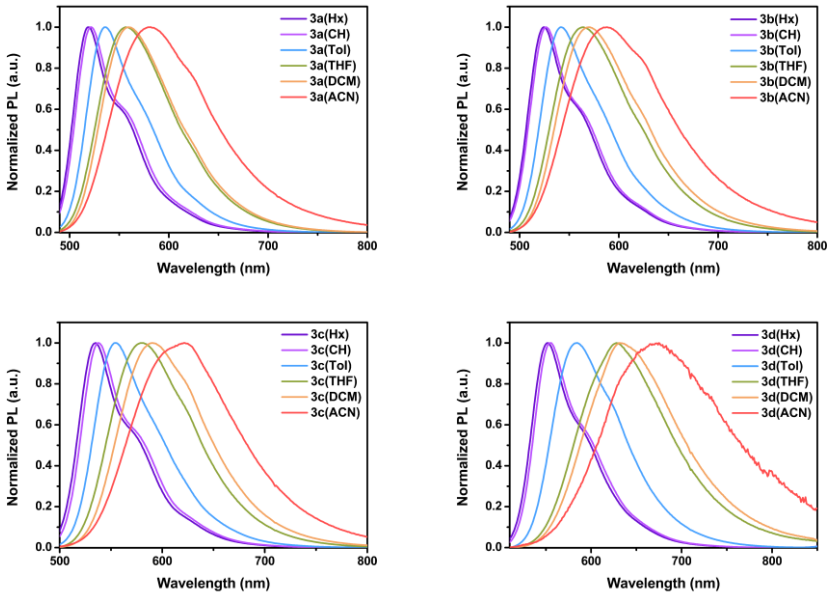

Figure S13. Emission spectra of **3a**–**3d** in *n*-Hexane, Cyclohexane, Toluene, THF, DCM, and ACN at room temperature

Stokes shifts ($\Delta\nu$) of compounds **3a–3d** were plotted as a function of solvent polarity parameters (Δf), according to the Lippert−Mataga method using Eq. (1):

$$\Delta\nu = \overline{\nu_a} - \overline{\nu_f} = \frac{2}{hca_0^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} + \frac{n^2 - 1}{2n^2 + 1}\right) \times \left(\mu_e - \mu_g\right)^2 + constant$$

$$= 2\Delta f \times \frac{\Delta\mu^2}{hca_0^3} + constant \qquad (1)$$

where, $\mu_e - \mu_g$ ($\Delta\mu$) is the difference between the dipole moments in the excited and ground states, c is the speed of light, h is Planck's constant, and a_0 is the radius of the Onsager cavity around the fluorophore. The dielectric constants (ε) (1.9 *n*-Hexane, 2.02 Cyclohexane, 2.38 Toluene, 7.6 THF, 9.1 DCM, and 37.5 ACN) and the refractive indices (n) of solvents are included in the term Δf, which is known as orientation polarizability. The Onsager radius was determined by DFT calculations (B3LYP method, 6-31G(d, p) basis) and was considered to be half of the average size of 24.5, 24.5, 25.3, and 25.4 Å for **3a–3d**, respectively. The ground-state dipole moment values (μ_g) for energy minimized structures obtained by the DFT method are above zero due to the asymmetry of these compounds. Using the values of the ground state dipole moment (μ_g) and dipole moment change ($\Delta\mu$), the excited state dipole moments (μ_e) are calculated to be 36.7, 36.8, 44.0, and 47.1 D for **3a–3d**. These values confirm that the excited state of **3a–3d** has a relatively larger dipole moment than the ground state, consistent with the observed solvatochromic behavior.

Table S2. Dipole moment values of **3a–3d** in the ground and excited states

Compounds	$\Delta\mu$	μ_g	μ_e
3a	35.1 D	1.5682 D	36.7 D
3b	36.6 D	0.1689 D	36.8 D
3c	43.1 D	0.8943 D	44.0 D
3d	46.8 D	0.3368 D	47.1 D

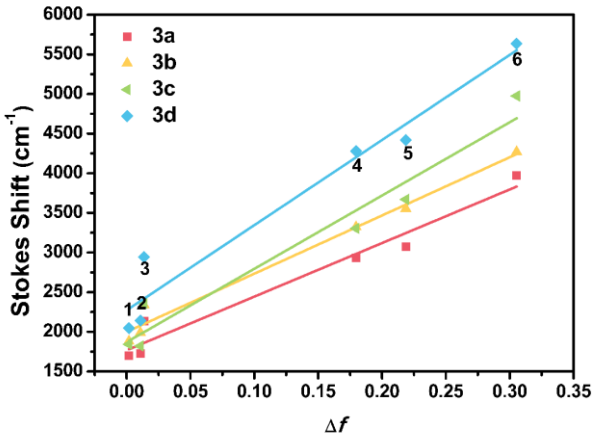

Figure S14. Comparison of Lippert−Mataga plots for **3a–3d** in different solvents: 1, *n*-Hexane; 2, Cyclohexane; 3, Toluene; 4, THF; 5, DCM; 6, ACN.

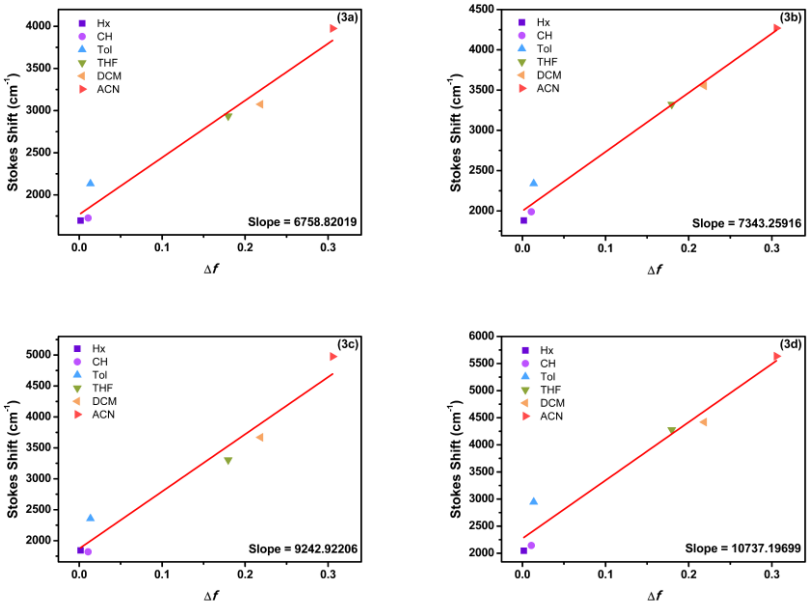

Figure S15. Lippert-Mataga plots for compounds **3a–3d**.

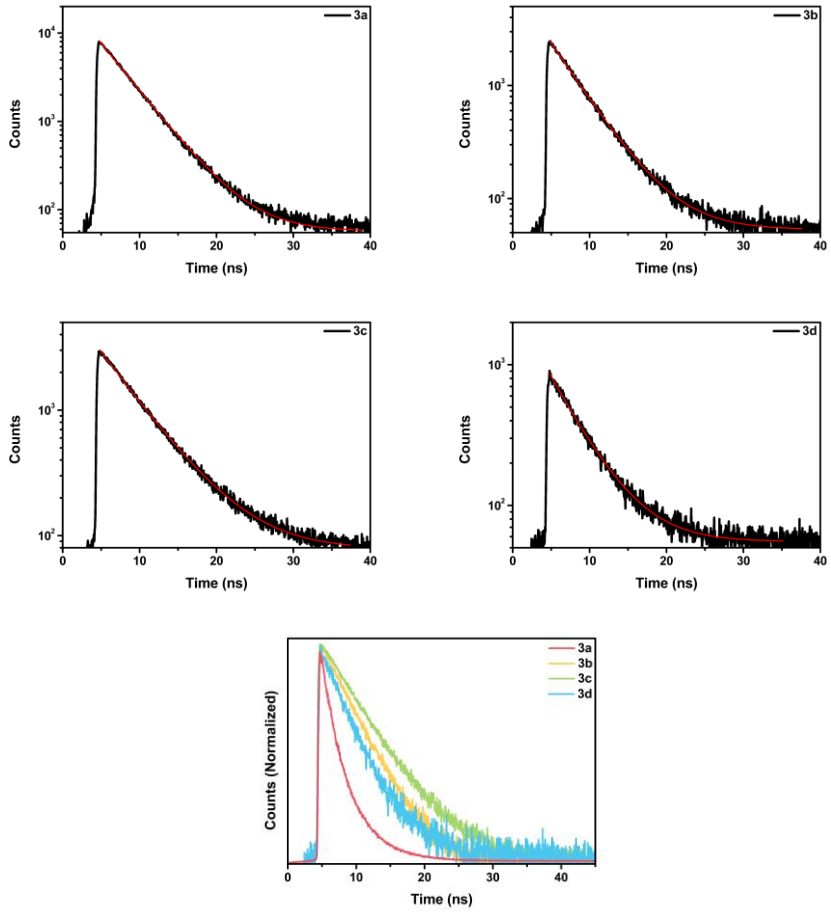

Figure S16. Fluorescence lifetimes (τ_F) of **3a–3d** in DCM solution at RT.

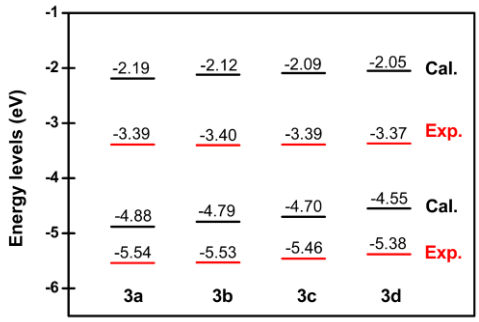

Figure S17. The experimental (red line) and calculated (black line) energy levels of HOMO–LUMO for **3a–3d**.

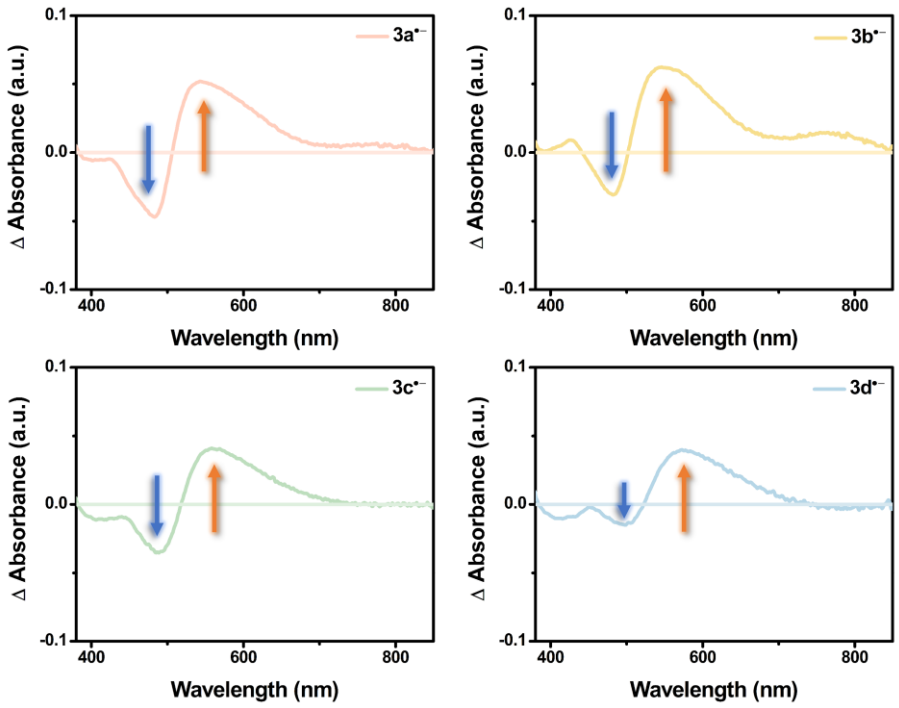

Figure S18. UV-vis absorption spectral change of **3a**$^{\bullet-}$**–3d**$^{\bullet-}$ formed during the electrochemical reduction from neutral to radical anion (0.1 mM / 0.1 M TBAP/ DCM).

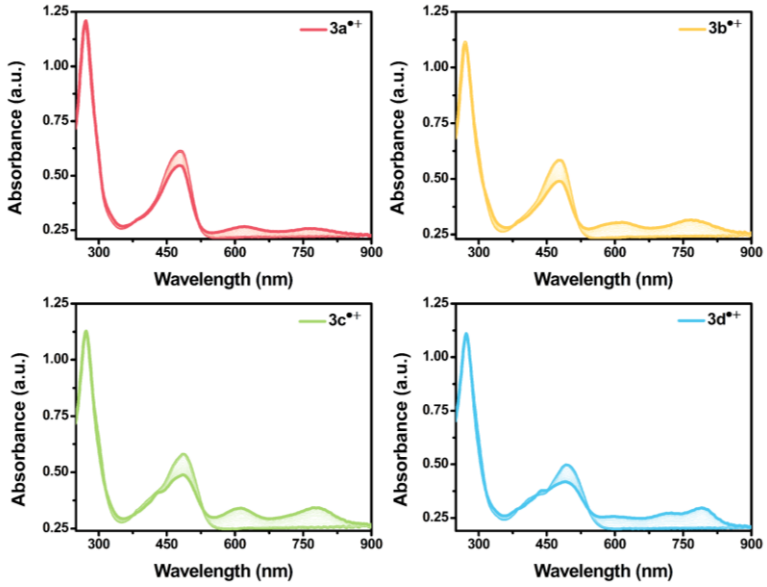

Figure S19. UV-vis absorption spectra of **3a**$^{\bullet+}$–**3d**$^{\bullet+}$ formed during the electrochemical oxidation from neutral to radical cation (0.1 mM / 0.1 M TBAP/ DCM).

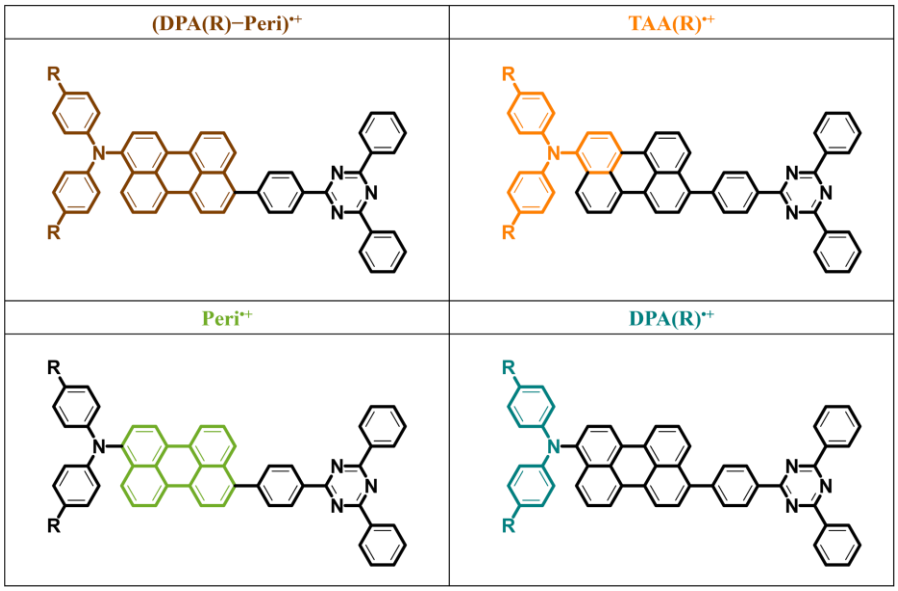

Figure S20. Schematic diagram of radical cation species.

DFT/TD-DFT Calculation Details

All the calculations were performed on the platform of the Gaussian 16 package.[1] The ground-state geometry of **3a–3d, 3a$^{\bullet-}$–3d$^{\bullet-}$** and **3a$^{\bullet+}$–3d$^{\bullet+}$** has been optimized at the density function theory (DFT) level. Full geometry optimizations in their ground singlet and doublet state were performed using B3LYP [2] / 6-31G [3](d,p) (for **3a**–**3d**) and ωB97XD [4]/ 6-31+G [3] (d) (for **3a$^{\bullet-}$**–**3d$^{\bullet-}$** and **3a$^{\bullet+}$**–**3d$^{\bullet+}$**) level theory for all atoms. The nature of the stationary points located was further checked by computations of harmonic vibrational frequencies at the same level of theory. The ground state energies obtained by DFT calculation (imaginary frequencies, total energies, and dipole moment) show in Table S3, S12 and S21. As well as, all of the Cartesian coordinates for optimized structure of **3a**–**3d** (Table S4, S6, S8 and S10), **3a$^{\bullet-}$–3d$^{\bullet-}$** (Table S13, S15, S17 and S19) and **3a$^{\bullet+}$–3d$^{\bullet+}$** (Table S22, S24, S26 and S28) are also summarized. The Isodensity plots (isodensity contour = 0.035 a.u.) of the selected frontier orbitals were visualized by Chem3D Ultra and GaussView 5.0 program (Figure S22-S33). The excitation energies and oscillator strengths for singlet–singlet and doublet–doublet electronic transitions at the optimized geometry in the ground state were obtained in TD-DFT calculations using the same basis set and functional as for the ground state. The simulated absorption spectra were obtained by the GaussSum program based on TD-DFT results. All of the Transition assignment for optimized structure of **3a**–**3d** (Table S5, S7, S9 and S11), **3a$^{\bullet-}$–3d$^{\bullet-}$** (Table S14, S16, S18 and S20) and **3a$^{\bullet+}$–3d$^{\bullet+}$** (Table S23, S25, S27 and S29) are also summarized.

Table S3. The number of imaginary frequencies, total energies, and dipole moments for the compound **3a−3d** as obtained in the geometry optimizations at B3LYP/6-31G(d,p) method

Entry	Number of imaginary frequencies	Total energies (Eh) (Hartrees)	Ground state dipole moment (field-independent basis, Debye)
3a	0	-2457.735353	1.568117
3b	0	-2259.274010	0.168921
3c	0	-2337.914648	0.894326
3d	0	-2488.321718	0.336753

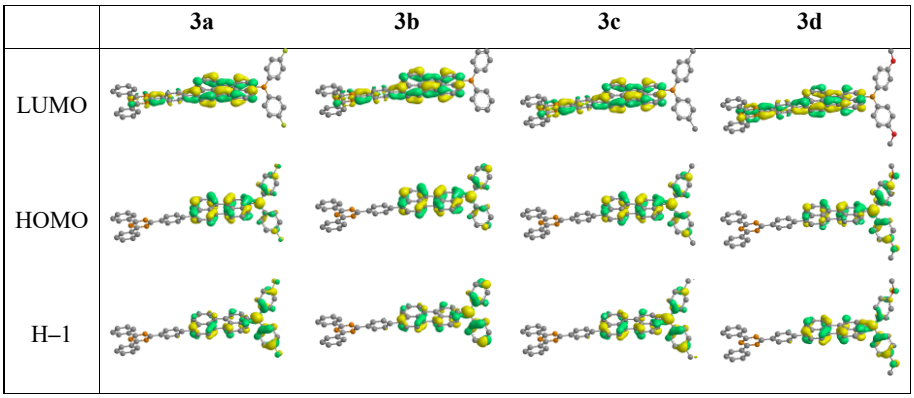

Figure S21. Frontier orbital distributions (HOMO–1, HOMO, LUMO) of **3a–3d** calculated by DFT using B3LYP function and 6-31G-(d, p) basis.

Table S4. Cartesian coordinates for optimized structure for **3a**

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.55196	0.85592	-1.73554	C	9.811938	-2.17344	0.238054
C	-5.92493	0.796475	-1.46475	C	11.20787	-2.04949	0.159654
C	-6.40673	0.117459	-0.36072	C	12.02037	-3.1747	0.270794
C	-5.48448	-0.54216	0.515147	C	11.45058	-4.43572	0.461231
C	-5.93181	-1.31319	1.61696	C	10.06213	-4.56655	0.540197
C	-5.02458	-1.93366	2.445268	C	9.246323	-3.4437	0.429585
C	-3.64534	-1.79719	2.222895	C	10.71566	2.747605	-0.45628
C	-3.14705	-1.0583	1.154536	C	11.28397	4.00419	-0.64764
C	-1.69851	-0.89802	0.925988	C	10.46942	5.133838	-0.75496
C	-0.75415	-1.39405	1.817432	C	9.081537	5.000841	-0.66999
C	0.621278	-1.24688	1.596923	C	8.509488	3.745927	-0.47886
C	1.11549	-0.6017	0.475338	F	-9.8869	2.478025	4.446396
C	0.181167	-0.09892	-0.4914	F	-11.091	-1.55001	-4.30257
C	0.614818	0.48291	-1.7114	H	-4.23752	1.41349	-2.60947
C	-0.2967	0.956643	-2.62727	H	-6.62522	1.293327	-2.12832
C	-1.67319	0.885919	-2.36526	H	-6.99507	-1.41556	1.793161
C	-2.16344	0.317256	-1.19412	H	-5.37277	-2.5339	3.280476
C	-1.23176	-0.22288	-0.24727	H	-2.9677	-2.29784	2.903893
C	-3.60835	0.256894	-0.90672	H	-1.06745	-1.89288	2.726606
C	-4.07454	-0.43897	0.254514	H	1.317168	-1.62123	2.341572
N	-7.81174	0.062251	-0.11199	H	1.674925	0.532276	-1.92709
C	2.587522	-0.44777	0.331414	H	0.046775	1.386268	-3.56359
C	-8.34822	0.697062	1.041127	H	-2.35565	1.271985	-3.11287
C	-8.66669	-0.33741	-1.17814	H	-10.0283	-0.64828	1.201997
C	-9.52505	0.208506	1.636651	H	-10.9588	0.443636	3.23913
C	-10.0509	0.812914	2.774898	H	-7.71839	3.243131	3.23656
C	-9.38373	1.897205	3.334659	H	-6.79666	2.187902	1.175514
C	-8.21306	2.394002	2.777731	H	-10.0419	1.313292	-0.98247
C	-7.70314	1.798456	1.624905	H	-11.5075	0.565312	-2.85582
C	-9.80253	0.408926	-1.53065	H	-8.9485	-2.80118	-3.53518
C	-10.6272	-0.00314	-2.5761	H	-7.49222	-2.0841	-1.63803
C	-10.2983	-1.15294	-3.2831	H	2.55845	1.694773	0.076879
C	-9.17284	-1.9055	-2.96635	H	5.019981	1.919369	-0.06932
C	-8.3658	-1.5	-1.90699	H	5.452253	-2.30908	0.449901
C	3.18595	0.81158	0.142651	H	2.987677	-2.54974	0.583221
C	4.567315	0.94433	0.066636	H	11.63746	-1.06588	0.011803
C	5.400332	-0.18004	0.175586	H	13.09944	-3.06895	0.208935
C	4.811887	-1.43878	0.368664	H	12.08576	-5.31264	0.547709
C	3.429883	-1.56744	0.447096	H	9.615407	-5.5453	0.688114
C	6.872799	-0.03985	0.090432	H	8.168083	-3.53185	0.489118
N	7.376642	1.190076	-0.09551	H	11.33645	1.863675	-0.37141
C	8.714469	1.268647	-0.16619	H	12.36342	4.103555	-0.71323
N	9.537678	0.213706	-0.06455	H	10.91426	6.113527	-0.9041
C	8.944629	-0.97598	0.119797	H	8.44494	5.876789	-0.75278
N	7.616826	-1.15103	0.204017	H	7.434414	3.62949	-0.41121
C	9.321824	2.606439	-0.37006				

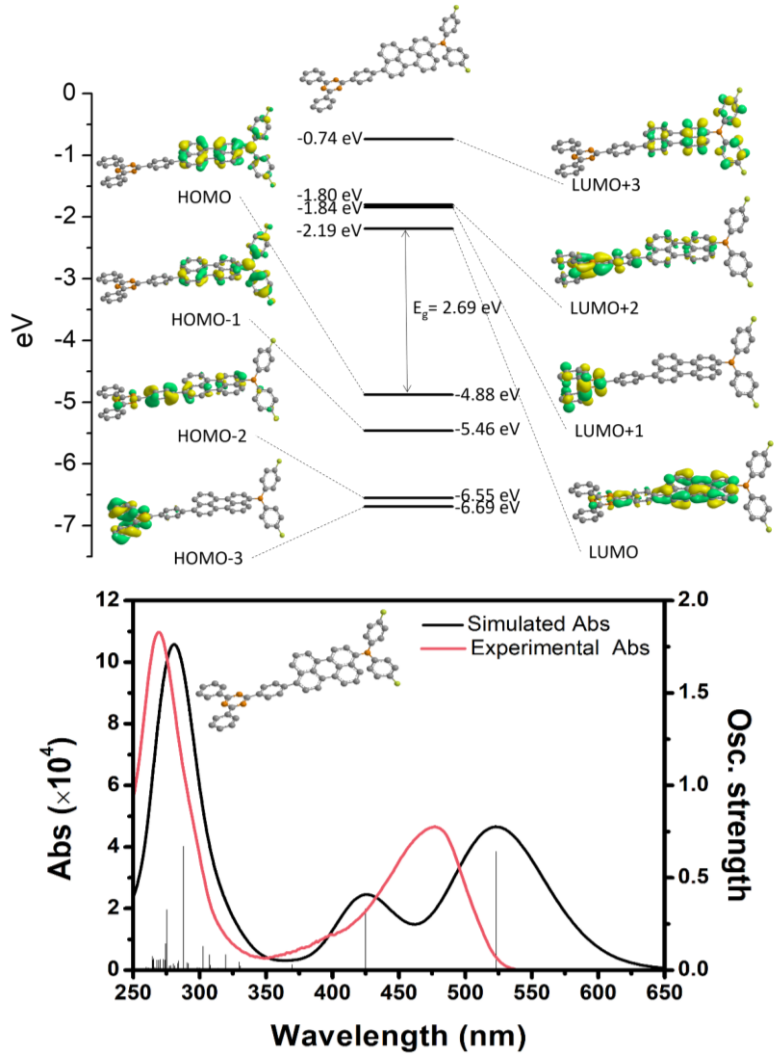

Figure S22. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3a** (Down): Electronic transition of the simulated/experimental absorption spectra of **3a**

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Table S5. TD-DFT calculation: Transition assignment of **3a**

No	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	19110.50064	523.27	0.6411	HOMO->LUMO (95%)
2	22227.02695	449.90	0.0067	H-1->LUMO (19%), HOMO->L+2 (76%)
3	22563.36015	443.19	0.0007	HOMO->L+1 (96%)
4	23536.87134	424.86	0.3321	H-1->LUMO (74%), HOMO->L+2 (20%)
5	27059.90109	369.55	0.0307	H-1->L+2 (92%)
6	27391.39496	365.07	0.0002	H-1->L+1 (96%)
7	28172.94620	354.95	0.0048	HOMO->L+3 (81%)
8	30250.63041	330.57	0.0227	H-4->LUMO (12%), HOMO->L+4 (42%), HOMO->L+5 (24%)
9	30326.44653	329.74	0.0439	HOMO->L+4 (29%), HOMO->L+5 (37%)
10	31285.43974	319.63	0.085	H-2->LUMO (66%)
11	31853.25406	313.93	0.01	H-7->LUMO (11%), H-6->LUMO (16%), HOMO->L+12 (10%)
12	32369.44889	308.93	0.0039	H-3->LUMO (30%), H-3->L+2 (15%), H-2->L+1 (17%)
13	32438.81258	308.27	0.0261	H-7->LUMO (19%), H-3->LUMO (14%)
14	32527.53356	307.43	0.0829	H-4->LUMO (13%), HOMO->L+4 (11%), HOMO->L+6 (28%), HOMO->L+8 (10%)
15	32558.18263	307.14	0.0121	H-14->LUMO (32%), H-14->L+2 (41%), H-13->L+1 (13%)
16	32925.16490	303.71	0.0041	H-13->LUMO (41%), H-13->L+2 (56%)
17	33054.21360	302.53	0.1292	HOMO->L+7 (66%)
18	33170.35744	301.47	0.0001	H-13->L+1 (83%)
19	33337.31421	299.96	0.0121	H-1->L+3 (31%), HOMO->L+6 (14%), HOMO->L+9 (16%)
20	33430.87452	299.12	0.0025	H-14->L+1 (92%)

Table S6. Cartesian coordinates for optimized structure for **3b**

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.99082	1.212403	-1.54909	C	9.357506	-2.203	-0.1341
C	-6.36438	1.109312	-1.29523	C	10.28892	2.757562	0.068044
C	-6.85003	0.243047	-0.33325	C	10.86434	4.024893	0.105368
C	-5.93132	-0.56765	0.408938	C	10.05567	5.160525	0.191966
C	-6.38349	-1.52313	1.353002	C	8.666534	5.022704	0.241159
C	-5.47998	-2.2878	2.055099	C	8.087402	3.757059	0.204095
C	-4.09984	-2.12044	1.860668	C	10.75427	-2.07503	-0.18679
C	-3.59704	-1.20268	0.943924	C	11.56055	-3.20672	-0.2754
C	-2.14752	-1.01127	0.747764	C	10.98364	-4.47829	-0.31246
C	-1.20622	-1.66823	1.53201	C	9.594321	-4.61316	-0.26042
C	0.169985	-1.49006	1.341974	C	8.784727	-3.48387	-0.17178
C	0.668488	-0.65152	0.358657	H	-4.67305	1.91879	-2.30648
C	-0.26251	0.025664	-0.49874	H	-7.06284	1.720257	-1.85772
C	0.174942	0.820226	-1.59066	H	-7.44742	-1.64904	1.508784
C	-0.73365	1.459078	-2.40331	H	-5.83184	-3.02716	2.768315
C	-2.11069	1.347725	-2.1591	H	-3.4252	-2.7395	2.439751
C	-2.60486	0.57516	-1.113	H	-1.52273	-2.32471	2.333515
C	-1.67637	-0.13419	-0.28147	H	0.863375	-1.99892	2.004725
C	-4.05045	0.468725	-0.84265	H	1.235426	0.903153	-1.79387
C	-4.52071	-0.4254	0.171692	H	-0.3873	2.052454	-3.24432
N	-8.25581	0.150195	-0.10161	H	-2.79073	1.868171	-2.8227
C	2.141411	-0.48158	0.246193	H	-10.5318	1.455911	-0.72701
C	-8.79172	0.563077	1.147585	H	-11.9757	1.01699	-2.68173
C	-9.10508	-0.08496	-1.21928	H	-11.3731	-0.76042	-4.31763
C	-10.2682	0.672979	-1.4296	H	-9.30254	-2.09825	-3.95947
C	-11.0797	0.420629	-2.53457	H	-7.87416	-1.67824	-1.98527
C	-10.7408	-0.57175	-3.45565	H	-10.4801	-0.77755	1.055088
C	-9.578	-1.31881	-3.25479	H	-11.4001	-0.09007	3.239293
C	-8.76957	-1.08664	-2.14491	H	-10.2308	1.627825	4.614037
C	-9.9724	-0.01973	1.642093	H	-8.13111	2.65344	3.753011
C	-10.4864	0.371366	2.875432	H	-7.22901	1.991263	1.553033
C	-9.83051	1.331818	3.649434	H	2.124273	1.671747	0.38351
C	-8.65305	1.90273	3.166409	H	4.587147	1.905574	0.283984
C	-8.13839	1.532126	1.924743	H	4.996362	-2.34948	0.030563
C	2.747017	0.787797	0.28917	H	2.530364	-2.59645	0.113571
C	4.129202	0.924495	0.240501	H	10.90506	1.868863	0.000968
C	4.956313	-0.2056	0.145938	H	11.94476	4.12796	0.066957
C	4.360784	-1.47524	0.107041	H	10.50604	6.148581	0.221049
C	2.977992	-1.60823	0.158399	H	8.034449	5.90323	0.308604
C	6.429508	-0.06064	0.091006	H	7.011282	3.636719	0.241599
N	6.940498	1.179929	0.128513	H	11.18938	-1.0832	-0.15729
C	8.2789	1.262179	0.077589	H	12.64032	-3.09776	-0.31567
N	9.096602	0.201425	-0.00713	H	11.61397	-5.36024	-0.38165
C	8.496694	-0.99864	-0.03988	H	9.142022	-5.60008	-0.28909
N	7.167812	-1.17841	0.007222	H	7.705871	-3.57502	-0.13079
C	8.893801	2.611511	0.117114				

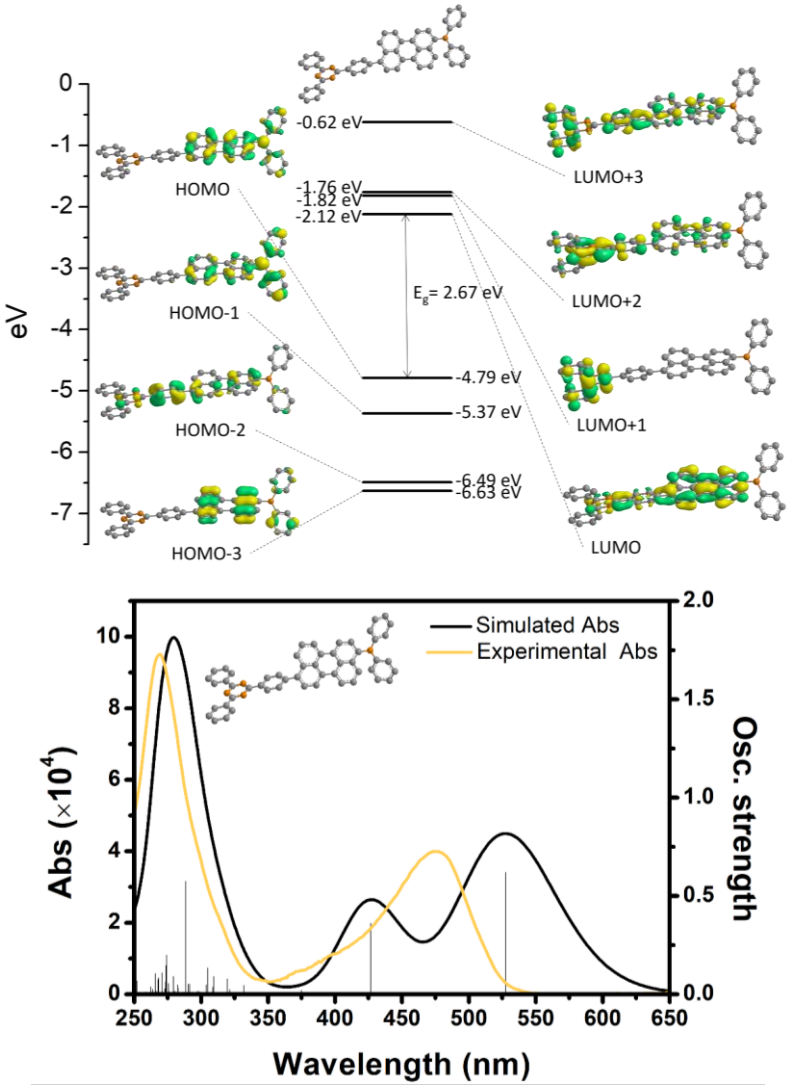


Figure S23. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3b** (Down): Electronic transition of the simulated/experimental absorption spectra of **3b**

Table S7. TD-DFT calculation: Transition assignment of **3b**

No	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	18960.48151	527.41	0.6198	HOMO->LUMO (96%)
2	21911.66417	456.37	0.0014	H-1->LUMO (17%), HOMO->L+2 (76%)
3	22098.78480	452.51	0.0004	HOMO->L+1 (93%)
4	23429.59960	426.81	0.3623	H-1->LUMO (76%), HOMO->L+2 (18%)
5	26672.75496	374.91	0.0202	H-1->L+2 (91%)
6	26896.17054	371.80	0.0003	H-1->L+1 (95%)
7	28415.71908	351.91	0.0031	H-3->LUMO (11%), HOMO->L+4 (81%)
8	30146.58489	331.71	0.046	HOMO->L+3 (73%), HOMO->L+6 (12%)
9	31107.19121	321.46	0.0229	H-6->LUMO (14%), HOMO->L+5 (25%)
10	31295.11839	319.53	0.0779	H-2->LUMO (58%)
11	32322.66874	309.38	0.0906	H-8->LUMO (13%), H-3->LUMO (21%), H-2->LUMO (21%)
12	32397.67830	308.66	0.036	H-4->LUMO (13%), HOMO->L+5 (11%), HOMO->L+6 (12%)
13	32443.65190	308.22	0.0109	H-4->LUMO (23%), H-4->L+2 (13%), H-2->L+1 (18%)
14	32580.76615	306.92	0.0015	H-15->L+1 (15%), H-14->LUMO (35%), H-14->L+2 (38%)
15	32787.24409	304.99	0.1338	HOMO->L+5 (30%), HOMO->L+6 (11%), HOMO->L+9 (10%)
16	32933.23044	303.64	0.048	HOMO->L+7 (48%), HOMO->L+8 (11%)
17	32973.55816	303.27	0.0012	H-15->LUMO (44%), H-15->L+2 (50%)
18	33176.80988	301.41	0.0001	H-15->L+1 (80%)
19	33404.25823	299.36	0.0026	H-14->L+1 (89%)
20	33500.23820	298.50	0.0147	H-5->LUMO (20%), H-3->LUMO (14%), HOMO->L+6 (22%)

Table S8. Cartesian coordinates for optimized structure for **3c**

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.54488	0.783743	-1.77443	C	11.45964	-4.41295	0.646253
C	-5.91749	0.736694	-1.50092	C	10.07104	-4.54096	0.727043
C	-6.4	0.106724	-0.36806	C	9.255197	-3.42375	0.569367
C	-5.47642	-0.51607	0.533675	C	10.72425	2.72655	-0.56786
C	-5.92349	-1.24064	1.666627	C	11.29243	3.974397	-0.81015
C	-5.01641	-1.82812	2.518818	C	10.47771	5.098469	-0.96442
C	-3.63716	-1.70266	2.289886	C	9.089796	4.968634	-0.87523
C	-3.13913	-1.0087	1.191744	C	8.517894	3.722434	-0.63326
C	-1.69054	-0.85945	0.955881	C	-11.2255	-1.78997	-4.37799
C	-0.74593	-1.31927	1.866458	C	-9.95755	2.723249	4.529201
C	0.629375	-1.18226	1.639298	H	-4.23059	1.304013	-2.67125
C	1.123619	-0.58363	0.492136	H	-6.61834	1.204923	-2.18424
C	0.189296	-0.12031	-0.49418	H	-6.98673	-1.33295	1.848164
C	0.622652	0.410719	-1.73726	H	-5.36479	-2.3932	3.378173
C	-0.28943	0.846917	-2.67108	H	-2.95933	-2.17602	2.990074
C	-1.6658	0.787798	-2.40591	H	-1.05923	-1.77993	2.795551
C	-2.15604	0.267923	-1.21216	H	1.325406	-1.52601	2.398508
C	-1.22374	-0.23336	-0.24445	H	1.682606	0.450416	-1.95574
C	-3.6006	0.220108	-0.9217	H	0.053778	1.237675	-3.62446
C	-4.06668	-0.42591	0.267708	H	-2.34859	1.143288	-3.16822
N	-7.80354	0.06453	-0.1176	H	-10.059	1.256166	-1.00969
C	2.59558	-0.43574	0.342573	H	-11.5087	0.455078	-2.83144
C	-8.33717	0.73491	1.016674	H	-8.89898	-2.89608	-3.44336
C	-8.65975	-0.37685	-1.16627	H	-7.46284	-2.11472	-1.59985
C	-9.80866	0.339482	-1.53258	H	-10.0242	-0.59496	1.220749
C	-10.625	-0.11957	-2.5645	H	-10.9379	0.534684	3.205591
C	-10.3234	-1.2869	-3.27633	H	-7.6782	3.323294	3.125004
C	-9.16423	-1.9856	-2.91135	H	-6.77812	2.219039	1.118863
C	-8.34908	-1.55034	-1.8712	H	2.566501	1.693499	-0.00547
C	-9.51531	0.271991	1.628797	H	5.027952	1.912551	-0.15835
C	-10.026	0.914896	2.751089	H	5.460901	-2.28929	0.544972
C	-9.38353	2.024737	3.319651	H	2.996368	-2.52451	0.685887
C	-8.20459	2.466871	2.710723	H	11.6466	-1.06382	0.061963
C	-7.6891	1.845637	1.573788	H	13.10872	-3.0568	0.343163
C	3.194227	0.814305	0.099615	H	12.09484	-5.28546	0.769475
C	4.575562	0.944124	0.019433	H	9.624164	-5.51313	0.913104
C	5.408995	-0.17411	0.178254	H	8.176825	-3.50976	0.629701
C	4.820503	-1.42345	0.425278	H	11.34513	1.846976	-0.44631
C	3.438494	-1.54893	0.507673	H	12.37192	4.071273	-0.87886
C	6.881157	-0.03721	0.089028	H	10.92243	6.071352	-1.15326
N	7.385393	1.18416	-0.14697	H	8.453001	5.840243	-0.99442
C	8.723123	1.260045	-0.21901	H	7.442798	3.608478	-0.5618
N	9.546706	0.210587	-0.07281	H	-11.8077	-0.97632	-4.82088
C	8.953436	-0.97058	0.159642	H	-10.6526	-2.26877	-5.17835
N	7.625759	-1.14248	0.249327	H	-11.94	-2.53397	-4.00308
C	9.820909	-2.16204	0.328206	H	-10.3508	2.00644	5.257743
C	9.330403	2.588613	-0.4771	H	-9.20294	3.334035	5.033054

C	11.21698	-2.04087	0.248253	H	-10.7859	3.388434	4.253893
C	12.02952	-3.1604	0.406596				

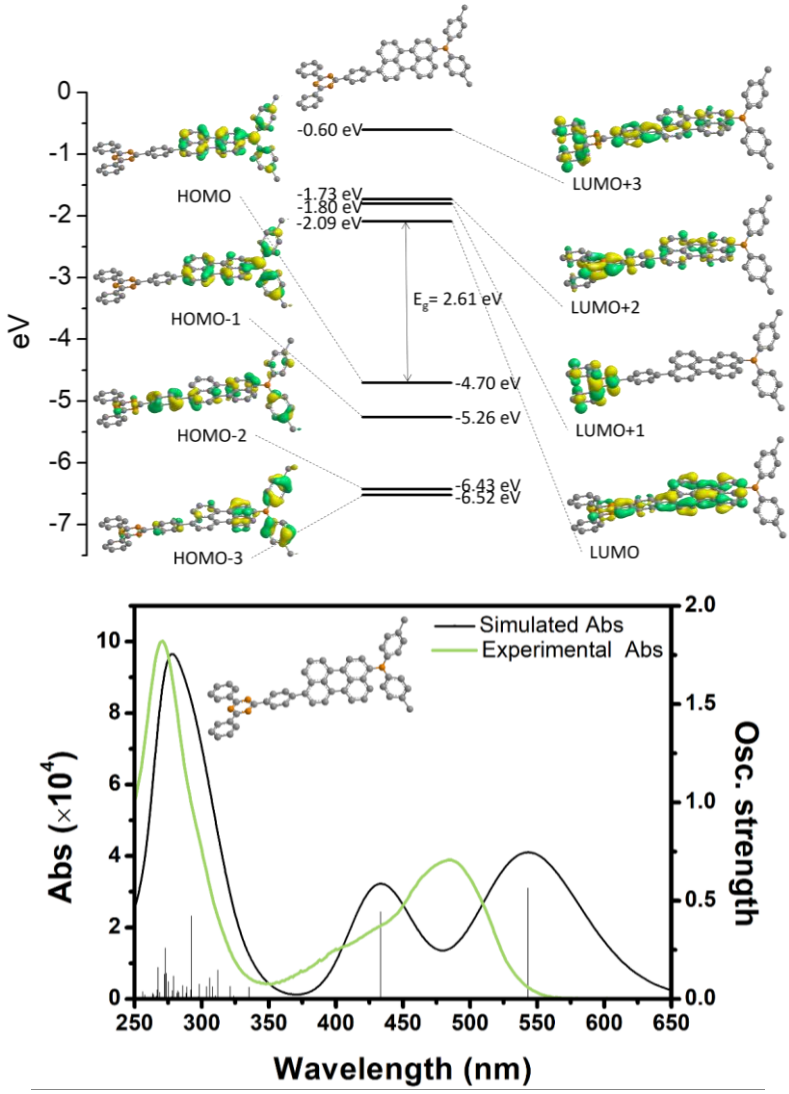


Figure S24. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3c** (Down): Electronic transition of the simulated/experimental absorption spectra of **3c**

Table S9. TD-DFT calculation: Transition assignment of **3c**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	18410.41139	543.17	0.5657	HOMO->LUMO (96%)
2	21393.04967	467.44	0.0012	H-1->LUMO (14%), HOMO->L+1 (10%), HOMO->L+2 (73%)
3	21522.09838	464.63	0.0004	HOMO->L+1 (89%)
4	23083.58775	433.20	0.4433	H-1->LUMO (80%), HOMO->L+2 (17%)
5	25973.47227	385.00	0.0058	H-1->L+1 (12%), H-1->L+2 (83%)
6	26084.77678	383.36	0.0006	H-1->L+1 (86%), H-1->L+2 (12%)
7	28186.65763	354.77	0.004	HOMO->L+4 (83%)
8	29814.28446	335.40	0.0598	HOMO->L+3 (76%), HOMO->L+6 (12%)
9	30889.42152	323.73	0.0147	H-8->LUMO (10%), H-4->LUMO (12%), H-1->L+4 (12%), HOMO->L+5 (40%)
10	31138.64684	321.14	0.0641	H-2->LUMO (63%)
11	32054.89267	311.96	0.1471	H-3->LUMO (39%), HOMO->L+3 (11%), HOMO->L+6 (15%)
12	32220.23632	310.36	0.016	H-9->LUMO (14%), H-8->LUMO (11%), H-4->LUMO (13%)
13	32422.68149	308.42	0.0036	H-6->LUMO (33%), H-6->L+2 (16%), H-2->L+1 (25%)
14	32435.58636	308.30	0.0621	H-4->LUMO (15%), HOMO->L+5 (19%), HOMO->L+12 (12%)
15	32595.28413	306.79	0.0034	H-15->L+1 (17%), H-14->LUMO (33%), H-14->L+2 (31%)
16	32687.23134	305.92	0.1083	HOMO->L+7 (51%), HOMO->L+8 (22%)
17	32944.52220	303.54	0.064	H-3->LUMO (23%), HOMO->L+6 (18%), HOMO->L+7 (10%), HOMO->L+12 (12%)
18	33004.20723	302.99	0.0005	H-15->LUMO (46%), H-15->L+2 (46%)
19	33180.84265	301.37	0.0001	H-15->L+1 (80%)
20	33374.41571	299.63	0.0023	HOMO->L+6 (12%), HOMO->L+7 (11%), HOMO->L+8 (33%)

Table S10. Cartesian coordinates for optimized structure for **3d**

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.1635	0.470224	1.841516	C	10.49949	3.135095	-3.32862
C	-5.53397	0.340669	1.586867	C	9.674761	2.35511	-2.52234
C	-6.01146	0.171539	0.298501	C	11.09491	-1.81379	2.155573
C	-5.07933	0.142075	-0.79186	C	11.65304	-2.65367	3.115666
C	-5.51693	0.059146	-2.13713	C	10.829	-3.43561	3.928452
C	-4.60363	0.03042	-3.16659	C	9.441863	-3.37371	3.776335
C	-3.22615	0.061392	-2.89905	C	8.880024	-2.53512	2.8173
C	-2.73699	0.149232	-1.5996	O	-10.8619	3.638525	2.646598
C	-1.29022	0.163501	-1.31158	O	-9.55149	-4.59715	-2.22964
C	-0.33988	-0.01974	-2.3098	C	-10.662	5.040043	2.568562
C	1.033646	0.002368	-2.03677	C	-8.93266	-5.86193	-2.06538
C	1.520599	0.212403	-0.75699	H	-3.85508	0.584765	2.873894
C	0.580177	0.437346	0.304075	H	-6.23791	0.367626	2.412005
C	1.005296	0.759967	1.6195	H	-6.57865	0.028696	-2.34573
C	0.086579	0.973382	2.621942	H	-4.94609	-0.01815	-4.19596
C	-1.28823	0.861052	2.366284	H	-2.54238	0.030035	-3.73892
C	-1.77064	0.558739	1.096623	H	-0.64758	-0.2098	-3.33099
C	-0.83126	0.379993	0.027512	H	1.734287	-0.18244	-2.84549
C	-3.21261	0.418854	0.826702	H	2.063903	0.859537	1.824931
C	-3.67136	0.228973	-0.51585	H	0.42365	1.234673	3.620758
N	-7.41007	0.051681	0.062557	H	-1.97643	1.03551	3.18466
C	2.991042	0.17876	-0.53979	H	-9.57523	-0.52865	1.577155
C	-7.93508	-1.1526	-0.48715	H	-11.0721	1.11559	2.684555
C	-8.28536	0.970829	0.713576	H	-8.67169	4.328285	1.138258
C	-9.3823	0.533979	1.476401	H	-7.21583	2.699173	0.014632
C	-10.2231	1.448356	2.096375	H	-9.60825	-0.17687	-1.44071
C	-9.98008	2.824985	1.99065	H	-10.5202	-2.26526	-2.42649
C	-8.88371	3.271037	1.243664	H	-7.27701	-4.48729	-0.69125
C	-8.05594	2.347074	0.604566	H	-6.40173	-2.42969	0.315963
C	-9.10419	-1.12261	-1.2712	H	2.946648	-1.30264	1.028384
C	-9.61811	-2.28563	-1.82383	H	5.405939	-1.39524	1.296951
C	-8.96854	-3.5144	-1.63036	H	5.870166	1.514591	-1.81033
C	-7.80144	-3.55487	-0.8629	H	3.407743	1.629018	-2.07754
C	-7.30096	-2.38283	-0.28877	H	12.04663	0.799011	-0.65201
C	3.580659	-0.67029	0.415065	H	13.52463	2.190729	-2.08996
C	4.960845	-0.73128	0.565395	H	12.52895	3.687869	-3.80572
C	5.802682	0.056675	-0.23512	H	10.06054	3.788104	-4.07717
C	5.223441	0.902348	-1.19305	H	8.597272	2.389703	-2.63073
C	3.842504	0.95921	-1.3418	H	11.72309	-1.20222	1.518944
C	7.273532	-0.00544	-0.07324	H	12.73197	-2.69906	3.230837
N	7.768236	-0.82828	0.864906	H	11.26588	-4.09036	4.677039
C	9.105248	-0.85222	0.974955	H	8.797808	-3.98016	4.406285
N	9.937218	-0.11849	0.219619	H	7.805639	-2.47802	2.689375
C	9.353237	0.675384	-0.69139	H	-11.4628	5.492643	3.155197
N	8.027024	0.764555	-0.87407	H	-9.69358	5.336726	2.992245
C	10.23018	1.507291	-1.55136	H	-10.7246	5.40267	1.534249
C	9.701921	-1.74649	1.997159	H	-9.54751	-6.57368	-2.61835

C	11.62501	1.455742	-1.40358	H	-7.91386	-5.87215	-2.47444
C	12.44646	2.237298	-2.2117	H	-8.8956	-6.16244	-1.01003
C	11.88681	3.078727	-3.176				

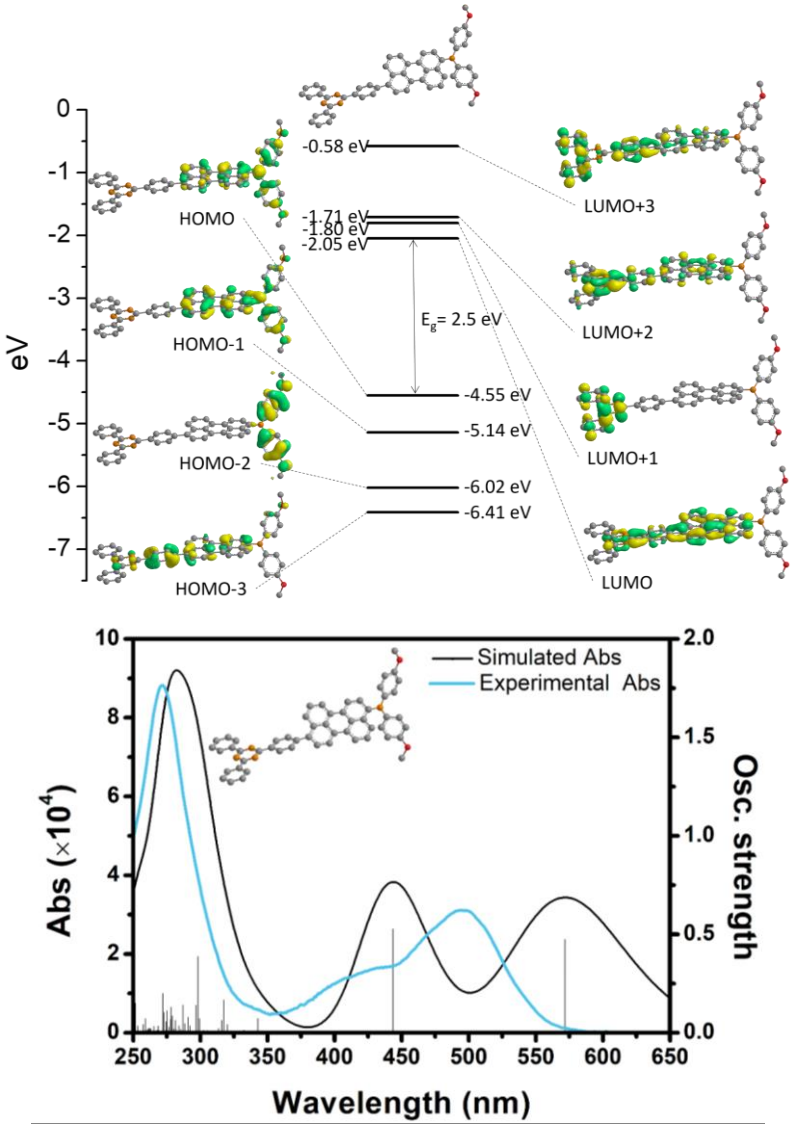


Figure S25. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3d** (Down): Electronic transition of the simulated/experimental absorption spectra of **3d**

Table S11. TD-DFT calculation: Transition assignment of **3d**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	17490.93934	571.72	0.4739	HOMO->LUMO (96%)
2	20538.10198	486.89	0.0006	HOMO->L+1 (72%), HOMO->L+2 (24%)
3	20614.72465	485.09	0.0006	HOMO->L+1 (27%), HOMO->L+2 (64%)
4	22552.06838	443.41	0.5278	H-1->LUMO (87%), HOMO->L+2 (11%)
5	25070.93787	398.86	0.0001	H-1->L+1 (95%)
6	25231.44220	396.33	0.0025	H-1->L+2 (93%)
7	27587.38768	362.48	0.0061	HOMO->L+4 (86%)
8	29019.02180	344.60	0.0092	H-2->LUMO (88%)
9	29167.42781	342.84	0.0726	HOMO->L+3 (80%), HOMO->L+6 (11%)
10	30082.86709	332.41	0.0127	H-4->LUMO (10%), H-1->L+4 (11%), HOMO->L+5 (67%)
11	31237.04648	320.13	0.042	H-4->LUMO (24%), H-3->LUMO (39%), HOMO->L+6 (10%), H-4->L+2 (3%), H-3->L+2 (2%), HOMO->L+5 (4%)
12	31509.66187	317.36	0.1677	H-3->LUMO (16%), HOMO->L+6 (39%), HOMO->L+11 (10%), HOMO->L+3 (9%)
13	31655.64822	315.89	0.0638	H-7->LUMO (16%), H-3->LUMO (12%), HOMO->L+10 (10%), HOMO->L+11 (13%), H-4->LUMO (6%), H-1->L+4 (3%)
14	31893.58178	313.54	0.0209	H-4->LUMO (14%), H-3->LUMO (15%), H-1->L+4 (19%)
15	32329.12117	309.31	0.0013	H-5->LUMO (28%), H-5->L+2 (12%), H-3->L+1 (33%), H-2->L+1 (14%)
16	32599.31691	306.75	0.0004	H-16->LUMO (40%), H-16->L+2 (33%), H-15->L+1 (17%)
17	32633.99875	306.42	0.0049	HOMO->L+6 (10%), HOMO->L+7 (37%), HOMO->L+10 (16%)
18	32763.04746	305.22	0.0116	H-2->L+2 (73%)
19	32859.83399	304.32	0.0022	H-2->L+1 (77%)
20	33021.95143	302.82	0.0018	H-15->LUMO (52%), H-15->L+2 (44%)

Table S12. The number of imaginary frequencies, total energies, and dipole moments for the compound **3a**$^{\bullet-}$**–3d**$^{\bullet-}$ as obtained in the geometry optimizations at ωB97XD/6-31+G method

Entry	Number of imaginary frequencies	Total energies (Eh) (Hartrees)	Doublet state dipole moment (field-independent basis, Debye)
3a$^{\bullet-}$	-1	-2456.99756154	9.2913
3b$^{\bullet-}$	-1	-2258.56417008	7.9921
3c$^{\bullet-}$	-1	-2337.17648297	4.9679
3d$^{\bullet-}$	-1	-2487.54389717	4.6622

Table S13. Cartesian coordinates for optimized structure for **3a**$^{\bullet-}$

Symbolic Z-matrix:
Charge = -1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.547349	1.281593	1.627884	C	-9.78605	-2.15976	-0.39447
C	5.904441	1.211848	1.340686	C	-11.1767	-2.01552	-0.37889
C	6.380869	0.359733	0.359167	C	-11.999	-3.12423	-0.55415
C	5.48665	-0.4602	-0.38133	C	-11.4401	-4.38695	-0.74643
C	5.949733	-1.36447	-1.36408	C	-10.0538	-4.5356	-0.76265
C	5.044227	-2.14474	-2.06453	C	-9.23002	-3.42821	-0.58767
C	3.67775	-2.04639	-1.83079	C	-10.6343	2.757606	0.352581
C	3.157946	-1.15932	-0.86629	C	-11.1864	4.020198	0.545367
C	1.737048	-1.02617	-0.62894	C	-10.3574	5.126379	0.727119
C	0.784143	-1.72713	-1.39946	C	-8.97267	4.963743	0.715091
C	-0.57203	-1.58103	-1.18395	C	-8.41877	3.702193	0.522191
C	-1.08561	-0.73564	-0.19363	F	9.702707	2.497677	-4.62534
C	-0.15439	-0.05567	0.666726	F	10.95507	-2.0748	3.984368
C	-0.57694	0.677794	1.796335	H	4.223938	1.972563	2.397303
C	0.337914	1.335301	2.603915	H	6.611987	1.830382	1.889047
C	1.69527	1.296759	2.317359	H	7.014041	-1.44274	-1.56132
C	2.185697	0.554584	1.229582	H	5.406742	-2.8458	-2.81352
C	1.261792	-0.17262	0.414369	H	3.012086	-2.68012	-2.40516
C	3.608674	0.502272	0.92582	H	1.102727	-2.367	-2.21424
C	4.077246	-0.36544	-0.10657	H	-1.26378	-2.09329	-1.84951
N	7.789256	0.30265	0.099587	H	-1.62915	0.700734	2.058003
C	-2.53889	-0.55943	-0.11038	H	-0.01168	1.882205	3.476991
C	8.297614	0.865758	-1.08132	H	2.377213	1.825062	2.973821
C	8.615809	-0.30295	1.064776	H	10.04054	-0.40465	-1.19836
C	9.487664	0.403523	-1.66605	H	10.88624	0.597302	-3.30116
C	9.966469	0.95576	-2.84982	H	7.489003	3.198287	-3.44509
C	9.238998	1.960008	-3.46504	H	6.64313	2.221465	-1.32104
C	8.047356	2.421206	-2.93321	H	10.22509	1.120225	0.89118
C	7.581646	1.875903	-1.74148	H	11.63646	0.036254	2.630973
C	9.870293	0.227413	1.396764	H	8.593237	-2.90711	3.277149
C	10.66496	-0.37152	2.370323	H	7.185901	-1.84548	1.513471
C	10.1856	-1.49179	3.027332	H	-2.5069	1.585749	0.126832
C	8.941829	-2.03058	2.740749	H	-4.95029	1.850907	0.162922
C	8.162392	-1.43686	1.754053	H	-5.42725	-2.38141	-0.34556
C	-3.1412	0.708101	0.047617	H	-2.98138	-2.6567	-0.35813
C	-4.51512	0.862118	0.05925	H	-11.6004	-1.02828	-0.22853
C	-5.36702	-0.24696	-0.08169	H	-13.0788	-3.00257	-0.54065
C	-4.78361	-1.51326	-0.24518	H	-12.0828	-5.25263	-0.88331
C	-3.40793	-1.6622	-0.25926	H	-9.61242	-5.51706	-0.9121
C	-6.82029	-0.08594	-0.06185	H	-8.1501	-3.53045	-0.59866
N	-7.32678	1.145922	0.12634	H	-11.2694	1.889706	0.21044
C	-8.65229	1.240629	0.133899	H	-12.2663	4.141234	0.55397
N	-9.49286	0.212303	-0.0282	H	-10.7891	6.112329	0.877861
C	-8.90374	-0.97555	-0.20799	H	-8.3215	5.821846	0.856513
N	-7.59034	-1.17576	-0.23354	H	-7.34303	3.562966	0.511265
C	-9.24622	2.589758	0.339475				

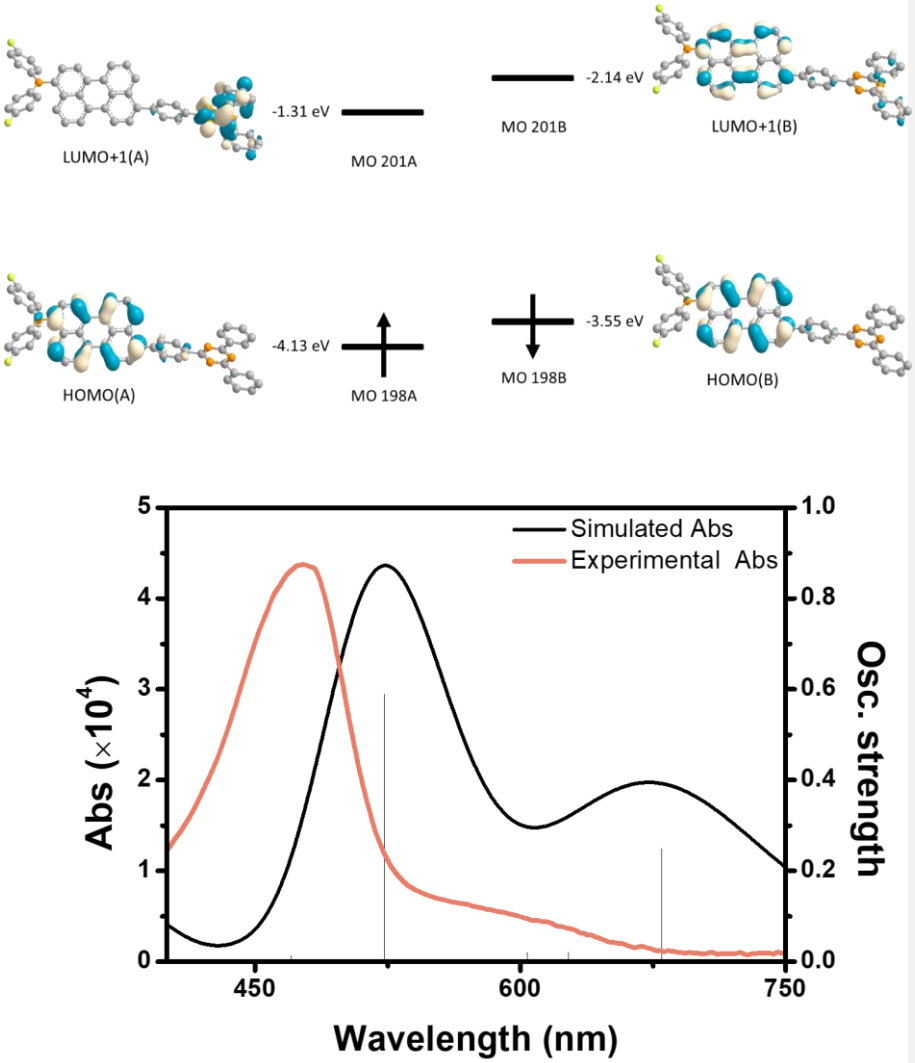


Figure S26. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3a**$^{\bullet-}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3a**$^{\bullet-}$

Table S14. TD-DFT calculation: Transition assignment of **3a**$^{\bullet-}$

Excited State 3: 2.130-?Sym 1.8235 eV 679.94 nm f=0.2485 <S**2>=0.884			
178A -> 263A	-0.01043	192B -> 230B	-0.01537
179A -> 263A	-0.01158	192B -> 237B	0.01622
179A -> 266A	0.01149	192B -> 242B	0.02099
179A -> 284A	-0.01401	192B -> 243B	-0.01200
179A -> 300A	-0.01122	192B -> 244B	-0.01034
188A -> 201A	0.01191	193B -> 216B	0.02402
191A -> 215A	0.01192	193B -> 217B	-0.01059
192A -> 213A	-0.02322	193B -> 231B	-0.01350
192A -> 217A	-0.01209	193B -> 232B	-0.03492
192A -> 234A	0.01221	193B -> 233B	0.03409
192A -> 237A	0.01167	193B -> 237B	0.01322
192A -> 242A	0.01666	194B -> 214B	0.01437
193A -> 213A	-0.01851	194B -> 216B	0.03005
193A -> 233A	-0.02068	194B -> 224B	-0.01041
194A -> 200A	-0.01512	194B -> 226B	0.01436
194A -> 202A	0.01461	194B -> 228B	-0.02142
194A -> 213A	-0.03494	194B -> 230B	0.08150
194A -> 215A	-0.02406	194B -> 231B	-0.04250
194A -> 216A	0.01040	194B -> 233B	-0.03754
194A -> 217A	0.01890	194B -> 236B	0.01371
194A -> 218A	0.01067	194B -> 240B	0.01056
194A -> 221A	0.01595	194B -> 259B	0.01022
194A -> 222A	-0.03814	195B -> 216B	-0.05175
194A -> 223A	-0.01160	195B -> 217B	0.03164
194A -> 224A	-0.01301	195B -> 218B	-0.01334
194A -> 233A	0.01244	195B -> 219B	0.01497
195A -> 202A	-0.01870	195B -> 232B	-0.01674
195A -> 212A	-0.01403	195B -> 233B	0.01386
195A -> 213A	0.03482	196B -> 200B	0.02888
196A -> 202A	-0.01682	196B -> 201B	0.05283
196A -> 213A	0.02660	196B -> 202B	0.05257
196A -> 221A	-0.01807	196B -> 203B	-0.01136
196A -> 222A	0.02815	196B -> 204B	0.03301
197A -> 200A	-0.01461	196B -> 205B	-0.01825
197A -> 213A	0.01921	196B -> 215B	-0.01022
197A -> 222A	0.01115	196B -> 216B	-0.02129
198A -> 200A	0.11761	196B -> 218B	0.01226
198A -> 201A	0.04742	196B -> 220B	0.04044
198A -> 202A	-0.04500	196B -> 221B	-0.03685
198A -> 203A	-0.01282	196B -> 222B	-0.01189
198A -> 205A	0.01640	196B -> 223B	-0.01014
198A -> 217A	0.01004	196B -> 227B	0.01279
198A -> 233A	-0.01237	196B -> 228B	0.01383
198A -> 256A	-0.01754	196B -> 229B	-0.01308
198A -> 259A	-0.01668	196B -> 230B	0.03442
198A -> 263A	-0.01525	196B -> 231B	-0.01901
198A -> 265A	-0.01001	196B -> 232B	0.01274
199A -> 200A	0.09745	196B -> 236B	0.01672
199A -> 201A	0.02694	196B -> 237B	-0.01444
199A -> 202A	0.09501	196B -> 239B	-0.01211
199A -> 203A	0.03618	196B -> 241B	-0.01168

199A -> 204A	-0.01986
199A -> 205A	-0.02924
199A -> 209A	-0.06337
199A -> 210A	-0.03446
199A -> 211A	-0.03863
199A -> 212A	0.05961
199A -> 213A	-0.09157
199A -> 215A	0.18146
199A -> 216A	-0.04063
199A -> 217A	-0.18218
199A -> 218A	-0.07642
199A -> 219A	0.05766
199A -> 220A	-0.01457
199A -> 221A	-0.05544
199A -> 222A	0.13789
199A -> 223A	0.03999
199A -> 224A	0.04855
199A -> 225A	0.03456
199A -> 227A	-0.01554
199A -> 228A	-0.01225
199A -> 229A	-0.01494
199A -> 232A	0.01355
199A -> 233A	-0.01618
199A -> 234A	0.03325
199A -> 236A	0.02191
199A -> 237A	0.04015
199A -> 239A	-0.02156
199A -> 241A	-0.01569
199A -> 242A	0.04381
199A -> 243A	0.01546
199A -> 244A	0.01501
199A -> 248A	0.01556
199A -> 249A	0.01352
199A -> 252A	0.01625
199A -> 256A	-0.01343
199A -> 299A	-0.01119
178B -> 269B	-0.01165
180B -> 201B	-0.01041
180B -> 284B	0.01126
191B -> 214B	-0.01486
192B -> 201B	0.02499
192B -> 220B	-0.02703
192B -> 221B	0.02127
196B -> 242B	-0.01489
196B -> 243B	0.01147
196B -> 244B	0.01221
196B -> 249B	-0.01135
197B -> 200B	0.03478
197B -> 201B	-0.02256
197B -> 202B	0.01599
197B -> 204B	0.01531
197B -> 215B	-0.01333
197B -> 216B	-0.01816
197B -> 218B	0.01314
197B -> 220B	0.03423
197B -> 221B	-0.02697
197B -> 230B	0.01235
197B -> 237B	-0.01365
197B -> 242B	-0.01220
198B -> 199B	-0.04890
198B -> 200B	-0.39435
198B -> 201B	0.75646
198B -> 202B	0.16021
198B -> 203B	-0.02261
198B -> 204B	0.05054
198B -> 205B	-0.08603
198B -> 208B	-0.01699
198B -> 209B	-0.01779
198B -> 210B	0.02796
198B -> 211B	0.01865
198B -> 214B	0.01479
198B -> 215B	0.01852
198B -> 220B	-0.02893
198B -> 221B	0.02052
198B -> 223B	0.01048
198B -> 228B	0.01430
198B -> 232B	0.01393
198B -> 235B	-0.01419
198B -> 237B	0.01173
198B -> 242B	0.01061
198B -> 249B	-0.01630
198B -> 257B	0.01426
198B -> 259B	0.01541
198B -> 261B	0.01083
198B -> 286B	0.01328

Table S15. Cartesian coordinates for optimized structure for **3b**$^{\bullet-}$

Symbolic Z-matrix:
Charge = -1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.989029	1.487718	1.431451	C	-9.35421	-2.18906	-0.05769
C	6.346722	1.377876	1.155288	C	-10.1942	2.787631	-0.09585
C	6.819436	0.409474	0.288346	C	-10.7434	4.066192	-0.10668
C	5.921824	-0.49571	-0.33965	C	-9.9119	5.185343	-0.10488
C	6.382917	-1.51674	-1.20198	C	-8.52755	5.019456	-0.09222
C	5.476449	-2.38006	-1.79296	C	-7.97673	3.741962	-0.08157
C	4.110116	-2.25659	-1.56468	C	-10.7447	-2.04206	-0.06209
C	3.592365	-1.25674	-0.71763	C	-11.569	-3.16315	-0.05762
C	2.172654	-1.10182	-0.48634	C	-11.0124	-4.44138	-0.04867
C	1.218644	-1.91656	-1.13485	C	-9.62632	-4.59293	-0.04426
C	-0.13655	-1.74652	-0.93677	C	-8.80062	-3.47317	-0.04873
C	-0.65175	-0.76006	-0.08567	H	4.669871	2.270576	2.109102
C	0.282168	0.041704	0.661826	H	7.056645	2.057763	1.621419
C	-0.13816	0.930218	1.673879	H	7.446646	-1.61595	-1.39247
C	0.776786	1.701881	2.373344	H	5.836565	-3.16849	-2.4507
C	2.133342	1.623317	2.09211	H	3.443594	-2.95815	-2.05265
C	2.622807	0.729193	1.125634	H	1.53641	-2.67255	-1.84359
C	1.698264	-0.10804	0.425005	H	-0.82764	-2.35675	-1.51443
C	4.047761	0.629783	0.835204	H	-1.18918	0.98808	1.934644
C	4.513795	-0.36724	-0.0741	H	0.427788	2.371132	3.156839
N	8.227482	0.318739	0.03439	H	2.814852	2.245742	2.660515
C	-2.10242	-0.57301	-0.03105	H	10.67546	1.205956	0.701499
C	8.731029	0.739382	-1.20605	H	12.07423	0.358671	2.546825
C	9.052879	-0.16452	1.067471	H	11.25022	-1.48155	4.009263
C	10.31537	0.390942	1.322083	H	8.99502	-2.45279	3.584401
C	11.09957	-0.08852	2.366706	H	7.607418	-1.61716	1.719471
C	10.63828	-1.1143	3.190073	H	10.4802	-0.52679	-1.17083
C	9.374997	-1.65516	2.951263	H	11.3131	0.205472	-3.36194
C	8.589672	-1.1921	1.901794	H	10.03544	1.866161	-4.71278
C	9.923684	0.216169	-1.73337	H	7.893116	2.765002	-3.80887
C	10.38793	0.628393	-2.9775	H	7.06892	2.048749	-1.60179
C	9.673292	1.553045	-3.73761	H	-2.07161	1.585497	-0.09282
C	8.476452	2.054337	-3.22892	H	-4.51247	1.854486	-0.10194
C	8.007939	1.659186	-1.98101	H	-4.99339	-2.40786	-0.01787
C	-2.70571	0.705247	-0.0501	H	-2.55048	-2.68476	0.010673
C	-4.07868	0.860325	-0.06505	H	-10.8317	1.909918	-0.09706
C	-4.93334	-0.25678	-0.05253	H	-11.823	4.189492	-0.11651
C	-4.34937	-1.5344	-0.03795	H	-10.3413	6.183746	-0.1133
C	-2.9747	-1.68521	-0.03005	H	-7.87427	5.887571	-0.09064
C	-6.38394	-0.09323	-0.05795	H	-6.90133	3.599808	-0.07161
N	-6.89024	1.154236	-0.06393	H	-11.1668	-1.04283	-0.06894
C	-8.21492	1.250331	-0.07219	H	-12.6485	-3.03893	-0.06104
N	-9.05795	0.210833	-0.07056	H	-11.6566	-5.31674	-0.04508
C	-8.46965	-0.9914	-0.06204	H	-9.18651	-5.58641	-0.03716
N	-7.15733	-1.19562	-0.05774	H	-7.72087	-3.57781	-0.0453
C	-8.8066	2.616395	-0.08332				

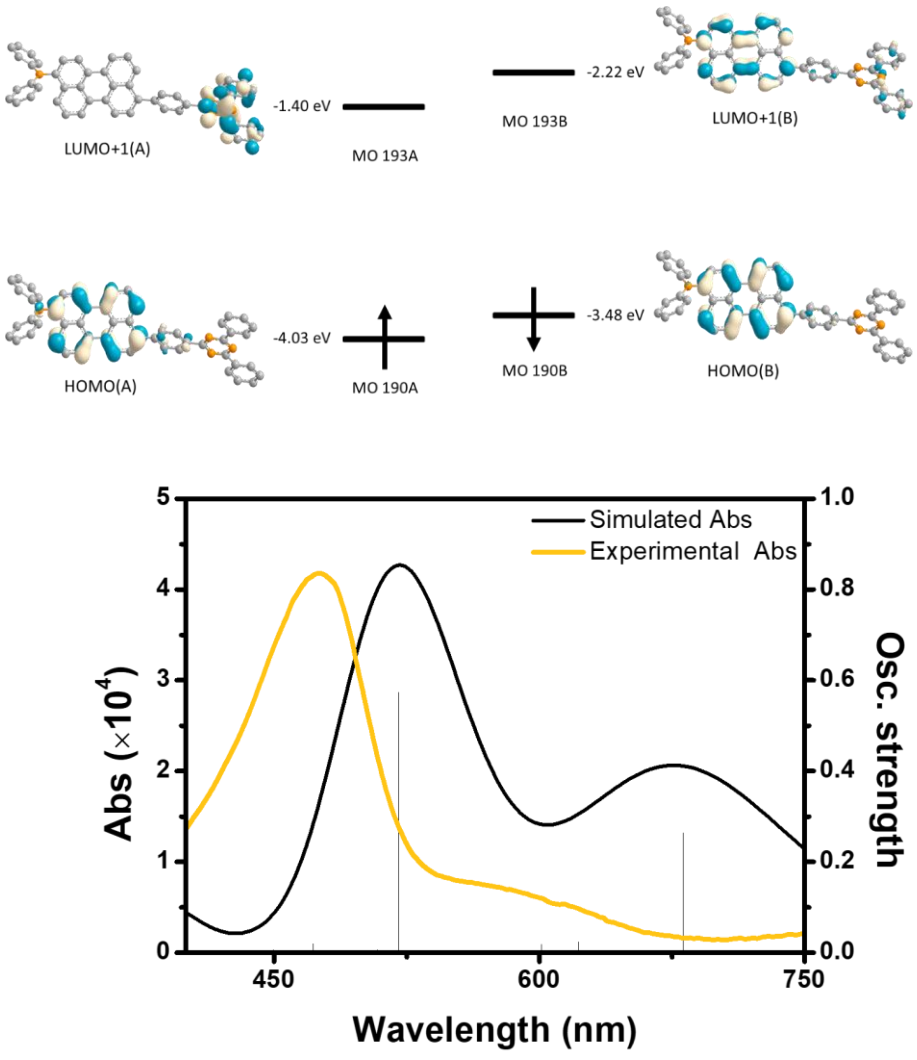


Figure S27. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3b**$^{\bullet-}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3b**$^{\bullet-}$

Table S16. TD-DFT calculation: Transition assignment of **3b**$^{\bullet-}$

Excited State 3: 2.159-?Sym 1.8194 eV 681.44 nm f=0.2634 <S**2>=0.915			
166A -> 300A	-0.01082	184B -> 193B	0.02407
170A -> 253A	-0.01166	184B -> 208B	0.01328
171A -> 255A	-0.01322	184B -> 210B	-0.01234
171A -> 258A	0.01271	184B -> 211B	0.01633
171A -> 276A	0.01136	184B -> 212B	-0.01082
171A -> 291A	-0.01044	184B -> 213B	-0.02440
179A -> 193A	0.01368	184B -> 221B	-0.01809
182A -> 205A	-0.01251	184B -> 228B	-0.01318
182A -> 206A	0.01071	184B -> 231B	0.01068
183A -> 208A	0.01071	184B -> 234B	-0.01501
184A -> 205A	-0.01663	184B -> 235B	-0.01125
184A -> 206A	0.01410	184B -> 236B	-0.01494
184A -> 228A	-0.01173	184B -> 237B	-0.01120
184A -> 234A	0.01283	185B -> 208B	0.01578
185A -> 205A	-0.01210	185B -> 223B	0.01284
185A -> 206A	0.01029	185B -> 224B	-0.01871
185A -> 225A	-0.01997	185B -> 225B	0.04701
186A -> 192A	-0.01766	185B -> 228B	-0.01161
186A -> 194A	0.01536	185B -> 229B	-0.01501
186A -> 205A	-0.02416	186B -> 206B	0.01006
186A -> 206A	0.02135	186B -> 207B	0.01505
186A -> 207A	0.02593	186B -> 208B	0.02896
186A -> 208A	-0.01765	186B -> 218B	0.01060
186A -> 210A	-0.01806	186B -> 219B	0.01430
186A -> 211A	0.01999	186B -> 221B	0.08712
186A -> 213A	0.01415	186B -> 223B	-0.02454
186A -> 214A	-0.02852	186B -> 224B	-0.02692
186A -> 215A	0.02432	186B -> 225B	-0.02389
186A -> 217A	-0.01416	186B -> 226B	0.02420
186A -> 219A	-0.01093	186B -> 227B	-0.01877
186A -> 225A	0.01101	186B -> 232B	0.01305
187A -> 194A	-0.01699	186B -> 251B	0.01260
187A -> 203A	-0.01028	187B -> 199B	0.01147
187A -> 205A	0.02497	187B -> 206B	-0.01498
187A -> 206A	-0.02229	187B -> 208B	-0.05837
187A -> 215A	0.01133	187B -> 209B	-0.02165
188A -> 194A	-0.02059	187B -> 211B	0.01603
188A -> 205A	0.02598	187B -> 214B	-0.01291
188A -> 206A	-0.02157	187B -> 221B	0.01188
188A -> 213A	-0.01264	187B -> 225B	0.01520
188A -> 214A	0.01751	188B -> 192B	0.02544
188A -> 215A	-0.02141	188B -> 193B	0.05912
188A -> 219A	0.01155	188B -> 194B	0.05347
189A -> 192A	0.01884	188B -> 195B	-0.01085
189A -> 205A	-0.01414	188B -> 196B	0.04071
189A -> 206A	0.01204	188B -> 208B	-0.02249
190A -> 192A	0.14806	188B -> 209B	-0.01365
190A -> 194A	-0.05352	188B -> 210B	0.01675
190A -> 195A	-0.01619	188B -> 211B	-0.01996
190A -> 205A	0.01453	188B -> 212B	0.01423
190A -> 206A	-0.01247	188B -> 213B	0.03490

190A -> 248A	0.01954
190A -> 252A	-0.01289
190A -> 253A	-0.01719
190A -> 257A	-0.01061
191A -> 192A	0.09303
191A -> 194A	0.11207
191A -> 195A	0.04154
191A -> 196A	0.02352
191A -> 200A	-0.01882
191A -> 201A	-0.01239
191A -> 203A	0.06971
191A -> 205A	-0.11773
191A -> 206A	0.10018
191A -> 207A	-0.10081
191A -> 208A	0.12517
191A -> 209A	-0.01243
191A -> 210A	0.11611
191A -> 211A	-0.13073
191A -> 212A	0.05988
191A -> 213A	-0.05075
191A -> 214A	0.09666
191A -> 215A	-0.08919
191A -> 216A	0.01997
191A -> 217A	0.04940
191A -> 218A	0.03447
191A -> 221A	-0.01826
191A -> 222A	-0.01810
191A -> 225A	-0.01887
191A -> 226A	0.01427
191A -> 228A	-0.04782
191A -> 229A	0.01611
191A -> 230A	-0.03332
191A -> 231A	0.01840
191A -> 232A	0.01410
191A -> 233A	-0.02633
191A -> 234A	0.02525
191A -> 235A	0.02376
191A -> 236A	0.01338
191A -> 240A	-0.02028
191A -> 241A	-0.01001
191A -> 244A	0.01678
191A -> 248A	0.01028
191A -> 251A	0.01740
191A -> 279A	0.01031
170B -> 257B	0.01099
170B -> 261B	-0.01260
172B -> 193B	-0.01061
172B -> 258B	-0.01220
172B -> 276B	0.01150
181B -> 221B	-0.01056
183B -> 207B	-0.01572
188B -> 214B	-0.01659
188B -> 218B	0.01945
188B -> 220B	0.02220
188B -> 221B	0.03684
188B -> 222B	-0.01291
188B -> 223B	0.01563
188B -> 224B	0.01206
188B -> 226B	0.01828
188B -> 228B	0.01475
188B -> 231B	-0.01433
188B -> 233B	-0.01148
188B -> 236B	0.01375
188B -> 240B	-0.01237
189B -> 192B	-0.03313
189B -> 193B	0.01958
189B -> 194B	-0.01580
189B -> 196B	-0.01540
189B -> 208B	0.02053
189B -> 210B	-0.01695
189B -> 211B	0.02359
189B -> 212B	-0.01369
189B -> 213B	-0.02968
189B -> 214B	0.01073
189B -> 220B	-0.01003
189B -> 221B	-0.01284
189B -> 228B	-0.01062
189B -> 236B	-0.01061
190B -> 191B	-0.05547
190B -> 192B	-0.39888
190B -> 193B	0.75348
190B -> 194B	0.16108
190B -> 195B	-0.02422
190B -> 196B	0.08327
190B -> 199B	-0.04852
190B -> 206B	-0.02512
190B -> 207B	0.01584
190B -> 208B	0.01582
190B -> 211B	0.02276
190B -> 212B	-0.01260
190B -> 213B	-0.03045
190B -> 216B	0.01074
190B -> 223B	0.01247
190B -> 224B	0.01639
190B -> 226B	0.01140
190B -> 228B	-0.01151
190B -> 234B	-0.01299
190B -> 241B	-0.01521
190B -> 249B	0.01813
190B -> 253B	0.01346
190B -> 269B	0.01008
190B -> 276B	-0.01356

Table S17. Cartesian coordinates for optimized structure for **3c**$^{\bullet-}$

Symbolic Z-matrix:
Charge = -1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.543415	1.27349	1.627652	C	-11.4559	-4.36278	-0.83517
C	5.90109	1.206804	1.335356	C	-10.0698	-4.51462	-0.84845
C	6.376043	0.357667	0.352615	C	-9.24393	-3.41252	-0.65126
C	5.479398	-0.46319	-0.38394	C	-10.6354	2.760587	0.387961
C	5.941524	-1.36594	-1.36943	C	-11.1853	4.021271	0.599296
C	5.035977	-2.14818	-2.06475	C	-10.3546	5.121835	0.805454
C	3.668855	-2.05447	-1.82458	C	-8.97027	4.955258	0.799117
C	3.150203	-1.16991	-0.85886	C	-8.4187	3.695629	0.587623
C	1.730187	-1.04046	-0.61517	C	11.07138	-2.11348	4.143746
C	0.774992	-1.74669	-1.37915	C	9.732562	2.57282	-4.82657
C	-0.57985	-1.60317	-1.16103	H	4.221757	1.963731	2.398596
C	-1.0954	-0.75241	-0.17331	H	6.609377	1.825965	1.881699
C	-0.15959	-0.07215	0.685445	H	7.005188	-1.43942	-1.57098
C	-0.57745	0.654553	1.819936	H	5.397022	-2.84799	-2.81567
C	0.338612	1.313009	2.625807	H	3.00297	-2.69037	-2.39641
C	1.694431	1.280226	2.331374	H	1.092361	-2.38802	-2.19343
C	2.18089	0.542045	1.240408	H	-1.27082	-2.11716	-1.82577
C	1.255991	-0.18639	0.428256	H	-1.62795	0.6712	2.088641
C	3.604941	0.493464	0.930542	H	-0.00874	1.855072	3.502751
C	4.071715	-0.37285	-0.10344	H	2.378401	1.809434	2.985113
N	7.783229	0.303232	0.089078	H	10.23261	1.118893	0.854258
C	-2.54446	-0.57235	-0.09386	H	11.63438	0.076198	2.584559
C	8.284805	0.863882	-1.0963	H	8.576937	-2.84359	3.30387
C	8.613982	-0.28687	1.060941	H	7.183266	-1.81635	1.552778
C	9.872369	0.237984	1.377277	H	10.03742	-0.3904	-1.21442
C	10.66041	-0.3555	2.360366	H	10.85808	0.582652	-3.30665
C	10.22176	-1.47095	3.074459	H	7.436284	3.159568	-3.45854
C	8.954212	-1.97645	2.764546	H	6.620558	2.206013	-1.34854
C	8.163222	-1.40568	1.776783	H	-2.51203	1.568495	0.193468
C	9.474539	0.410002	-1.68444	H	-4.95148	1.83948	0.221657
C	9.932186	0.961455	-2.87673	H	-5.43877	-2.3795	-0.38767
C	9.225315	1.964802	-3.54175	H	-2.99751	-2.66244	-0.39563
C	8.027457	2.391779	-2.96246	H	-11.6088	-1.01281	-0.26031
C	7.561763	1.862396	-1.7655	H	-13.0916	-2.97764	-0.61209
C	-3.14692	0.693601	0.0925	H	-12.1003	-5.22433	-0.98937
C	-4.51933	0.851469	0.098888	H	-9.63028	-5.49456	-1.01288
C	-5.3764	-0.25113	-0.07275	H	-8.16415	-3.51687	-0.65949
C	-4.79345	-1.5155	-0.26423	H	-11.2717	1.896889	0.226661
C	-3.41957	-1.66831	-0.27616	H	-12.265	4.145154	0.603231
C	-6.82556	-0.0867	-0.05638	H	-10.7845	6.106298	0.970634
N	-7.33186	1.143902	0.152169	H	-8.31754	5.808888	0.959477
C	-8.65617	1.241308	0.154533	H	-7.34333	3.553113	0.5806
N	-9.50018	0.218799	-0.02975	H	12.00749	-1.56411	4.290615
C	-8.91209	-0.9673	-0.22785	H	10.54711	-2.14297	5.106518
N	-7.6003	-1.17137	-0.2516	H	11.32975	-3.14699	3.881639
C	-9.79719	-2.14601	-0.43853	H	10.49566	1.939144	-5.29182
C	-9.24783	2.588778	0.380438	H	8.921936	2.707218	-5.55186

C	-11.1875	-1.9986	-0.42599	H	10.1832	3.558749	-4.65339
C	-12.0121	-3.10201	-0.62348				

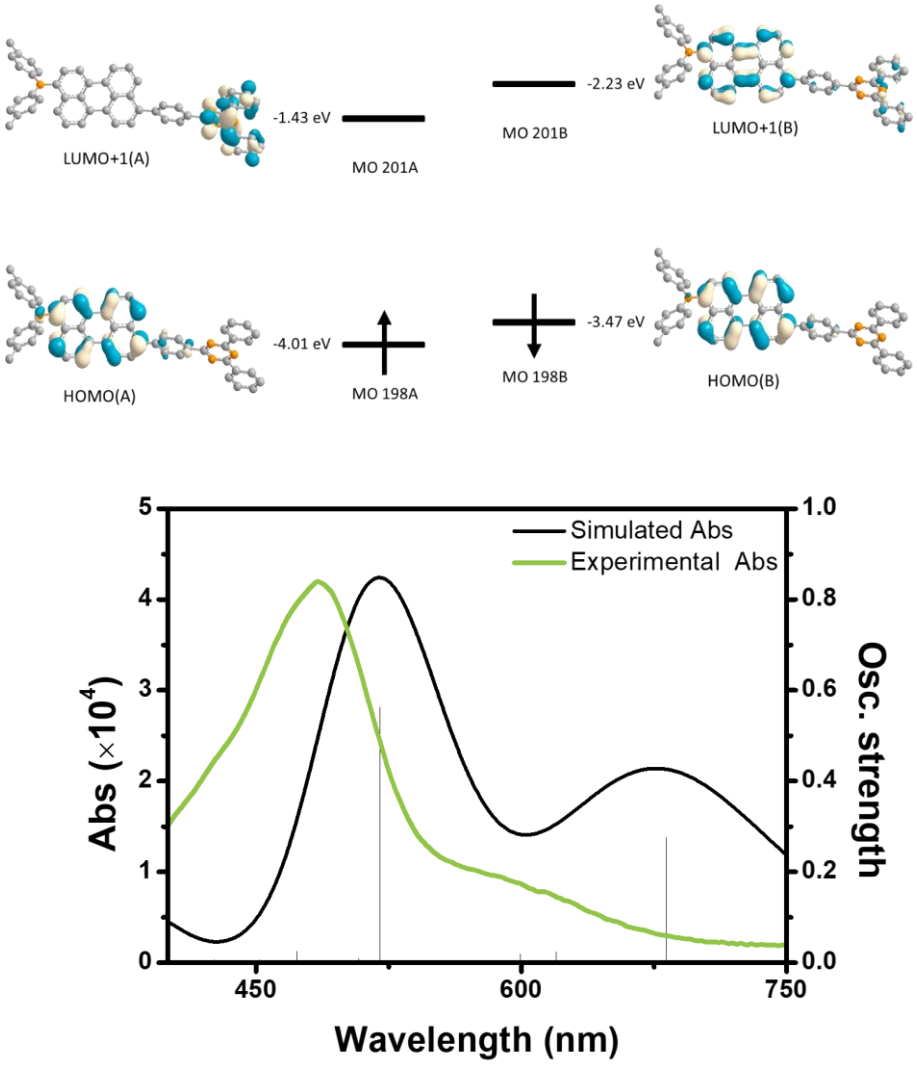


Figure S28. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3c**$^{\bullet-}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3c**$^{\bullet-}$

Table S18. TD-DFT calculation: Transition assignment of **3c**$^{\bullet-}$

Excited State 3: 2.177-?Sym 1.8179 eV 682.01 nm f=0.2755 <S**2>=0.935			
178A -> 265A	0.01290	199A -> 259A	0.01172
178A -> 272A	-0.01008	199A -> 262A	0.01110
179A -> 269A	-0.01013	199A -> 263A	-0.01082
179A -> 281A	-0.01053	199A -> 281A	-0.01254
187A -> 201A	0.01407	199A -> 294A	-0.01146
189A -> 212A	-0.01308	199A -> 300A	-0.01231
189A -> 213A	0.01558	178B -> 267B	0.01137
190A -> 217A	0.01152	178B -> 273B	-0.01320
192A -> 212A	-0.01121	180B -> 201B	-0.01005
192A -> 213A	0.01405	180B -> 288B	-0.01002
193A -> 213A	-0.01169	190B -> 231B	-0.01202
193A -> 216A	-0.01003	191B -> 217B	-0.01587
193A -> 233A	-0.02176	192B -> 201B	-0.02453
194A -> 200A	-0.01812	192B -> 215B	-0.01065
194A -> 202A	0.01584	192B -> 216B	0.01557
194A -> 212A	0.01565	192B -> 222B	-0.02710
194A -> 213A	-0.02536	192B -> 228B	-0.02383
194A -> 216A	-0.02678	192B -> 231B	0.01689
194A -> 217A	-0.02474	192B -> 237B	-0.01103
194A -> 219A	-0.01804	192B -> 240B	-0.01173
194A -> 221A	0.01746	192B -> 246B	0.01172
194A -> 223A	-0.04001	192B -> 247B	0.01142
194A -> 226A	0.01190	192B -> 248B	-0.01688
194A -> 227A	0.01973	193B -> 218B	0.01212
194A -> 233A	0.01168	193B -> 232B	0.01377
195A -> 202A	-0.01513	193B -> 233B	0.05021
195A -> 212A	-0.01781	193B -> 234B	0.01493
195A -> 213A	0.02149	193B -> 237B	0.01323
195A -> 217A	-0.01119	193B -> 238B	-0.01495
195A -> 218A	0.01206	194B -> 216B	-0.02194
195A -> 223A	-0.01772	194B -> 217B	0.01343
196A -> 202A	-0.02365	194B -> 218B	0.02101
196A -> 212A	-0.02206	194B -> 229B	0.02271
196A -> 213A	0.02925	194B -> 230B	0.02359
196A -> 221A	0.01080	194B -> 231B	0.07519
196A -> 223A	0.02763	194B -> 232B	0.05071
196A -> 227A	-0.01812	194B -> 233B	-0.02523
197A -> 200A	0.02534	194B -> 234B	-0.01278
197A -> 213A	-0.01234	194B -> 235B	-0.01956
197A -> 223A	-0.01115	194B -> 237B	-0.01356
198A -> 200A	0.15786	194B -> 240B	-0.01431
198A -> 202A	-0.05769	195B -> 206B	-0.01158
198A -> 203A	-0.01723	195B -> 215B	-0.01014
198A -> 206A	0.01006	195B -> 216B	-0.02314
198A -> 212A	-0.01404	195B -> 218B	0.05440
198A -> 213A	0.01567	195B -> 219B	-0.02988
198A -> 217A	-0.01317	195B -> 231B	-0.01133
198A -> 218A	0.01003	195B -> 232B	-0.01133
198A -> 256A	-0.01002	195B -> 233B	-0.01501
198A -> 259A	-0.01262	196B -> 200B	0.02356
198A -> 260A	0.01388	196B -> 201B	0.06368

198A -> 263A	0.01859
198A -> 265A	-0.01481
198A -> 272A	0.01115
199A -> 200A	-0.08958
199A -> 202A	-0.11925
199A -> 203A	-0.04313
199A -> 204A	-0.02272
199A -> 209A	-0.02213
199A -> 210A	-0.01550
199A -> 211A	0.01045
199A -> 212A	-0.11279
199A -> 213A	0.11226
199A -> 214A	-0.01341
199A -> 215A	-0.02243
199A -> 216A	-0.04350
199A -> 217A	-0.17477
199A -> 218A	0.05858
199A -> 219A	-0.08304
199A -> 220A	-0.02138
199A -> 221A	0.11765
199A -> 222A	-0.01873
199A -> 223A	-0.14196
199A -> 225A	-0.01683
199A -> 226A	0.05734
199A -> 227A	0.02154
199A -> 228A	0.02469
199A -> 230A	0.01640
199A -> 232A	0.01799
199A -> 233A	0.02318
199A -> 236A	0.03641
199A -> 237A	0.01977
199A -> 238A	-0.01226
199A -> 239A	-0.03500
199A -> 240A	0.02475
199A -> 242A	0.01442
199A -> 243A	0.01016
199A -> 244A	-0.02231
199A -> 246A	-0.01089
199A -> 247A	-0.01671
199A -> 248A	0.02282
199A -> 250A	-0.01457
199A -> 252A	-0.01021
199A -> 253A	0.01013
199A -> 254A	0.01627

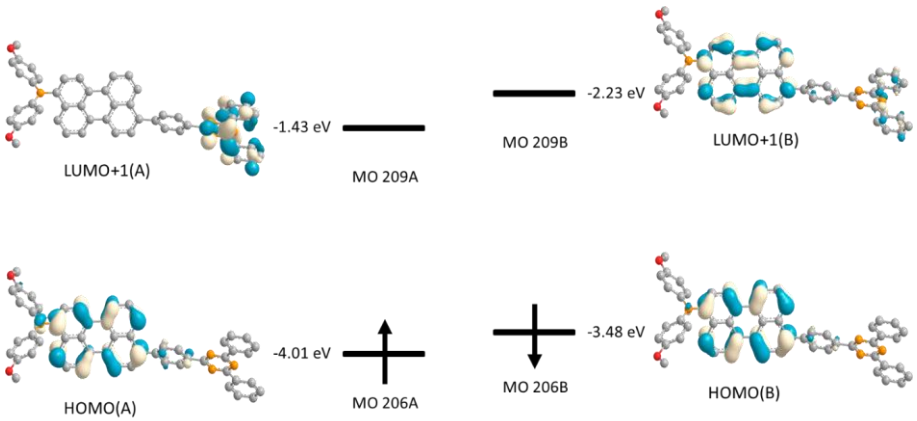
196B -> 202B	0.05515
196B -> 203B	-0.01103
196B -> 204B	0.04199
196B -> 216B	0.01745
196B -> 217B	0.01016
196B -> 219B	0.01389
196B -> 222B	-0.04033
196B -> 226B	0.01627
196B -> 228B	-0.04736
196B -> 231B	0.03462
196B -> 235B	-0.01925
196B -> 237B	-0.01311
196B -> 240B	-0.01566
196B -> 248B	-0.01756
196B -> 250B	0.01114
197B -> 200B	-0.03558
197B -> 201B	0.02713
197B -> 202B	-0.01339
197B -> 204B	-0.01403
197B -> 215B	0.01364
197B -> 216B	-0.02371
197B -> 222B	0.03332
197B -> 228B	0.02616
197B -> 231B	-0.01349
197B -> 248B	0.01016
198B -> 199B	-0.07344
198B -> 200B	-0.40366
198B -> 201B	0.74918
198B -> 202B	0.15496
198B -> 203B	-0.02294
198B -> 204B	0.07973
198B -> 206B	-0.05443
198B -> 215B	0.03345
198B -> 216B	-0.02510
198B -> 222B	0.03226
198B -> 232B	-0.01266
198B -> 235B	-0.01551
198B -> 246B	-0.01022
198B -> 255B	-0.01033
198B -> 256B	0.01025
198B -> 260B	-0.01289
198B -> 264B	-0.01350
198B -> 279B	0.01267
198B -> 284B	0.01212

Table S19. Cartesian coordinates for optimized structure for **3d**$^{\bullet-}$

Symbolic Z-matrix:
Charge = -1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.169027	0.396438	2.042733	C	-10.4254	-3.69563	-2.76947
C	5.527499	0.464763	1.753079	C	-9.60575	-2.79098	-2.10209
C	6.00268	0.156876	0.491357	C	-11.0299	2.255316	1.588895
C	5.103867	-0.23323	-0.53875	C	-11.587	3.285541	2.340365
C	5.565828	-0.58787	-1.82761	C	-10.7624	4.186514	3.012709
C	4.659928	-0.96409	-2.80376	C	-9.37703	4.051955	2.92959
C	3.292567	-0.98765	-2.54754	C	-8.81832	3.022639	2.178568
C	2.774042	-0.64057	-1.28462	O	10.67891	-3.60906	2.660149
C	1.354159	-0.63689	-1.00841	O	9.412312	4.290523	-3.04779
C	0.399373	-0.92421	-2.00882	C	10.25851	-4.94708	2.772632
C	-0.95541	-0.89657	-1.74973	C	8.695144	5.487015	-3.22671
C	-1.47201	-0.5819	-0.48498	H	3.84873	0.658351	3.044267
C	-0.5367	-0.35914	0.588358	H	6.236481	0.762429	2.522683
C	-0.95522	-0.21928	1.92811	H	6.629865	-0.56374	-2.039
C	-0.03976	0.006479	2.944479	H	5.020512	-1.24443	-3.79139
C	1.316466	0.106796	2.668006	H	2.626598	-1.29087	-3.34706
C	1.803979	-0.06394	1.362332	H	0.717183	-1.13061	-3.02443
C	0.879305	-0.34588	0.308157	H	-1.64579	-1.05802	-2.57483
C	3.229264	0.025977	1.06591	H	-2.00572	-0.32426	2.175631
C	3.695969	-0.27626	-0.24882	H	-0.38794	0.098158	3.971064
N	7.408864	0.223442	0.23211	H	1.999656	0.285759	3.490441
C	-2.92151	-0.46221	-0.33381	H	9.836395	0.597019	1.338857
C	7.916951	1.264043	-0.56361	H	11.24198	-1.14945	2.393904
C	8.238338	-0.75411	0.817898	H	8.201524	-4.07105	1.566775
C	9.486588	-0.43061	1.37247	H	6.835422	-2.3444	0.492411
C	10.27665	-1.4036	1.965848	H	9.669313	0.193926	-1.2381
C	9.83161	-2.72526	2.046203	H	10.50433	2.030233	-2.65866
C	8.584631	-3.05746	1.518676	H	7.07517	4.390858	-1.60487
C	7.804511	-2.07827	0.903895	H	6.267682	2.583638	-0.17397
C	9.110424	1.122954	-1.29352	H	-2.89872	1.321341	0.88505
C	9.581795	2.148737	-2.09768	H	-5.33896	1.53893	1.030693
C	8.866877	3.341881	-2.2216	H	-5.80777	-1.9587	-1.41003
C	7.670125	3.487386	-1.52459	H	-3.36616	-2.19571	-1.54311
C	7.20776	2.459804	-0.70184	H	-11.9844	-0.84545	-0.66634
C	-3.5296	0.581908	0.401388	H	-13.456	-2.45877	-1.8557
C	-4.90274	0.713529	0.477148	H	-12.4518	-4.28723	-3.20518
C	-5.75531	-0.19842	-0.172	H	-9.98023	-4.49313	-3.35803
C	-5.16667	-1.23889	-0.91109	H	-8.52533	-2.86963	-2.16047
C	-3.79225	-1.36319	-0.9899	H	-11.6616	1.548331	1.061689
C	-7.20513	-0.06705	-0.08352	H	-12.6674	3.385439	2.401518
N	-7.71766	0.937893	0.652586	H	-11.1978	4.990994	3.599688
C	-9.04246	1.014995	0.699245	H	-8.72903	4.750742	3.451392
N	-9.88145	0.176052	0.079345	H	-7.74207	2.907572	2.106638
C	-9.28738	-0.79273	-0.62805	H	11.06277	-5.47396	3.289399
N	-7.97462	-0.95544	-0.74203	H	9.334193	-5.03091	3.360323
C	-10.1662	-1.7601	-1.34148	H	10.1014	-5.40452	1.786207
C	-9.6413	2.116463	1.50249	H	9.282125	6.090883	-3.92135

C	-11.5574	-1.6479	-1.25839	H	7.702025	5.300854	-3.65797
C	-12.3758	-2.55381	-1.92634	H	8.57999	6.033973	-2.28054
C	-11.8123	-3.57991	-2.68358				



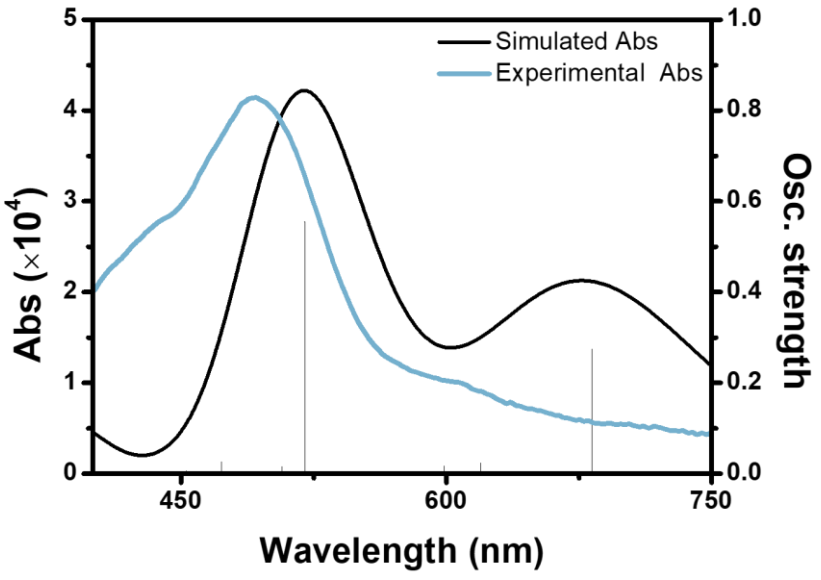


Figure S29. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3d**$^{\bullet-}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3d**$^{\bullet-}$

Table S20. TD-DFT calculation: Transition assignment of **3d**$^{\bullet-}$

Excited State 3: 2.181-?Sym 1.8172 eV 682.30 nm f=0.2746 <S**2>=0.939			
185A -> 271A	-0.01019	199B -> 209B	0.01976
186A -> 274A	0.01436	199B -> 230B	-0.01810
186A -> 298A	-0.01109	199B -> 232B	-0.02664
195A -> 209A	0.01404	199B -> 233B	0.01679
198A -> 222A	0.01728	199B -> 235B	0.01833
198A -> 223A	-0.01124	199B -> 236B	-0.01094
198A -> 225A	-0.01605	199B -> 239B	-0.01355
198A -> 244A	0.01055	199B -> 242B	0.01330
198A -> 248A	0.01018	199B -> 249B	0.01655
198A -> 254A	-0.01378	199B -> 255B	0.01152
198A -> 255A	0.01128	199B -> 256B	-0.02148
200A -> 224A	0.01562	200B -> 209B	0.01870
200A -> 225A	-0.01214	201B -> 209B	-0.01052
200A -> 232A	0.01413	201B -> 239B	-0.01111
201A -> 242A	-0.01681	201B -> 240B	-0.01241
201A -> 243A	0.01079	201B -> 241B	-0.02636
201A -> 244A	-0.01028	201B -> 242B	0.03894
201A -> 245A	-0.01223	201B -> 243B	-0.02041
202A -> 208A	-0.01717	201B -> 245B	0.02888
202A -> 210A	0.01721	201B -> 249B	0.01010
202A -> 219A	-0.01482	202B -> 224B	0.02046
202A -> 222A	-0.01686	202B -> 226B	-0.01896
202A -> 223A	0.01797	202B -> 233B	0.01159
202A -> 224A	0.03184	202B -> 234B	0.01197
202A -> 225A	-0.02497	202B -> 236B	-0.01809
202A -> 228A	-0.01519	202B -> 237B	0.01704
202A -> 229A	0.01346	202B -> 238B	-0.01739
202A -> 231A	0.01200	202B -> 239B	0.05319
202A -> 232A	0.03642	202B -> 240B	0.04524
202A -> 236A	-0.01408	202B -> 241B	-0.03216
203A -> 210A	-0.01296	202B -> 242B	-0.05230
203A -> 222A	0.01781	202B -> 244B	0.02076
203A -> 223A	-0.01237	202B -> 246B	0.01234
203A -> 224A	-0.01565	203B -> 215B	-0.01023
203A -> 225A	-0.01033	203B -> 219B	0.01264
203A -> 231A	0.01241	203B -> 224B	0.01852
203A -> 232A	0.01608	203B -> 225B	0.01793
204A -> 210A	-0.02428	203B -> 226B	-0.04896
204A -> 222A	0.02782	203B -> 227B	0.03570
204A -> 223A	-0.02063	203B -> 228B	0.01748
204A -> 224A	-0.02249	203B -> 234B	-0.01106
204A -> 229A	0.01042	203B -> 241B	0.01276
204A -> 232A	-0.02847	204B -> 208B	0.02442
205A -> 208A	0.03548	204B -> 209B	0.06310
205A -> 232A	0.01113	204B -> 210B	0.05555
206A -> 208A	0.15773	204B -> 211B	-0.01047
206A -> 210A	-0.05847	204B -> 212B	0.04317
206A -> 211A	-0.01780	204B -> 226B	0.01174
206A -> 222A	0.01832	204B -> 228B	-0.01409
206A -> 223A	-0.01301	204B -> 229B	-0.01146
206A -> 224A	-0.01228	204B -> 230B	0.02466

206A -> 225A	-0.01359
206A -> 268A	-0.01264
206A -> 269A	-0.01216
206A -> 270A	-0.01101
206A -> 271A	-0.01386
206A -> 272A	0.01281
206A -> 274A	0.01118
207A -> 208A	0.08784
207A -> 210A	0.11839
207A -> 211A	0.04292
207A -> 212A	0.02205
207A -> 217A	-0.01056
207A -> 218A	-0.01062
207A -> 219A	-0.03505
207A -> 220A	0.04903
207A -> 221A	-0.02261
207A -> 222A	-0.13722
207A -> 223A	0.06941
207A -> 224A	0.02126
207A -> 225A	0.18596
207A -> 226A	-0.02378
207A -> 228A	0.10177
207A -> 229A	-0.09538
207A -> 230A	0.03560
207A -> 231A	-0.07220
207A -> 232A	-0.11305
207A -> 236A	0.05178
207A -> 237A	0.05754
207A -> 238A	-0.01141
207A -> 241A	-0.01088
207A -> 242A	-0.02885
207A -> 244A	-0.02302
207A -> 247A	-0.01687
207A -> 248A	-0.01054
207A -> 249A	-0.04431
207A -> 252A	-0.01149
207A -> 254A	0.02708
207A -> 255A	-0.02883
207A -> 256A	0.01663
207A -> 257A	0.01254
207A -> 261A	-0.01891
207A -> 264A	0.01472
207A -> 268A	-0.01615
207A -> 271A	-0.01146
207A -> 283A	0.01218
198B -> 224B	-0.01541
204B -> 232B	0.04296
204B -> 233B	-0.03130
204B -> 234B	0.01068
204B -> 235B	-0.02861
204B -> 236B	0.01363
204B -> 239B	0.01761
204B -> 240B	0.01306
204B -> 242B	-0.02860
204B -> 248B	0.01447
204B -> 249B	-0.02156
204B -> 256B	0.01863
204B -> 257B	0.01010
204B -> 261B	-0.01343
204B -> 264B	0.01102
205B -> 208B	-0.04123
205B -> 209B	0.04331
205B -> 229B	0.01095
205B -> 230B	-0.02000
205B -> 232B	-0.02768
205B -> 233B	0.01928
205B -> 235B	0.01823
205B -> 236B	-0.01290
205B -> 256B	-0.01013
206B -> 207B	-0.06920
206B -> 208B	-0.40383
206B -> 209B	0.74908
206B -> 210B	0.15720
206B -> 211B	-0.02231
206B -> 212B	0.08465
206B -> 215B	-0.03393
206B -> 217B	0.01552
206B -> 219B	0.01643
206B -> 223B	-0.02521
206B -> 224B	0.01374
206B -> 229B	0.01007
206B -> 230B	-0.01738
206B -> 232B	-0.02440
206B -> 235B	0.01419
206B -> 239B	-0.01174
206B -> 245B	0.01556
206B -> 248B	0.01564
206B -> 261B	-0.01366
206B -> 263B	-0.01121
206B -> 270B	0.01363
206B -> 272B	-0.01358
206B -> 298B	-0.01707

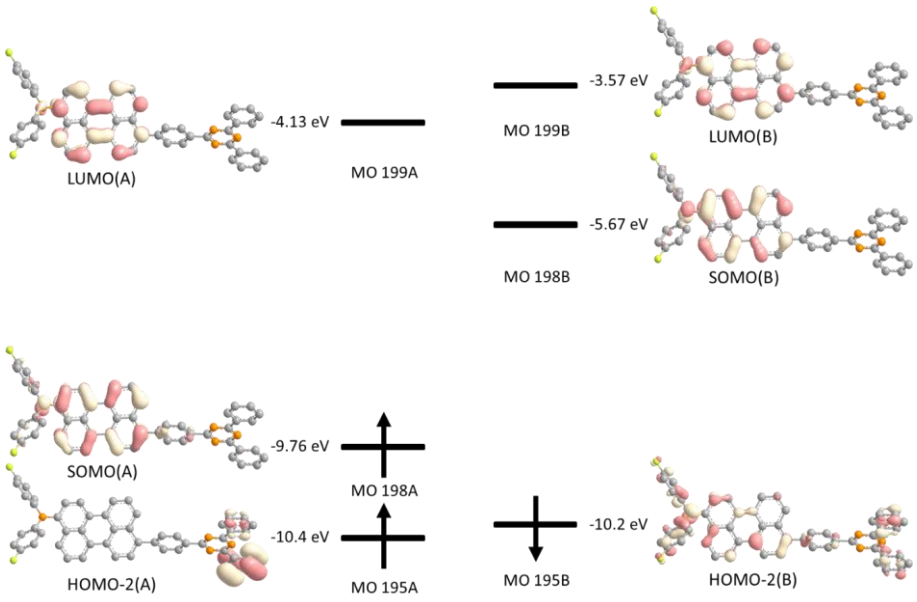
Table S21. The number of imaginary frequencies, total energies, and dipole moments for the compound **3a**$^{\bullet+}$–**3d**$^{\bullet+}$ as obtained in the geometry optimizations at ωB97XD/6-31+G method

Entry	Number of imaginary frequencies	Total energies (Eh) (Hartrees)	Doublet state dipole moment (field-independent basis, Debye)
3a$^{\bullet+}$	1	-2456.71649265	15.8004
3b$^{\bullet+}$	1	-2258.29152659	20.5553
3c$^{\bullet+}$	1	-2336.90879867	20.5266
3d$^{\bullet+}$	1	-2487.27978747	19.3941

Table S22. Cartesian coordinates for optimized structure for **3a**$^{\bullet+}$

Symbolic Z-matrix:
Charge = 1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.50031	1.280098	1.478604	C	-9.8118	-1.90943	0.833731
C	5.85107	1.140307	1.282819	C	-11.198	-1.71858	0.845443
C	6.364009	0.149977	0.420583	C	-12.0389	-2.73006	1.295946
C	5.442626	-0.81482	-0.14248	C	-11.504	-3.93911	1.738157
C	5.893711	-1.97206	-0.79473	C	-10.1234	-4.13429	1.72855
C	4.99505	-2.8911	-1.30993	C	-9.27985	-3.12486	1.278538
C	3.628967	-2.67244	-1.20454	C	-10.5951	2.739003	-0.9262
C	3.119412	-1.5552	-0.5329	C	-11.1363	3.942253	-1.36521
C	1.683616	-1.33164	-0.39666	C	-10.3008	4.955258	-1.83359
C	0.742264	-2.16544	-1.00819	C	-8.92038	4.761453	-1.86157
C	-0.62539	-1.93856	-0.89388	C	-8.37618	3.559666	-1.42263
C	-1.12185	-0.87034	-0.15992	F	9.774641	-1.02908	-4.83501
C	-0.19621	-0.02074	0.517538	F	11.26409	2.081161	3.906475
C	-0.64592	1.016256	1.368155	H	4.177142	2.09872	2.109018
C	0.251331	1.843564	2.016901	H	6.531849	1.846377	1.743962
C	1.619314	1.664758	1.842615	H	6.953655	-2.16694	-0.89364
C	2.129592	0.634444	1.035751	H	5.362147	-3.78532	-1.80274
C	1.209353	-0.24017	0.377063	H	2.961417	-3.40755	-1.63666
C	3.549211	0.440358	0.856445	H	1.059011	-3.0042	-1.61632
C	4.034962	-0.62896	0.046535	H	-1.31865	-2.59029	-1.41676
N	7.709417	0.134238	0.154056	H	-1.71067	1.150509	1.523545
C	-2.58633	-0.64275	-0.11565	H	-0.10973	2.633068	2.66758
C	8.239149	-0.16923	-1.14032	H	2.286122	2.342304	2.361357
C	8.628961	0.65239	1.1237	H	9.857191	-1.35388	-0.35323
C	9.382207	-0.96307	-1.24806	H	10.7952	-1.86985	-2.6118
C	9.909255	-1.25449	-2.50031	H	7.693568	0.453776	-4.44247
C	9.274589	-0.74431	-3.6249	H	6.758087	0.992513	-2.19021
C	8.145758	0.059085	-3.53927	H	9.474382	2.11406	-0.21494
C	7.632797	0.355556	-2.28234	H	11.08196	2.983169	1.491338
C	9.498308	1.690056	0.784293	H	9.595457	0.157673	4.351904
C	10.39611	2.176805	1.726547	H	7.989844	-0.7276	2.648135
C	10.40106	1.61262	2.995574	H	-2.49148	1.35944	-0.91528
C	9.548123	0.577323	3.353119	H	-4.94744	1.689477	-0.88841
C	8.659402	0.091327	2.401475	H	-5.47901	-2.25674	0.679765
C	-3.14084	0.568608	-0.54865	H	-3.02427	-2.60594	0.660715
C	-4.51668	0.756011	-0.54297	H	-11.6056	-0.77505	0.499488
C	-5.36583	-0.26023	-0.09672	H	-13.1137	-2.57524	1.302072
C	-4.81689	-1.47092	0.333002	H	-12.1621	-4.72846	2.089758
C	-3.44114	-1.66309	0.316458	H	-9.70439	-5.07532	2.072487
C	-6.84052	-0.05572	-0.08338	H	-8.205	-3.26904	1.26775
N	-7.30212	1.117426	-0.51335	H	-11.2379	1.945612	-0.56098
C	-8.63404	1.257701	-0.48438	H	-12.2118	4.090163	-1.34242
N	-9.47245	0.309936	-0.05896	H	-10.7251	5.89445	-2.17689
C	-8.91653	-0.83181	0.353514	H	-8.26756	5.548724	-2.22702
N	-7.59637	-1.05941	0.358212	H	-7.30353	3.400455	-1.44179
C	-9.21038	2.539676	-0.95174				



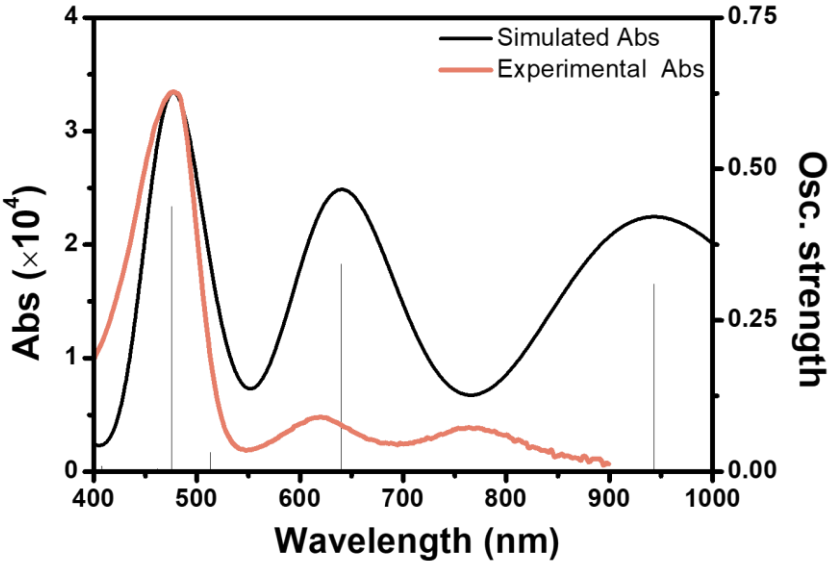


Figure S30. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3a**$^{\bullet+}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3a**$^{\bullet+}$

Table S23. TD-DFT calculation: Transition assignment of **3a**$^{\bullet+}$

Excited State 1: 2.087-?Sym 1.3141 eV 943.51 nm f=0.3097 <S**2>=0.839			
175A -> 199A	-0.02858	182B -> 200B	-0.01747
175A -> 209A	0.01043	182B -> 201B	-0.01723
182A -> 199A	0.02520	182B -> 208B	0.02339
182A -> 200A	0.03313	183B -> 198B	-0.01103
182A -> 201A	0.01935	184B -> 198B	0.04820
182A -> 207A	-0.01350	184B -> 199B	-0.02789
183A -> 200A	0.02116	184B -> 201B	-0.01056
183A -> 202A	-0.01388	184B -> 208B	0.01219
184A -> 199A	-0.02414	185B -> 198B	-0.06152
184A -> 200A	-0.02089	185B -> 202B	-0.01104
184A -> 202A	0.01332	186B -> 198B	-0.01630
184A -> 207A	0.01994	186B -> 199B	0.03163
186A -> 208A	0.01693	186B -> 200B	0.01158
187A -> 199A	-0.01318	186B -> 202B	0.01579
188A -> 199A	-0.01032	186B -> 204B	-0.01300
188A -> 206A	0.01142	186B -> 206B	-0.01666
191A -> 201A	0.01491	187B -> 198B	-0.14102
193A -> 199A	0.04353	187B -> 199B	0.05311
193A -> 201A	0.01762	187B -> 200B	-0.01688
193A -> 204A	-0.01509	187B -> 201B	0.02735
196A -> 199A	-0.01346	187B -> 202B	-0.01248
198A -> 199A	0.17842	187B -> 205B	0.02429
198A -> 200A	-0.02661	187B -> 207B	0.01370
198A -> 201A	0.01010	187B -> 208B	-0.01250
198A -> 202A	0.01182	188B -> 198B	0.02092
198A -> 203A	-0.01309	188B -> 199B	-0.06270
198A -> 206A	0.01308	188B -> 202B	-0.01416
198A -> 207A	0.01926	188B -> 206B	-0.03031
198A -> 227A	-0.01238	188B -> 208B	-0.01418
161B -> 198B	-0.01129	189B -> 199B	0.01339
164B -> 199B	0.01028	192B -> 198B	0.16056
166B -> 198B	-0.01341	192B -> 199B	0.09991
167B -> 198B	0.01305	192B -> 202B	-0.01339
167B -> 201B	-0.01378	193B -> 198B	0.07646
167B -> 205B	-0.01597	193B -> 199B	0.01155
170B -> 202B	0.01257	194B -> 198B	-0.04114
174B -> 199B	0.01047	195B -> 198B	0.82177
176B -> 198B	-0.07231	195B -> 199B	0.08013
176B -> 199B	-0.06732	195B -> 201B	0.01350
176B -> 208B	0.01398	195B -> 210B	-0.01051
176B -> 210B	0.01575	196B -> 198B	0.42682
179B -> 198B	0.05180	196B -> 199B	0.03185
179B -> 199B	0.03124	197B -> 198B	-0.02197
182B -> 198B	-0.01273		
Excited State 2: 2.291-?Sym 1.9371 eV 640.05 nm f=0.3426 <S**2>=1.063			
168A -> 199A	0.01694	167B -> 229B	-0.01452
168A -> 225A	-0.01274	170B -> 198B	-0.01392
168A -> 227A	0.02495	170B -> 199B	-0.02414
168A -> 228A	0.02159	170B -> 227B	-0.01808
168A -> 231A	-0.01082	170B -> 231B	0.01643
175A -> 199A	0.02502	170B -> 232B	0.01253

175A -> 201A	0.01307
175A -> 209A	-0.01963
175A -> 227A	0.01780
175A -> 228A	-0.01333
179A -> 199A	-0.01141
179A -> 204A	-0.01216
182A -> 199A	-0.02843
182A -> 200A	-0.05835
182A -> 201A	-0.01686
182A -> 202A	0.06493
182A -> 203A	-0.03230
182A -> 204A	0.02898
182A -> 205A	-0.01420
182A -> 206A	0.02273
182A -> 207A	0.01129
182A -> 208A	-0.01815
183A -> 199A	-0.01062
183A -> 200A	0.02067
183A -> 201A	-0.05128
183A -> 202A	-0.03586
183A -> 204A	0.01471
183A -> 207A	0.02585
183A -> 209A	0.02086
184A -> 200A	0.04324
184A -> 202A	0.01308
184A -> 204A	0.02794
184A -> 206A	-0.01309
184A -> 207A	-0.03978
185A -> 199A	-0.01258
185A -> 200A	0.01127
185A -> 201A	-0.02563
185A -> 202A	0.05507
185A -> 203A	-0.03331
185A -> 204A	0.06320
185A -> 207A	-0.01501
185A -> 209A	0.01769
186A -> 200A	0.02975
186A -> 201A	-0.02535
186A -> 203A	-0.01856
186A -> 204A	0.02159
186A -> 209A	0.01185
187A -> 200A	-0.05031
187A -> 201A	-0.01558
187A -> 203A	0.03773
187A -> 204A	0.01674
187A -> 205A	0.02735
187A -> 206A	-0.02042
187A -> 207A	-0.02459
188A -> 199A	-0.01236
188A -> 200A	0.01565
188A -> 201A	0.01022
188A -> 202A	-0.01892
188A -> 203A	0.01133
188A -> 204A	-0.01564
170B -> 238B	0.01264
170B -> 239B	-0.01152
173B -> 198B	0.01302
174B -> 198B	-0.01122
176B -> 198B	0.02996
176B -> 199B	0.01634
176B -> 200B	-0.01033
176B -> 201B	0.01309
176B -> 205B	0.01504
176B -> 210B	-0.01752
179B -> 199B	-0.01670
182B -> 198B	-0.04780
182B -> 201B	0.01945
182B -> 202B	-0.02223
182B -> 208B	-0.02237
183B -> 200B	0.01241
183B -> 208B	-0.01180
184B -> 198B	-0.01874
184B -> 200B	-0.01881
184B -> 201B	0.02318
184B -> 202B	-0.02741
184B -> 203B	-0.01099
184B -> 205B	0.01220
185B -> 198B	0.08557
185B -> 199B	0.01177
185B -> 200B	0.03394
185B -> 202B	0.03745
185B -> 203B	0.01032
185B -> 204B	-0.01583
185B -> 206B	0.01132
185B -> 208B	0.01823
186B -> 198B	-0.12238
186B -> 201B	0.02099
186B -> 202B	-0.03658
186B -> 203B	-0.01574
186B -> 205B	-0.02307
186B -> 207B	-0.02097
186B -> 208B	0.01415
187B -> 198B	-0.04882
187B -> 199B	0.02394
187B -> 200B	0.01312
187B -> 201B	-0.04519
187B -> 202B	0.02936
187B -> 203B	0.01758
187B -> 204B	0.01830
187B -> 205B	-0.03305
187B -> 206B	-0.01099
187B -> 207B	0.01386
187B -> 210B	0.01469
187B -> 214B	0.01025
188B -> 198B	0.20421
188B -> 199B	0.01079
188B -> 200B	0.01022
188B -> 201B	-0.01725

189A -> 199A	-0.03199
189A -> 202A	0.01010
190A -> 199A	-0.05347
191A -> 199A	-0.19168
191A -> 202A	0.01698
191A -> 203A	0.01110
191A -> 204A	-0.03688
191A -> 209A	0.01389
191A -> 212A	-0.01234
193A -> 199A	-0.08532
193A -> 200A	-0.04657
193A -> 201A	0.07331
193A -> 202A	-0.01393
193A -> 203A	0.02395
193A -> 204A	-0.05910
196A -> 199A	-0.04187
198A -> 199A	0.86238
198A -> 200A	0.01108
198A -> 204A	0.04098
157B -> 265B	-0.01105
161B -> 265B	-0.01056
167B -> 198B	0.01046
167B -> 228B	-0.01257
188B -> 202B	0.04425
188B -> 203B	0.01662
188B -> 205B	0.02588
188B -> 206B	0.03971
188B -> 207B	0.01589
189B -> 198B	-0.03838
189B -> 211B	-0.01320
192B -> 198B	-0.05855
192B -> 199B	-0.07078
193B -> 198B	-0.01080
193B -> 199B	-0.01778
195B -> 198B	-0.10494
195B -> 199B	-0.16362
195B -> 201B	0.01765
195B -> 202B	-0.03271
195B -> 203B	-0.01366
195B -> 205B	0.01673
195B -> 210B	-0.01141
196B -> 198B	-0.05262
196B -> 199B	-0.07882
196B -> 201B	0.01139
196B -> 202B	-0.01626

Table S24. Cartesian coordinates for optimized structure for **3b**$^{\bullet+}$

Symbolic Z-matrix:
Charge = 1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.93614	1.139538	1.606968	C	-9.35451	-2.03413	0.56244
C	6.287175	1.033585	1.396885	C	-10.1707	2.802248	-0.55623
C	6.806635	0.160257	0.417969	C	-10.7211	4.049916	-0.82775
C	5.890634	-0.73608	-0.25761	C	-9.89401	5.121643	-1.16082
C	6.349265	-1.80463	-1.04173	C	-8.51266	4.941958	-1.22147
C	5.456061	-2.66099	-1.66354	C	-7.95917	3.695737	-0.94972
C	4.088635	-2.46336	-1.53597	C	-10.742	-1.85633	0.601008
C	3.572331	-1.4366	-0.73769	C	-11.5749	-2.9245	0.914847
C	2.134558	-1.23668	-0.58015	C	-11.0307	-4.17764	1.19262
C	1.199102	-1.9894	-1.29528	C	-9.64894	-4.36001	1.155587
C	-0.17043	-1.78423	-1.15715	C	-8.81334	-3.29391	0.841981
C	-0.6731	-0.82097	-0.29467	H	4.607676	1.872636	2.332692
C	0.246954	-0.05875	0.486285	H	6.964008	1.68214	1.940792
C	-0.20923	0.862084	1.458998	H	7.410367	-1.98044	-1.16179
C	0.682795	1.605951	2.207189	H	5.828878	-3.48852	-2.25803
C	2.05245	1.457571	2.014013	H	3.425482	-3.14589	-2.05288
C	2.568871	0.538886	1.086237	H	1.521504	-2.74272	-2.00406
C	1.653696	-0.25216	0.322492	H	-0.85953	-2.36759	-1.76022
C	3.989834	0.376893	0.885361	H	-1.27488	0.970871	1.627612
C	4.48207	-0.58258	-0.049	H	0.317055	2.306391	2.950674
N	8.148749	0.190253	0.14906	H	2.714943	2.069045	2.614008
C	-2.13936	-0.60947	-0.22236	H	9.903266	2.201255	-0.00258
C	8.680992	0.038255	-1.1723	H	11.49741	2.884184	1.772323
C	9.067873	0.601013	1.171398	H	11.55585	1.659396	3.930494
C	9.931556	1.672373	0.945464	H	10.02132	-0.25545	4.310278
C	10.8252	2.049177	1.942925	H	8.431248	-0.94245	2.529697
C	10.85561	1.362251	3.156221	H	10.30911	-1.2079	-0.51567
C	9.992123	0.289401	3.371863	H	11.24961	-1.45956	-2.79769
C	9.098751	-0.09866	2.378088	H	10.14486	-0.35367	-4.72753
C	9.832055	-0.72601	-1.36406	H	8.116596	1.031972	-4.36265
C	10.35535	-0.8633	-2.64572	H	7.185931	1.295521	-2.08045
C	9.734149	-0.24299	-3.72899	H	-2.05828	1.476184	-0.76976
C	8.592694	0.531192	-3.52538	H	-4.5157	1.786148	-0.69683
C	8.067223	0.68254	-2.24643	H	-5.02047	-2.32688	0.373269
C	-2.70222	0.642279	-0.50249	H	-2.56367	-2.65541	0.307986
C	-4.07911	0.819524	-0.47044	H	-10.8063	1.962759	-0.29679
C	-4.92128	-0.24902	-0.15095	H	-11.7972	4.186717	-0.77986
C	-4.36408	-1.50011	0.124848	H	-10.3254	6.095632	-1.37325
C	-2.98715	-1.68011	0.082818	H	-7.86638	5.775096	-1.48174
C	-6.39683	-0.05674	-0.10773	H	-6.88575	3.547345	-0.99515
N	-6.867	1.160301	-0.37711	H	-11.1569	-0.87834	0.383321
C	-8.1994	1.287386	-0.32537	H	-12.6507	-2.77949	0.942682
N	-9.03121	0.286627	-0.02731	H	-11.6827	-5.01119	1.437557
C	-8.46718	-0.89639	0.227823	H	-9.22258	-5.33523	1.371464
N	-7.14596	-1.11457	0.198778	H	-7.7375	-3.42752	0.810929
C	-8.78499	2.616848	-0.61513				

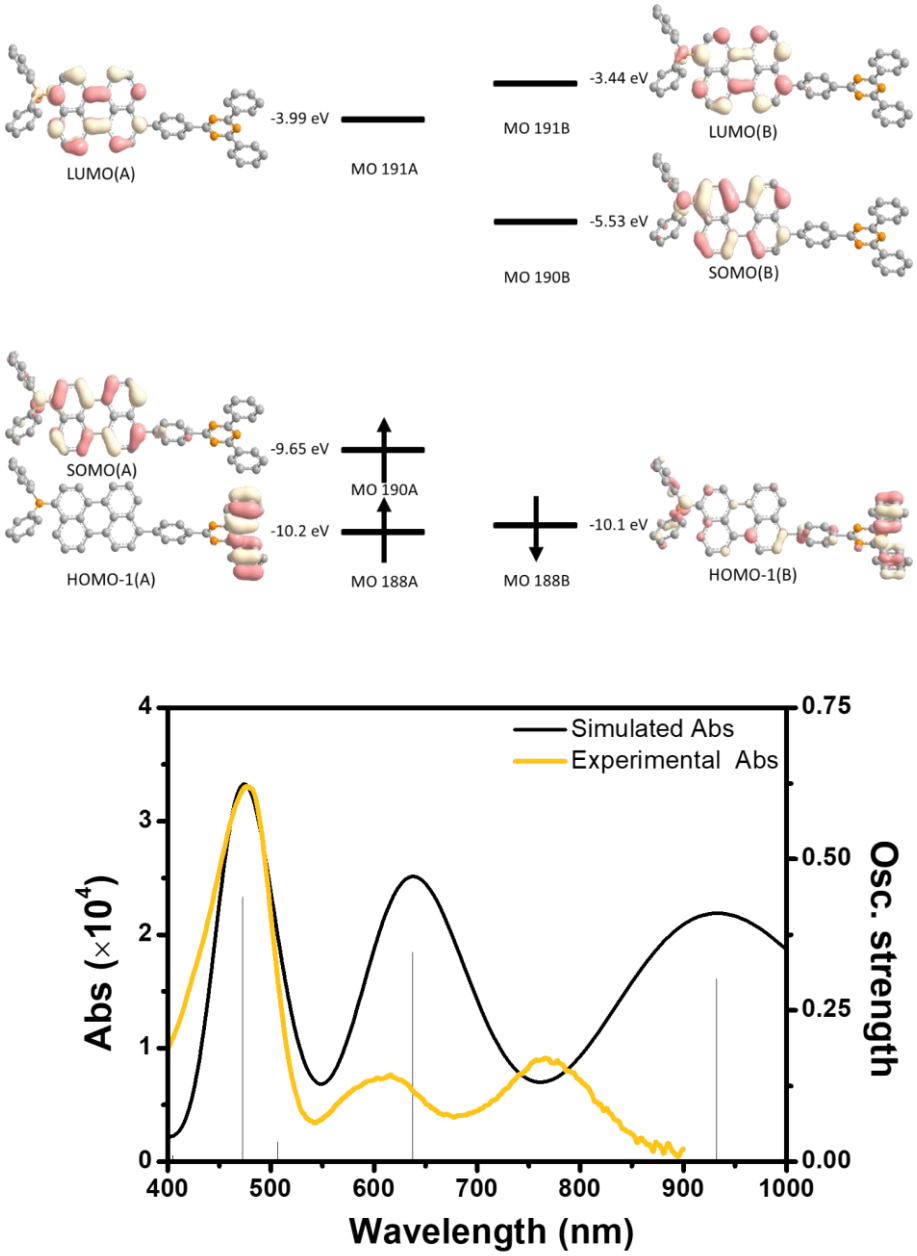


Figure S31. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of $\mathbf{3b}^{\bullet+}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of $\mathbf{3b}^{\bullet+}$

Table S25. TD-DFT calculation: Transition assignment of **3b**$^{\bullet+}$

Excited State 1:	2.088-?Sym	1.3299 eV	932.32 nm	f=0.3019	<S**2>=0.840
167A -> 191A	-0.02863		172B -> 191B	0.02926	
167A -> 201A	0.01095		174B -> 190B	0.01503	
174A -> 191A	0.02806		174B -> 193B	0.02631	
174A -> 192A	0.01327		174B -> 195B	-0.01028	
174A -> 193A	0.03593		174B -> 199B	-0.02474	
174A -> 197A	0.01224		175B -> 196B	-0.02028	
174A -> 199A	-0.01366		175B -> 197B	-0.01221	
175A -> 192A	0.02170		175B -> 198B	0.01592	
175A -> 193A	0.01751		176B -> 190B	0.08940	
175A -> 194A	-0.01408		176B -> 191B	-0.03601	
176A -> 191A	-0.01731		176B -> 192B	0.02305	
176A -> 193A	-0.01617		176B -> 195B	0.01785	
178A -> 191A	0.01111		176B -> 197B	-0.01402	
178A -> 196A	0.01099		176B -> 198B	-0.01241	
179A -> 191A	-0.01316		177B -> 190B	-0.03601	
179A -> 193A	-0.01145		177B -> 191B	0.04668	
179A -> 199A	0.01809		177B -> 193B	0.01271	
180A -> 200A	0.01976		177B -> 196B	-0.01809	
183A -> 193A	0.01376		178B -> 190B	0.02747	
183A -> 196A	-0.01292		178B -> 191B	-0.04812	
185A -> 191A	-0.04832		178B -> 192B	0.01559	
185A -> 192A	0.01922		178B -> 197B	-0.01486	
185A -> 194A	-0.01194		179B -> 190B	0.01223	
185A -> 196A	0.01657		179B -> 191B	-0.06365	
185A -> 201A	0.01030		179B -> 195B	-0.01343	
188A -> 191A	-0.01297		179B -> 196B	-0.01244	
190A -> 191A	0.18615		179B -> 197B	-0.01499	
190A -> 192A	-0.02618		179B -> 198B	0.01518	
190A -> 194A	0.01188		179B -> 199B	-0.01541	
190A -> 196A	0.01134		180B -> 190B	0.08958	
190A -> 197A	-0.01358		180B -> 191B	-0.02193	
190A -> 198A	-0.01848		180B -> 192B	0.01885	
190A -> 199A	0.01491		180B -> 195B	0.01377	
190A -> 220A	-0.01231		180B -> 199B	0.01179	
152B -> 190B	0.01174		181B -> 190B	0.01050	
155B -> 191B	0.01102		181B -> 191B	0.01441	
159B -> 190B	0.02317		184B -> 190B	0.17861	
159B -> 192B	0.01067		184B -> 191B	0.09721	
159B -> 196B	0.01020		184B -> 195B	-0.01333	
159B -> 197B	-0.01435		185B -> 190B	0.06130	
163B -> 195B	0.01348		186B -> 190B	-0.03214	
163B -> 197B	0.01375		187B -> 190B	0.62422	
166B -> 191B	0.01095		187B -> 191B	0.05998	
168B -> 190B	-0.07128		188B -> 190B	0.68402	
168B -> 191B	-0.06205		188B -> 191B	0.05305	
168B -> 199B	0.01076		188B -> 202B	-0.01069	
168B -> 202B	0.01586		189B -> 190B	-0.04823	
172B -> 190B	0.05230				
Excited State 2:	2.316-?Sym	1.9457 eV	637.22 nm	f=0.3463	<S**2>=1.091
147A -> 254A	0.01015		152B -> 257B	-0.01139	
158A -> 220A	-0.01625		159B -> 222B	0.01824	

160A -> 191A	0.01652
160A -> 219A	0.02900
160A -> 220A	0.01124
160A -> 225A	-0.01270
167A -> 191A	0.02524
167A -> 192A	-0.01131
167A -> 201A	-0.01950
167A -> 220A	0.01803
167A -> 221A	-0.01146
171A -> 191A	-0.01119
171A -> 196A	-0.01131
174A -> 191A	-0.02872
174A -> 192A	-0.04179
174A -> 193A	-0.05311
174A -> 194A	0.06310
174A -> 196A	0.05870
174A -> 198A	-0.03327
174A -> 199A	0.01168
174A -> 200A	-0.01356
175A -> 191A	-0.01720
175A -> 192A	0.04726
175A -> 193A	-0.03638
175A -> 194A	-0.03190
175A -> 195A	-0.01312
175A -> 196A	0.02904
175A -> 199A	0.02154
175A -> 200A	0.01038
175A -> 201A	0.02518
176A -> 191A	-0.01238
176A -> 192A	0.03583
176A -> 193A	0.01429
176A -> 194A	0.03281
176A -> 196A	0.07726
176A -> 197A	0.03103
176A -> 199A	-0.02979
176A -> 201A	0.01812
177A -> 196A	-0.01191
178A -> 192A	0.03960
178A -> 193A	0.04379
178A -> 196A	0.01720
178A -> 197A	-0.04220
178A -> 198A	-0.03361
178A -> 199A	0.01282
179A -> 191A	-0.01471
179A -> 193A	0.02713
179A -> 194A	-0.01785
179A -> 196A	-0.03135
179A -> 199A	-0.01231
180A -> 192A	0.01298
180A -> 194A	-0.01249
181A -> 191A	-0.03105
182A -> 191A	-0.03981
183A -> 191A	-0.18306
183A -> 193A	-0.01097
163B -> 190B	-0.01470
163B -> 191B	-0.02190
163B -> 220B	-0.01977
163B -> 226B	-0.01369
163B -> 227B	-0.01388
163B -> 229B	-0.01326
163B -> 231B	-0.01199
165B -> 190B	0.01064
166B -> 190B	-0.01233
168B -> 190B	0.02720
168B -> 191B	0.01470
168B -> 192B	-0.01483
168B -> 197B	0.01446
168B -> 202B	-0.01768
168B -> 222B	-0.01102
172B -> 191B	-0.01637
174B -> 190B	0.05130
174B -> 193B	-0.02289
174B -> 195B	0.02583
174B -> 199B	0.02146
174B -> 200B	-0.01017
176B -> 190B	-0.04512
176B -> 191B	-0.01533
176B -> 192B	-0.04982
176B -> 194B	0.01055
176B -> 195B	-0.05698
176B -> 196B	-0.01291
176B -> 198B	0.01250
176B -> 202B	-0.01144
176B -> 206B	-0.01022
177B -> 190B	-0.10909
177B -> 195B	-0.02332
177B -> 197B	-0.03291
177B -> 198B	-0.01105
177B -> 199B	0.01876
178B -> 190B	0.08325
178B -> 193B	0.03158
178B -> 196B	-0.02100
178B -> 197B	0.01996
178B -> 198B	-0.02059
178B -> 199B	0.01894
179B -> 190B	0.20762
179B -> 191B	0.01215
179B -> 192B	0.01998
179B -> 194B	-0.01159
179B -> 195B	0.04978
179B -> 197B	0.05216
179B -> 199B	-0.01065
180B -> 191B	-0.01980
180B -> 192B	-0.02620
180B -> 193B	0.01247
180B -> 195B	-0.03309
180B -> 196B	-0.01644
181B -> 190B	-0.03968

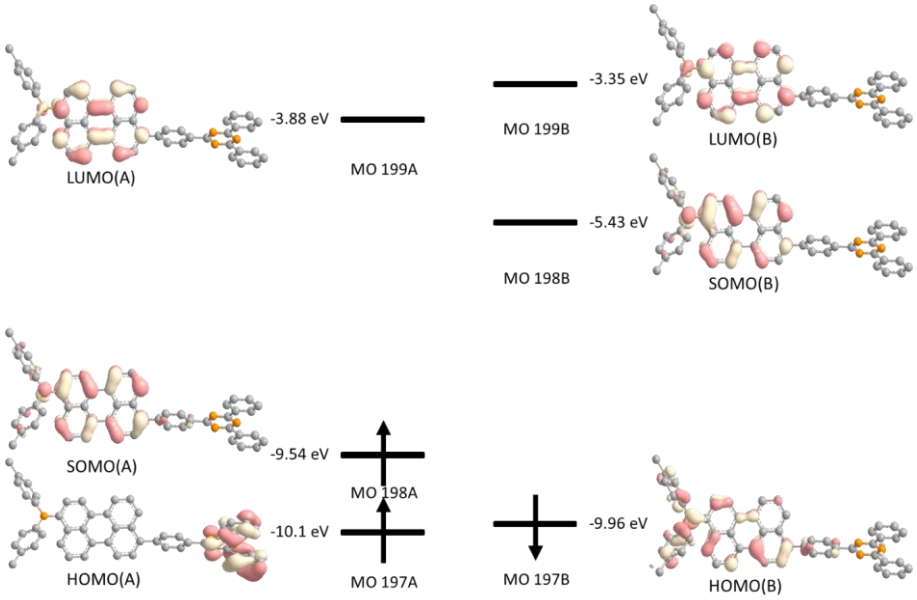
183A -> 194A	0.02678	181B -> 195B	-0.01137
183A -> 196A	-0.03473	181B -> 203B	-0.01328
183A -> 201A	0.01448	184B -> 190B	-0.05946
183A -> 204A	-0.01193	184B -> 191B	-0.07298
185A -> 191A	0.07069	184B -> 192B	0.01291
185A -> 192A	0.08126	184B -> 197B	-0.01025
185A -> 193A	-0.02907	185B -> 191B	-0.01538
185A -> 195A	-0.01270	187B -> 190B	-0.08316
185A -> 196A	0.06437	187B -> 191B	-0.13322
185A -> 197A	0.01416	187B -> 195B	-0.02954
185A -> 201A	0.01045	187B -> 196B	-0.01257
188A -> 191A	-0.03529	188B -> 190B	-0.08860
190A -> 191A	0.86380	188B -> 191B	-0.13827
190A -> 192A	0.01339	188B -> 192B	-0.01311
190A -> 194A	-0.01683	188B -> 195B	-0.03048
190A -> 196A	0.04145	188B -> 196B	-0.01315
190A -> 197A	0.01197		

Table S26. Cartesian coordinates for optimized structure for **3c**$^{\bullet+}$

Symbolic Z-matrix:
Charge = 1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.489272	1.281403	1.479125	C	-11.5005	-3.91604	1.826207
C	5.839675	1.140949	1.288243	C	-10.1196	-4.10879	1.813019
C	6.355591	0.155355	0.41947	C	-9.28016	-3.1056	1.341757
C	5.434183	-0.80727	-0.15197	C	-10.6157	2.718115	-0.95678
C	5.886567	-1.96208	-0.80667	C	-11.1605	3.913063	-1.41371
C	4.988053	-2.88056	-1.32209	C	-10.3284	4.919622	-1.90165
C	3.621312	-2.66327	-1.21626	C	-8.94777	4.72763	-1.93121
C	3.111469	-1.54778	-0.54457	C	-8.39998	3.534107	-1.47442
C	1.673344	-1.32418	-0.40986	C	11.40818	2.104212	4.078312
C	0.734256	-2.15496	-1.02393	C	9.888614	-1.0707	-5.00972
C	-0.63522	-1.92786	-0.91032	H	4.164295	2.097371	2.111961
C	-1.13144	-0.86291	-0.17485	H	6.520693	1.843974	1.753561
C	-0.20677	-0.01276	0.503111	H	6.946613	-2.15456	-0.90905
C	-0.65748	1.027579	1.350561	H	5.355741	-3.77372	-1.8165
C	0.238672	1.853564	1.999445	H	2.954045	-3.39845	-1.64884
C	1.60829	1.671993	1.82898	H	1.051393	-2.99281	-1.63322
C	2.118548	0.641194	1.025602	H	-1.32794	-2.57953	-1.43417
C	1.198544	-0.23309	0.364835	H	-1.72257	1.164686	1.501145
C	3.539536	0.445338	0.849929	H	-0.12227	2.64543	2.647427
C	4.026557	-0.62243	0.036854	H	2.274485	2.350151	2.347754
N	7.698105	0.146245	0.156619	H	9.512387	2.082859	-0.20007
C	-2.59724	-0.63727	-0.12685	H	11.09508	2.92723	1.499378
C	8.234759	-0.16396	-1.13336	H	9.509394	0.152817	4.365298
C	8.616153	0.649832	1.135194	H	7.928166	-0.69832	2.665408
C	9.51365	1.664474	0.802144	H	9.851417	-1.34191	-0.33603
C	10.40206	2.132051	1.761638	H	10.78608	-1.87391	-2.56023
C	10.41827	1.603921	3.059011	H	7.683919	0.436495	-4.42012
C	9.51168	0.585455	3.368472	H	6.753998	0.980643	-2.19971
C	8.618861	0.103078	2.417435	H	-2.50881	1.353396	-0.95372
C	9.378339	-0.95604	-1.23441	H	-4.96537	1.68047	-0.9213
C	9.898196	-1.25116	-2.48844	H	-5.48369	-2.24389	0.705535
C	9.298779	-0.76701	-3.65728	H	-3.02792	-2.58869	0.680571
C	8.160184	0.035585	-3.52928	H	-11.6139	-0.77352	0.534638
C	7.632591	0.346927	-2.28172	H	-13.1148	-2.56258	1.375083
C	-3.15585	0.566523	-0.57466	H	-12.1554	-4.7005	2.194432
C	-4.53191	0.752351	-0.56497	H	-9.69702	-5.04308	2.17078
C	-5.37768	-0.25862	-0.10035	H	-8.20508	-3.24781	1.328106
C	-4.82466	-1.46189	0.34449	H	-11.2557	1.929689	-0.57622
C	-3.44841	-1.6517	0.324925	H	-12.2362	4.059512	-1.3896
C	-6.85214	-0.05624	-0.08331	H	-10.7555	5.852346	-2.2589
N	-7.31862	1.108915	-0.53044	H	-8.29748	5.509835	-2.31177
C	-8.65027	1.247345	-0.49755	H	-7.32716	3.376143	-1.49453
N	-9.48561	0.305846	-0.05248	H	11.51588	3.192031	4.026264
C	-8.92533	-0.8278	0.376267	H	11.10566	1.839431	5.095178
N	-7.6052	-1.05342	0.378394	H	12.39779	1.667382	3.900644
C	-9.81653	-1.89887	0.879057	H	10.31796	-2.07658	-5.04053
C	-9.23075	2.520669	-0.98389	H	9.136975	-0.99559	-5.80063

C	-11.203	-1.71039	0.894456	H	10.69152	-0.3628	-5.24689
C	-12.0398	-2.7156	1.366224				



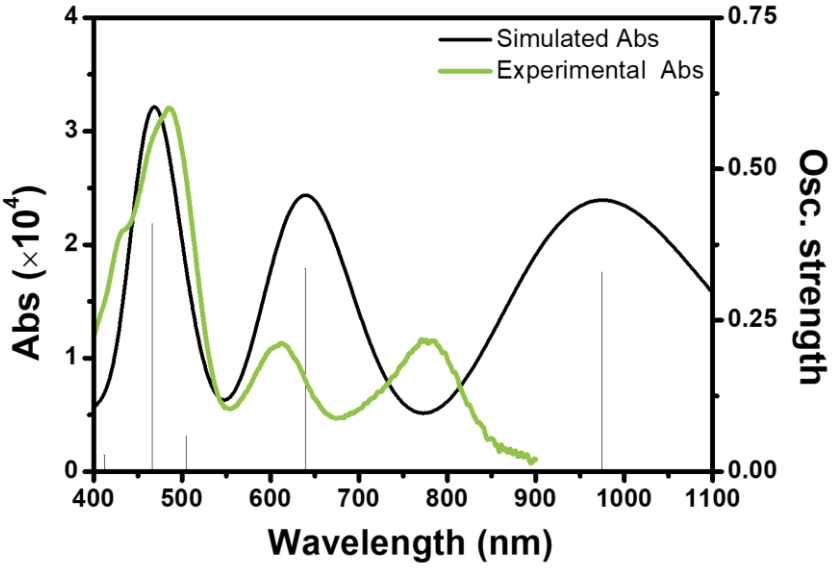


Figure S32. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3c**$^{\bullet+}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3c**$^{\bullet+}$

Table S27. TD-DFT calculation: Transition assignment of **3c**$^{\bullet+}$

Excited State 1: 2.089-?Sym 1.2716 eV 975.06 nm f=0.3301 <S**2>=0.841			
150A -> 199A	0.01087	182B -> 198B	-0.01400
175A -> 199A	-0.02966	182B -> 201B	-0.02714
175A -> 209A	0.01054	182B -> 207B	-0.02548
182A -> 199A	0.02651	183B -> 198B	0.04772
182A -> 200A	0.01257	183B -> 203B	0.01342
182A -> 201A	0.04018	183B -> 206B	-0.01260
182A -> 205A	-0.01166	184B -> 198B	0.05859
182A -> 206A	0.01186	184B -> 199B	-0.02269
182A -> 207A	-0.01393	184B -> 200B	0.01287
183A -> 200A	-0.01871	184B -> 203B	0.01348
183A -> 201A	-0.01748	184B -> 207B	-0.01040
183A -> 203A	0.01211	185B -> 198B	0.01319
184A -> 199A	0.01680	185B -> 199B	-0.02229
184A -> 201A	0.01309	185B -> 200B	0.01275
185A -> 207A	-0.01868	185B -> 205B	-0.01459
187A -> 208A	0.01959	185B -> 207B	-0.01124
188A -> 206A	-0.01105	186B -> 198B	0.03430
192A -> 201A	-0.01221	186B -> 199B	-0.07698
192A -> 204A	0.01089	186B -> 201B	-0.01162
193A -> 199A	-0.04245	186B -> 203B	-0.01135
193A -> 200A	0.01797	186B -> 204B	-0.01420
193A -> 203A	-0.01556	187B -> 198B	-0.10808
193A -> 204A	0.01808	187B -> 199B	0.04157
196A -> 199A	-0.01221	187B -> 200B	-0.02355
198A -> 199A	-0.17130	187B -> 203B	-0.01729
198A -> 200A	0.02585	187B -> 205B	0.01490
198A -> 201A	0.01035	187B -> 207B	0.01428
198A -> 204A	-0.01236	188B -> 199B	-0.03531
198A -> 205A	-0.01231	188B -> 204B	0.02393
198A -> 206A	0.01545	188B -> 205B	-0.01179
198A -> 207A	-0.01268	188B -> 206B	0.03150
198A -> 229A	0.01112	188B -> 207B	0.01303
159B -> 198B	-0.01353	189B -> 199B	0.01533
163B -> 199B	0.01062	192B -> 198B	-0.12894
167B -> 198B	0.02101	192B -> 199B	-0.09124
171B -> 203B	0.01514	192B -> 203B	0.01403
171B -> 205B	0.01534	193B -> 198B	0.03196
174B -> 199B	0.01097	194B -> 198B	-0.01679
177B -> 198B	-0.06443	195B -> 198B	0.15406
177B -> 199B	-0.05359	195B -> 199B	0.02331
177B -> 210B	-0.01442	197B -> 198B	0.92672
180B -> 198B	0.07553	197B -> 199B	0.08557
180B -> 199B	0.04695	197B -> 200B	-0.01093
180B -> 210B	0.01051	197B -> 210B	0.01353
Excited State 2: 2.377-?Sym 1.9397 eV 639.18 nm f=0.3358 <S**2>=1.163			
153A -> 266A	0.01462	163B -> 198B	0.01006
163A -> 229A	0.01161	165B -> 198B	-0.01111
167A -> 199A	0.01469	165B -> 230B	0.01045
167A -> 227A	-0.01816	167B -> 230B	0.01058
167A -> 229A	0.02349	171B -> 198B	0.01605
167A -> 233A	0.01204	171B -> 199B	0.02006

168A -> 227A	0.01423
174A -> 204A	-0.01001
175A -> 199A	-0.02411
175A -> 200A	0.01571
175A -> 209A	0.02054
175A -> 228A	0.01066
175A -> 229A	-0.01673
179A -> 199A	0.01379
182A -> 199A	0.02975
182A -> 200A	0.02766
182A -> 201A	0.06044
182A -> 202A	-0.03112
182A -> 203A	-0.03597
182A -> 204A	-0.07117
182A -> 206A	0.03293
182A -> 207A	-0.01380
182A -> 208A	0.01384
183A -> 200A	0.04264
183A -> 201A	-0.02500
183A -> 202A	-0.02381
183A -> 203A	-0.04994
183A -> 204A	-0.01071
183A -> 205A	0.01161
183A -> 207A	0.02912
183A -> 209A	0.01706
184A -> 199A	-0.01313
184A -> 200A	0.05084
184A -> 201A	0.01144
184A -> 204A	0.08811
184A -> 205A	-0.02567
184A -> 207A	-0.02490
184A -> 209A	0.02427
185A -> 201A	0.01234
185A -> 204A	-0.02573
185A -> 206A	0.01252
185A -> 207A	-0.01205
186A -> 200A	0.03493
186A -> 201A	0.04923
186A -> 204A	0.01522
186A -> 205A	0.04489
186A -> 206A	-0.03013
186A -> 207A	0.01398
187A -> 200A	-0.01416
187A -> 203A	0.01401
188A -> 199A	0.01765
188A -> 201A	-0.01616
188A -> 204A	0.02336
189A -> 199A	0.02563
190A -> 199A	0.02255
192A -> 199A	-0.18016
192A -> 200A	0.01603
192A -> 201A	-0.01486
192A -> 202A	0.01205
192A -> 203A	0.02398
171B -> 228B	0.01185
171B -> 229B	-0.01645
171B -> 234B	0.01404
171B -> 235B	0.01457
171B -> 236B	0.01105
171B -> 240B	-0.01201
171B -> 243B	-0.01248
174B -> 198B	0.01534
177B -> 198B	-0.02985
177B -> 200B	0.01532
177B -> 204B	-0.01129
177B -> 205B	-0.01584
177B -> 210B	-0.01563
180B -> 198B	0.01486
180B -> 199B	0.01836
180B -> 200B	-0.01061
180B -> 210B	0.01320
182B -> 198B	0.05410
182B -> 201B	-0.02266
182B -> 203B	0.02913
182B -> 206B	-0.01233
182B -> 207B	-0.02102
182B -> 208B	-0.01002
183B -> 198B	0.06704
183B -> 199B	0.01571
183B -> 200B	0.03219
183B -> 203B	0.04993
183B -> 205B	0.01003
183B -> 206B	-0.01302
184B -> 198B	0.01872
184B -> 199B	0.01643
184B -> 200B	0.02803
184B -> 203B	0.04012
184B -> 205B	-0.01363
185B -> 198B	-0.01908
185B -> 199B	0.01056
185B -> 200B	0.01237
185B -> 201B	-0.02960
185B -> 203B	0.02281
185B -> 204B	-0.01953
185B -> 206B	0.01678
185B -> 207B	0.02513
186B -> 198B	-0.19157
186B -> 200B	-0.01174
186B -> 203B	-0.04283
186B -> 204B	-0.01935
186B -> 205B	-0.05167
186B -> 206B	0.01312
186B -> 207B	-0.01491
187B -> 198B	0.05167
187B -> 199B	-0.03326
187B -> 200B	-0.02837
187B -> 201B	0.01338
187B -> 203B	-0.03913

192A -> 204A	-0.01758	187B -> 204B	0.02232
192A -> 209A	0.01662	187B -> 205B	0.01779
192A -> 212A	-0.01305	188B -> 198B	-0.10480
193A -> 199A	-0.14103	188B -> 203B	-0.02250
193A -> 200A	-0.07687	188B -> 205B	-0.02573
193A -> 201A	0.01597	188B -> 206B	0.02112
193A -> 203A	0.02742	189B -> 198B	0.03731
193A -> 204A	-0.06736	189B -> 203B	0.01102
193A -> 205A	0.01661	189B -> 211B	0.01319
194A -> 200A	-0.01324	192B -> 198B	-0.06907
196A -> 199A	0.02022	192B -> 199B	-0.05502
196A -> 200A	-0.01287	192B -> 200B	0.01843
198A -> 199A	0.85350	192B -> 205B	-0.01354
198A -> 200A	0.01327	193B -> 199B	0.01002
198A -> 202A	-0.01001	195B -> 198B	0.02152
198A -> 203A	-0.02366	195B -> 199B	0.04195
198A -> 204A	0.04205	197B -> 198B	0.10357
198A -> 205A	-0.01229	197B -> 199B	0.22692
156B -> 268B	-0.01074	197B -> 203B	0.04405
156B -> 270B	-0.01210	197B -> 204B	-0.01249

Table S28. Cartesian coordinates for optimized structure for **3d**$^{\bullet+}$

Symbolic Z-matrix:
Charge = 1 Multiplicity = 2

Atom	X	Y	Z	Atom	X	Y	Z
C	4.098477	-1.83832	0.610646	C	-10.5076	-0.01131	-4.49887
C	5.448867	-1.60184	0.559089	C	-9.66987	0.011052	-3.38938
C	5.963481	-0.42299	-0.01931	C	-11.0096	-0.27935	2.864701
C	5.042277	0.483136	-0.67633	C	-11.554	-0.35452	4.142019
C	5.491732	1.54456	-1.47704	C	-10.7219	-0.32073	5.260115
C	4.591133	2.373192	-2.12128	C	-9.34149	-0.21156	5.097047
C	3.223266	2.184434	-1.96602	C	-8.79409	-0.13675	3.821116
C	2.717694	1.130051	-1.20312	O	10.91788	-4.41502	0.182393
C	1.277729	0.918598	-1.04412	O	9.469437	4.869113	0.892065
C	0.339123	1.820419	-1.54222	C	10.92496	-5.43687	-0.8016
C	-1.03171	1.621975	-1.37934	C	8.916256	5.792001	1.816115
C	-1.52513	0.511066	-0.71673	H	3.774192	-2.73445	1.12404
C	-0.59879	-0.456	-0.22188	H	6.132025	-2.29684	1.034005
C	-1.0469	-1.65893	0.376134	H	6.551282	1.722572	-1.60713
C	-0.14921	-2.58829	0.85852	H	4.956343	3.179773	-2.74871
C	1.22146	-2.35205	0.767623	H	2.55362	2.866085	-2.47584
C	1.727495	-1.19267	0.166755	H	0.654965	2.722793	-2.0522
C	0.805591	-0.23579	-0.36445	H	-1.72547	2.368505	-1.75414
C	3.150521	-0.94126	0.07362	H	-2.11164	-1.85479	0.439027
C	3.635307	0.231214	-0.58352	H	-0.50718	-3.5084	1.308638
N	7.31081	-0.18637	0.065481	H	1.889321	-3.10481	1.168163
C	-2.99123	0.368836	-0.53224	H	9.240075	-0.63307	1.872632
C	7.848284	1.114653	0.301688	H	10.82564	-2.54715	1.870042
C	8.222774	-1.28489	0.083954	H	8.989834	-4.05171	-1.72104
C	9.189308	-1.38673	1.092562	H	7.429717	-2.15431	-1.71586
C	10.07352	-2.44765	1.094631	H	9.460018	0.873083	-1.11241
C	10.01178	-3.42618	0.088413	H	10.38323	3.144869	-0.7032
C	9.050521	-3.32053	-0.92358	H	7.285786	3.867804	2.196429
C	8.165351	-2.24685	-0.92157	H	6.384349	1.620561	1.793747
C	8.987574	1.5365	-0.39396	H	-2.90384	0.308836	1.622139
C	9.503682	2.798467	-0.1709	H	-5.35934	0.135635	1.906627
C	8.89284	3.66167	0.753078	H	-5.87611	0.253517	-2.3406
C	7.764136	3.231742	1.460957	H	-3.42056	0.426501	-2.64308
C	7.253878	1.957098	1.236301	H	-12.0067	-0.20927	-0.93433
C	-3.55056	0.283095	0.748858	H	-13.5047	-0.24908	-2.913
C	-4.92629	0.192147	0.913928	H	-12.5422	-0.12206	-5.19767
C	-5.77158	0.177996	-0.19911	H	-10.0836	0.044423	-5.49716
C	-5.21797	0.266033	-1.4787	H	-8.59457	0.083751	-3.51109
C	-3.84182	0.366654	-1.64298	H	-11.6493	-0.30436	1.989405
C	-7.2454	0.073691	-0.02247	H	-12.6295	-0.43932	4.265759
N	-7.71307	0.001948	1.223251	H	-11.1488	-0.37899	6.25729
C	-9.04423	-0.08944	1.335046	H	-8.69115	-0.18419	5.966443
N	-9.87924	-0.11238	0.293602	H	-7.72151	-0.05097	3.684701
C	-9.31798	-0.03697	-0.91568	H	11.73041	-6.1129	-0.51758
N	-7.99835	0.058421	-1.12164	H	9.974366	-5.9829	-0.80842
C	-10.208	-0.0604	-2.09974	H	11.12835	-5.02334	-1.79621
C	-9.62492	-0.1701	2.695767	H	9.539437	6.683017	1.750931

C	-11.5945	-0.15436	-1.93589	H	7.884253	6.047035	1.547828
C	-12.4296	-0.17628	-3.0474	H	8.951842	5.395291	2.837422
C	-11.8885	-0.10491	-4.33029				

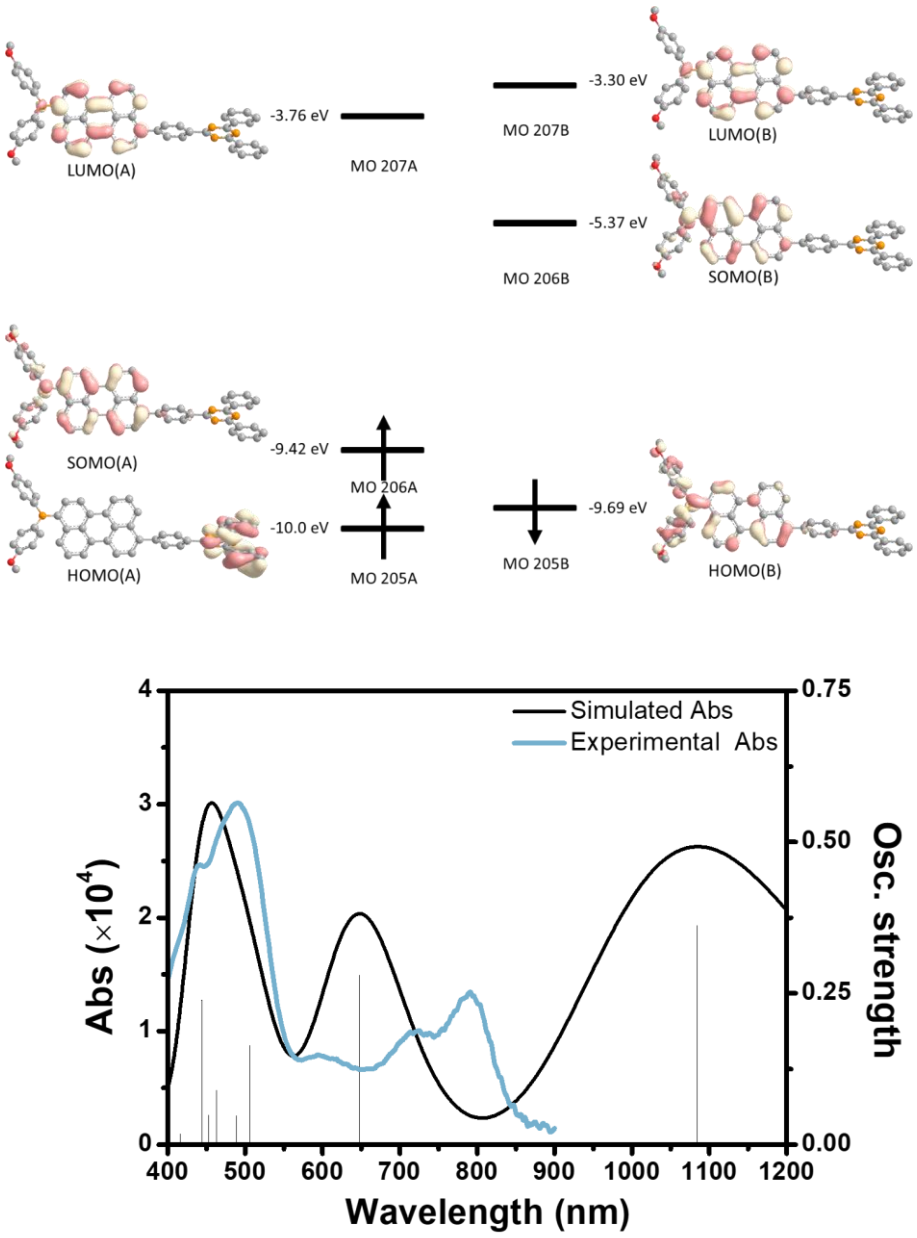


Figure S33. (Up): Energy levels and isodensity plots (isodensity contour = 0.035 a.u.) of **3d**$^{\bullet+}$ (Down): Electronic transition of the simulated/SEC experimental absorption spectra of **3d**$^{\bullet+}$

Table S29. TD-DFT calculation: Transition assignment of **3d**$^{\bullet+}$

Excited State 1: 2.075-?Sym 1.1431 eV 1084.60 nm f=0.3624 <S**2>=0.826			
185A -> 207A	0.02348	186B -> 207B	0.02819
188A -> 207A	0.01484	189B -> 206B	0.11015
190A -> 207A	-0.01784	189B -> 207B	-0.06534
190A -> 208A	0.02118	189B -> 215B	-0.01292
190A -> 209A	0.03055	189B -> 218B	0.01263
190A -> 214A	0.01383	190B -> 206B	-0.01010
191A -> 208A	-0.01749	190B -> 209B	0.02350
191A -> 211A	0.01357	190B -> 215B	0.02104
192A -> 207A	-0.01648	191B -> 212B	-0.01011
192A -> 208A	0.01211	191B -> 215B	-0.01059
192A -> 209A	0.01860	192B -> 206B	-0.02803
192A -> 214A	0.01218	192B -> 207B	0.01171
192A -> 215A	-0.01728	193B -> 206B	-0.04860
193A -> 207A	-0.01502	193B -> 207B	0.03620
193A -> 209A	0.01029	193B -> 211B	0.01650
194A -> 216A	-0.01381	193B -> 215B	-0.01137
198A -> 214A	-0.01172	194B -> 207B	0.04181
200A -> 207A	-0.01478	194B -> 211B	0.01159
200A -> 209A	-0.01079	194B -> 215B	-0.01876
203A -> 207A	0.02399	195B -> 206B	-0.11478
203A -> 209A	-0.01341	195B -> 207B	-0.07600
203A -> 211A	-0.01560	195B -> 208B	0.02885
203A -> 212A	0.01813	195B -> 211B	0.02024
204A -> 207A	0.01761	195B -> 213B	-0.01824
206A -> 207A	0.14671	195B -> 215B	-0.01396
206A -> 208A	0.02666	196B -> 207B	0.01475
206A -> 211A	-0.01328	199B -> 206B	0.01715
206A -> 213A	-0.01300	199B -> 207B	-0.01323
206A -> 214A	0.01203	199B -> 212B	0.01644
163B -> 206B	-0.01594	199B -> 214B	0.04550
167B -> 206B	0.01066	200B -> 206B	0.08299
174B -> 213B	0.01197	200B -> 207B	-0.08300
175B -> 213B	-0.01079	200B -> 211B	0.01435
176B -> 211B	-0.01555	201B -> 206B	0.01746
177B -> 213B	0.01092	203B -> 206B	0.05583
178B -> 211B	-0.01439	203B -> 207B	-0.01417
179B -> 206B	0.01096	205B -> 206B	0.95097
182B -> 207B	0.01190	205B -> 207B	-0.08264
186B -> 206B	-0.03395	205B -> 218B	0.01119
Excited State 2: 2.523-?Sym 1.9142 eV 647.72 nm f=0.2803 <S**2>=1.342			
165A -> 277A	0.01120	204A -> 211A	-0.01481
170A -> 239A	-0.01107	204A -> 212A	0.02949
173A -> 207A	-0.01648	206A -> 207A	0.81122
173A -> 236A	0.01825	206A -> 208A	-0.01206
173A -> 238A	-0.01043	206A -> 211A	0.02922
173A -> 239A	0.01562	206A -> 212A	-0.04801
173A -> 240A	-0.01138	166B -> 278B	0.01467
173A -> 242A	0.02028	170B -> 241B	0.01124
173A -> 244A	0.01035	174B -> 206B	0.01244
174A -> 239A	0.01221	175B -> 206B	-0.01264
174A -> 240A	0.01088	175B -> 241B	0.01153

182A -> 207A	-0.01127
182A -> 212A	0.01016
185A -> 207A	-0.01707
185A -> 208A	-0.01831
185A -> 209A	0.01066
185A -> 211A	0.01241
185A -> 212A	-0.01192
185A -> 218A	0.01795
185A -> 223A	0.01002
185A -> 239A	0.01138
188A -> 207A	-0.01991
188A -> 218A	0.01236
188A -> 239A	0.01186
190A -> 207A	0.02486
190A -> 208A	-0.03078
190A -> 209A	-0.04503
190A -> 211A	0.02909
190A -> 212A	0.05607
190A -> 213A	0.02795
190A -> 214A	-0.02571
190A -> 216A	0.01567
191A -> 207A	0.01673
191A -> 208A	-0.01525
191A -> 209A	0.02471
191A -> 211A	0.05392
191A -> 212A	0.05265
191A -> 213A	0.02558
191A -> 214A	0.01995
191A -> 215A	-0.03421
192A -> 208A	-0.02608
192A -> 209A	-0.03062
192A -> 211A	0.02290
192A -> 212A	0.03586
192A -> 213A	0.01617
192A -> 214A	-0.02226
192A -> 215A	0.01006
193A -> 208A	-0.05802
193A -> 209A	0.01350
193A -> 211A	0.02641
193A -> 212A	-0.08481
193A -> 215A	0.01527
193A -> 218A	0.02193
193A -> 223A	0.01441
194A -> 208A	0.03444
194A -> 211A	-0.03104
194A -> 212A	0.01540
195A -> 208A	0.03731
195A -> 209A	0.03489
195A -> 211A	-0.01429
195A -> 213A	0.04863
195A -> 214A	-0.03655
195A -> 215A	0.01729
196A -> 207A	0.02472
197A -> 207A	0.01622
176B -> 236B	0.01014
176B -> 242B	0.01373
176B -> 244B	0.01122
176B -> 246B	0.01214
176B -> 251B	-0.01158
177B -> 206B	0.01367
182B -> 206B	0.02180
186B -> 206B	0.02574
186B -> 208B	0.01003
186B -> 211B	0.01027
186B -> 213B	-0.01523
189B -> 206B	-0.03809
189B -> 207B	0.01618
189B -> 208B	-0.02298
189B -> 211B	-0.01053
189B -> 213B	0.02641
189B -> 218B	-0.01858
189B -> 223B	-0.01466
190B -> 206B	-0.05316
190B -> 209B	-0.02261
190B -> 211B	0.03302
190B -> 213B	0.01321
190B -> 215B	-0.01513
190B -> 216B	0.01305
191B -> 209B	0.01155
191B -> 215B	0.01500
192B -> 206B	0.04369
192B -> 207B	-0.01242
192B -> 208B	-0.01300
192B -> 211B	-0.03018
192B -> 213B	-0.01018
193B -> 206B	0.10806
193B -> 207B	-0.01881
193B -> 208B	-0.02969
193B -> 209B	-0.01428
193B -> 211B	-0.06569
193B -> 212B	-0.02418
193B -> 213B	-0.02669
193B -> 214B	0.01589
193B -> 216B	-0.01312
194B -> 206B	0.10298
194B -> 208B	-0.01278
194B -> 209B	0.02558
194B -> 211B	-0.04777
194B -> 212B	0.01696
194B -> 213B	-0.04117
194B -> 215B	-0.03967
195B -> 206B	-0.14572
195B -> 207B	-0.06632
195B -> 208B	-0.02738
195B -> 209B	0.01728
195B -> 211B	-0.04155
195B -> 212B	0.01775
195B -> 213B	0.04778

198A -> 207A	0.03489	195B -> 223B	-0.01402
198A -> 212A	-0.01340	196B -> 206B	0.03005
200A -> 207A	-0.16136	196B -> 219B	-0.01111
200A -> 208A	-0.02797	199B -> 206B	-0.05250
200A -> 209A	0.02501	199B -> 207B	0.01009
200A -> 211A	-0.01658	199B -> 214B	-0.02214
200A -> 218A	0.01782	200B -> 206B	-0.09423
200A -> 220A	0.01263	200B -> 207B	0.02589
201A -> 207A	-0.03502	200B -> 208B	-0.02562
202A -> 207A	0.01830	200B -> 211B	-0.01707
203A -> 207A	-0.23732	200B -> 213B	0.02425
203A -> 208A	0.05456	200B -> 218B	-0.01118
203A -> 209A	-0.02640	203B -> 206B	-0.01356
203A -> 211A	-0.03780	203B -> 207B	0.01920
203A -> 212A	0.06477	205B -> 206B	-0.07733
204A -> 207A	-0.07757	205B -> 207B	0.30003
204A -> 208A	0.03059	205B -> 211B	0.04433
204A -> 209A	-0.01624	205B -> 214B	-0.01033

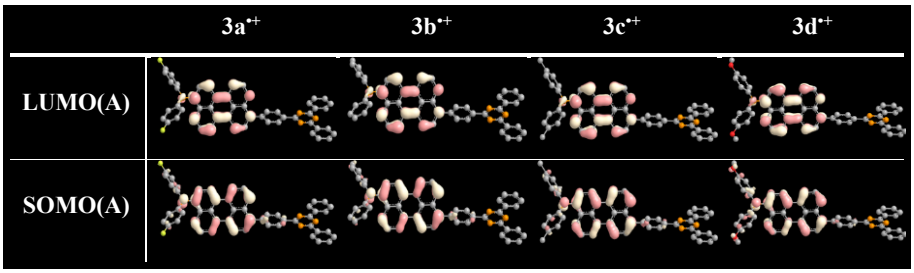


Figure S34. Frontier orbital distributions (SOMO(A), LUMO(A)) of **3a**$^{\bullet+}$**–3d**$^{\bullet+}$ calculated by DFT using ωB97XD function and 6-31+G+(d) basis

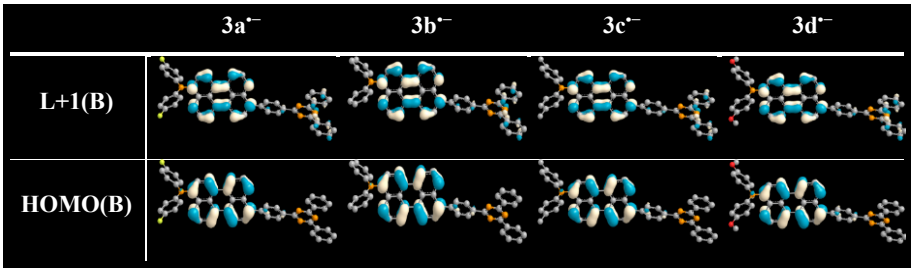
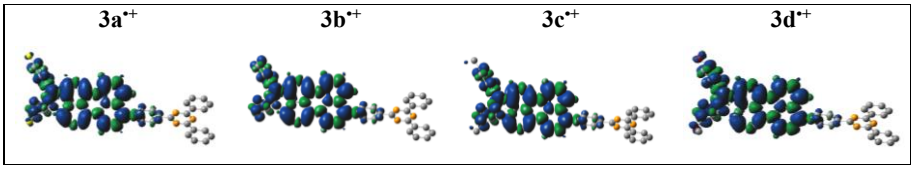


Figure S35. Frontier orbital distributions (HOMO(B), LUMO+1(B)) of **3a**$^{\bullet-}$**–3d**$^{\bullet-}$ calculated by DFT using ωB97XD function and 6-31+G+(d) basis

■ Spin density plots: Radical cations



■ Spin density plots: Radical anions

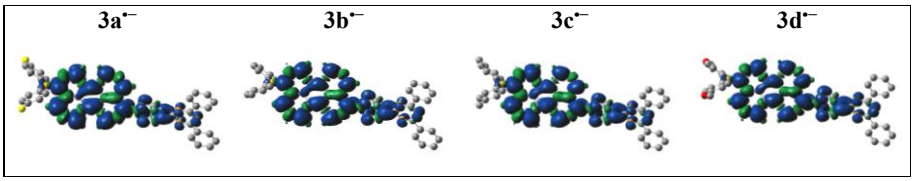


Figure S36. DFT calculated spin density distribution plots of radical cations **3a**$^{\bullet+}$–**3d**$^{\bullet+}$ and radical anions **3a**$^{\bullet-}$–**3d**$^{\bullet-}$ (ωB97XD/6-31+G(d), isosurface value= 0.0004 a.u.)

Table S30. Calculated Vertical Ionization Potential (IP) and Vertical Electron Affinity (EA) according to the conceptual density functional theory at the ωB97XD/6-31+G(d) level

Compounds	$E_{Neutral}$ [a] (Hartrees)	E_{Cation} [b] (Hartrees)	E_{Anion} [c] (Hartrees)	IP [d] (eV)	EA [e] (eV)
3a / **3a**$^{\bullet+}$ / **3a**$^{\bullet-}$	-2456.94775	-2456.71649	-2456.99756	6.29	1.36
3b / **3b**$^{\bullet+}$ / **3b**$^{\bullet-}$	-2258.51809	-2258.29153	-2258.56417	6.16	1.25
3c / **3c**$^{\bullet+}$ / **3c**$^{\bullet-}$	-2337.13168	-2336.9088	-2337.17648	6.06	1.22
3d / **3d**$^{\bullet+}$ / **3d**$^{\bullet-}$	-2487.4995	-2487.27979	-2487.5439	5.98	1.21

[a] The total energy for neutral state **3a**–**3d**. [b] The total energy for radical cationic state **3a**$^{\bullet+}$–**3d**$^{\bullet+}$. [c] The total energy for radical anionic state **3a**$^{\bullet-}$–**3d**$^{\bullet-}$. [d] $E_{Cation} - E_{Neutral}$. [e] $E_{Neutral} - E_{Anion}$.

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