Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information for

Isolation and Characterization of Annelated N-Heterocyclic Carbene Stabilized Breslow Enolate

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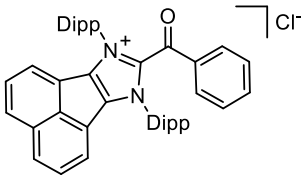
1. Experimental section

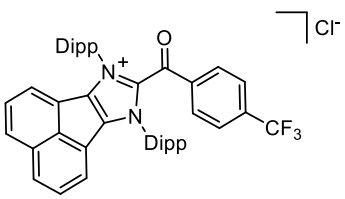
1.1 Materials and methods

All manipulations were carried out in an argon atmosphere using standard Schlenk techniques and a glove box. All solvents were dried over Na/benzophenone or CaH_2 and distilled before use. Glassware was heated in a box furnace at 130°C before use. The starting material IPr(BIAN) (**1**) was synthesized using the literature procedure.[1,2] Radicals **C** and **D** derived from classical NHCs have been synthesized based on literature methods.[3,4] NMR spectra were recorded on Bruker AVANCE III 400, and chemical shifts are reported relative to the solvent residual peak: CD_3CN (^1H, δ = 1.94 ppm and ^{13}C, δ = 118.3, 1.3 ppm). Mass spectra were obtained with Bruker Micro TOF-Q II mass spectrometer (Bruker Daltonics Corp., USA) in the electrospray ionization (ESI) mode. UV–vis spectra were recorded using a UV–3600 Plus in the 200-900 nm range. The TGA spectra were carried on the NETZSCH STA 449C microanalyzer from room temperature to 800°C at the heating rate of 10°C min^{-1}.

1.2 Synthesis of compounds 2a–d

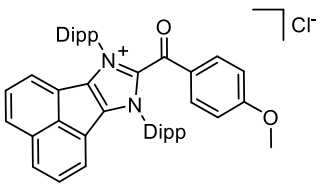


2a: Benzoyl chloride (37.9 mg, 0.270 mmol) was added to a stirred solution of carbene **1** (115.4 mg, 0.225 mmol) in 25 mL of dry THF at room temperature. A lot of light green precipitate was immediately formed. After stirring for 20 min, the supernatant was removed by filtration, the resulting solid was washed with hexanes (3×10 mL). Then dried under vacuum to yield **2a** as a yellow solid. Yield: 110.1 mg, 75%. ^1H NMR (400 MHz, CD_3CN): δ = 8.22 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.76–7.67 (m, 5H), 7.49–7.54 (m, 6H), 7.39 (d, J = 7.2 Hz, 2H), 2.88 (sept, J = 6.7 Hz, 4H), 1.20 (d, J = 6.7 Hz, 12H), 1.05 (d, J = 6.7 Hz, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 181.8, 146.6, 143.9, 140.2, 137.8, 134.7, 134.0, 132.7, 132.1, 131.0, 130.5, 129.6, 128.8, 126.8, 126.0, 123.0, 30.2, 25.8, 23.4 ppm. HRMS (ESI, positive ions): m/z = 617.3518 (calcd for [**2a**-Cl]$^+$ 617.3526). UV–vis (DMF, λ): 286, 321, 370 nm.

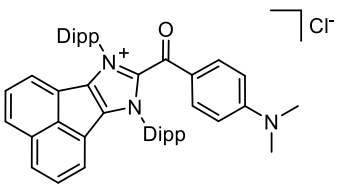


2b: 4-(trifluoromethyl)-benzoyl chloride (56.2 mg, 0.270 mmol) was added to a stirred solution of carbene **1** (115.4 mg, 0.225 mmol) in 25 mL of dry THF at room temperature. A lot of light green precipitate was immediately formed. After stirring for 10 min, the supernatant was removed by filtration, the resulting solid was washed with hexanes (3×10 mL). Then dried under vacuum to yield **2b** as a yellow solid. Yield: 105.3 mg, 65%. ^1H NMR (400 MHz, CD_3CN): δ = 8.24 (d, J = 8.4 Hz, 2H), 7.77–7.83 (m, 4H),

7.71 (t, J = 7.9 Hz, 4H), 7.50 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 7.1 Hz, 2H), 2.82 (sept, J = 6.7 Hz, 4H), 1.22 (d, J = 6.7 Hz, 12H), 1.05 (d, J = 6.7 Hz, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 181.0, 146.4, 142.5, 140.9, 138.2, 136.7, 136.4, 134.0, 133.0, 132.8, 131.1, 130.5, 129.7, 129.0, 127.7, 127.0, 126.4, 122.8, 30.2, 25.7, 23.4 ppm. HRMS (ESI, positive ions): m/z = 685.3384 (calcd for [**2b**-Cl]$^+$ 685.3340). UV–vis (DMF, λ): 286, 322, 369 nm.

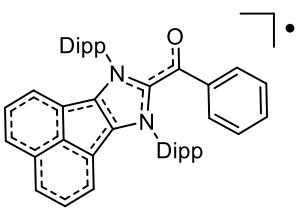


2c: 4-(methoxy)-benzoyl chloride (46.0 mg, 0.270 mmol) was added to a stirred solution of carbene **1** (115.4 mg, 0.225 mmol) in 25 mL of dry THF at room temperature. A lot of light green precipitate was immediately formed. After stirring for 10 min, the supernatant was removed by filtration, the resulting solid was washed with hexanes (3×10 mL). Then dried under vacuum to yield **2c** as a green solid. Yield: 75.2 mg, 49%. ^1H NMR (400 MHz, CD_3CN): δ = 8.19 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.66–7.72 (m, 4H), 7.51 (d, J = 7.9 Hz, 4H), 7.37 (d, J = 7.2 Hz, 2H), 7.02 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 2.92 (sept, J = 6.7 Hz, 4H), 1.20 (d, J = 6.7 Hz, 12H), 1.05 (d, J = 6.7 Hz, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 178.4, 167.9, 146.8, 144.9, 139.8, 133.9, 133.8, 132.5, 131.7, 131.0, 129.6, 128. 7, 127.3, 126.8, 125.8, 123.1, 116.6, 56.9, 30.2, 25.8, 23.5 ppm. HRMS (ESI, positive ions): m/z = 647.3617 (calcd for [**2c**-Cl]$^+$ 647.3632). UV–vis (DMF, λ): 286, 321, 381 nm.

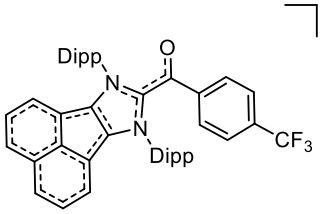


2d: 4-(dimethylamino)-benzoyl chloride (47.5 mg, 0.270 mmol) was added to a stirred solution of carbene **1** (115.4 mg, 0.225 mmol) in 25 mL of dry THF at room temperature. A lot of yellow-brown precipitate was immediately formed. After stirring for 30 min, the supernatant was removed by filtration, the resulting solid was washed with hexanes (3 x 10 mL). Then dried under vacuum to yield **2d** as an orange-red solid. Yield: 73.4 mg, 47%. ^1H NMR (400 MHz, CD_3CN): δ = 8.16 (d, J = 8.4 Hz, 2H), 7.71–7.64 (m, 6H), 7.50 (d, J = 7.9 Hz, 4H), 7.33 (d, J = 7.0 Hz, 2H), 6.67 (d, J = 9.2 Hz, 2H), 3.06 (s, 6H), 2.96 (sept, J = 6.7 Hz, 4H), 1.21 (d, J = 6.7 Hz, 12H), 1.04 (d, J = 6.7 Hz, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 174.9, 156.8, 147.0, 146.8, 139.3, 133.7, 133.6, 132.1, 131.4, 130.9, 129.5, 129.0, 126.7, 125.5, 123.6, 121.3, 112.9, 40.5, 30.2, 25.9, 23.6 ppm. HRMS (ESI, positive ions): m/z = 660.3927 (calcd for [**2d**-Cl]$^+$ 660.3948). UV–vis (DMF, λ): 288, 322, 400 nm.

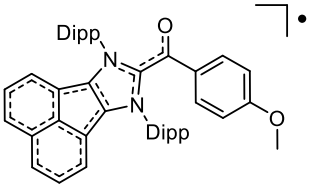
1.3 Synthesis of compounds 3a–d



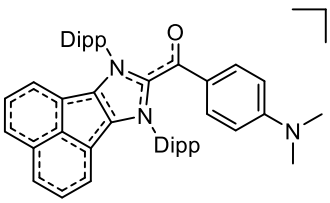
3a: Zn powder (5.0 mg, 0.077 mmol) was added to a THF (5.0 mL) solution of **2a** (100 mg, 0.153 mmol). The mixture was stirred at room temperature for 2 days. After which removal of the solvent under reduced pressure. The residual solid was extracted with diethyl ether and then filtered over celite and removal of all volatiles afforded compound **3a** as a brick-red solid. Yield: 66.2 mg, 70%. UV–vis (DMF, λ): 275, 321, 395 nm.



3b: Zn powder (4.6 mg, 0.070 mmol) was added to a THF (5.0 mL) solution of **2b** (100 mg, 0.139 mmol). The mixture was stirred at room temperature for 8 h. After which removal of the solvent under reduced pressure. The residual solid was extracted with diethyl ether and then filtered over celite and removal of all volatiles afforded compound **3b** as a bottle-green solid. Yield: 68.5 mg, 72%. UV–vis (DMF, λ): 275, 320, 428 nm.

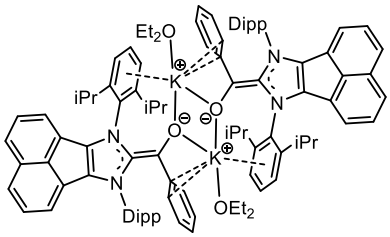


3c: KC_8 (23.8 mg, 0.176 mmol) was added to a THF (10.0 mL) solution of **2c** (100 mg, 0.147 mmol) at -35°C. The mixture was stirred at room temperature for 6 h. After which removal of the solvent under reduced pressure. The residual solid was extracted with diethyl ether and then filtered over celite and removal of all volatiles afforded compound **3c** as a brick-red solid. Yield: 76.8 mg, 81%. UV–vis (DMF, λ): 285, 322, 414, 440 nm.



3d: KC_8 (23.4 mg, 0.173 mmol) was added to a THF (8.0 mL) solution of **2d** (100 mg, 0.144 mmol) at -35°C. The mixture was stirred at room temperature for 6 h. After which removal of the solvent under reduced pressure. The residual solid was extracted with diethyl ether and then filtered over celite and removal of all volatiles afforded compound **3d** as a brick-red solid. Yield: 79.8 mg, 84%. UV–vis (DMF, λ): 285, 320, 428 nm.

1.4 Synthesis of compound $[(4a)K]_2(Et_2O)_2$



$[(\mathbf{4a})K]_2(Et_2O)_2$: KC_8 (32.4 mg, 0.24 mmol) was added to a THF (5.0 mL) solution of **3a** (124 mg, 0.2 mmol) at -35℃. The mixture was stirred at room temperature for 2 h. After which removal of the solvent under reduced pressure. The residual solid was extracted with diethyl ether and then filtered over celite and removal of all volatiles afforded compound $[(\mathbf{4a})K]_2(Et_2O)_2$. Yield: 104.54 mg, 65%. UV–vis (DMF, λ): 290, 319, 417, 550, 780 nm. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.31–7.24 (4H), 7.12 (d, J = 7.8 Hz, 4H), 7.10 (d, J = 7.8 Hz, 4H), 6.95–6.88 (12H), 6.87–6.85 (m, 2H), 6.30 (dt, J = 9.8, 2.0 Hz, 2H), 5.11 (dt, J = 9.7, 3.9 Hz, 2H), 4.27 (4H), 2.85 (sept, J = 6.9 Hz, 4H), 2.70 (sept, J = 6.9 Hz, 4H), 1.16 (d, J = 6.8 Hz, 12H), 1.07 (d, J = 6.9 Hz, 12H), 1.03 (d, J = 6.9 Hz, 12H), 0.98 (d, J = 6.8 Hz, 12H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 146.8, 146.4, 140.3, 138.8, 137.5, 130.8, 130.7, 130.6, 129.4, 129.2, 128.1, 127.1, 125.3, 124.2, 121.1, 118.4, 117.7, 117.3, 113,2, 111.6, 108.7, 29.0, 28.9, 24.6, 24.3, 24.1, 23.9 ppm.

2. NMR spectra

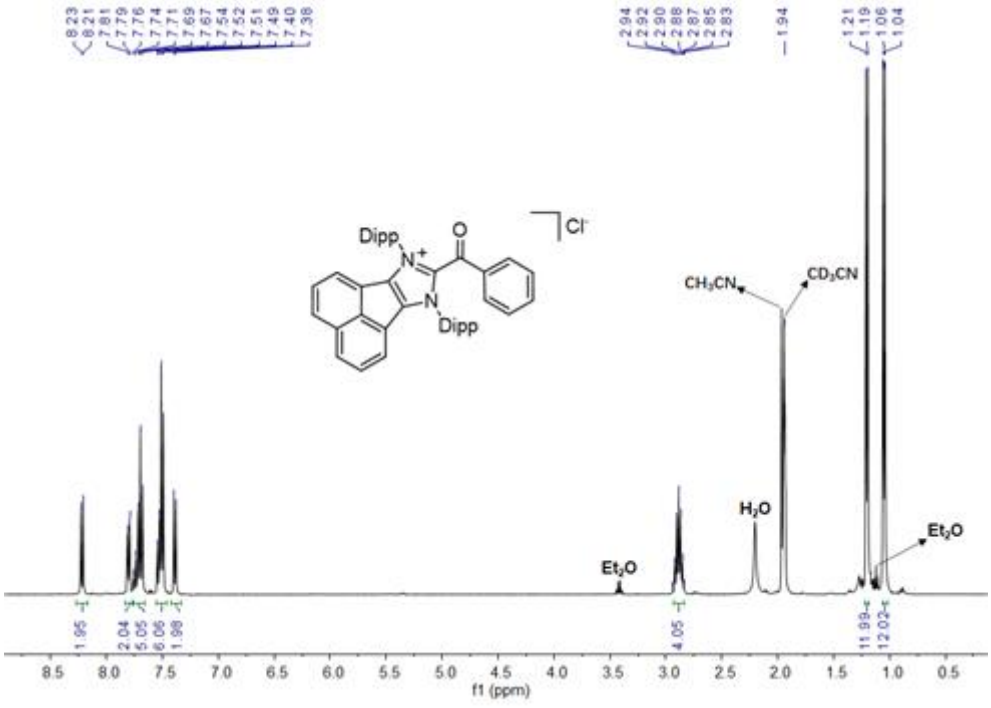


Figure S1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of **2a**.

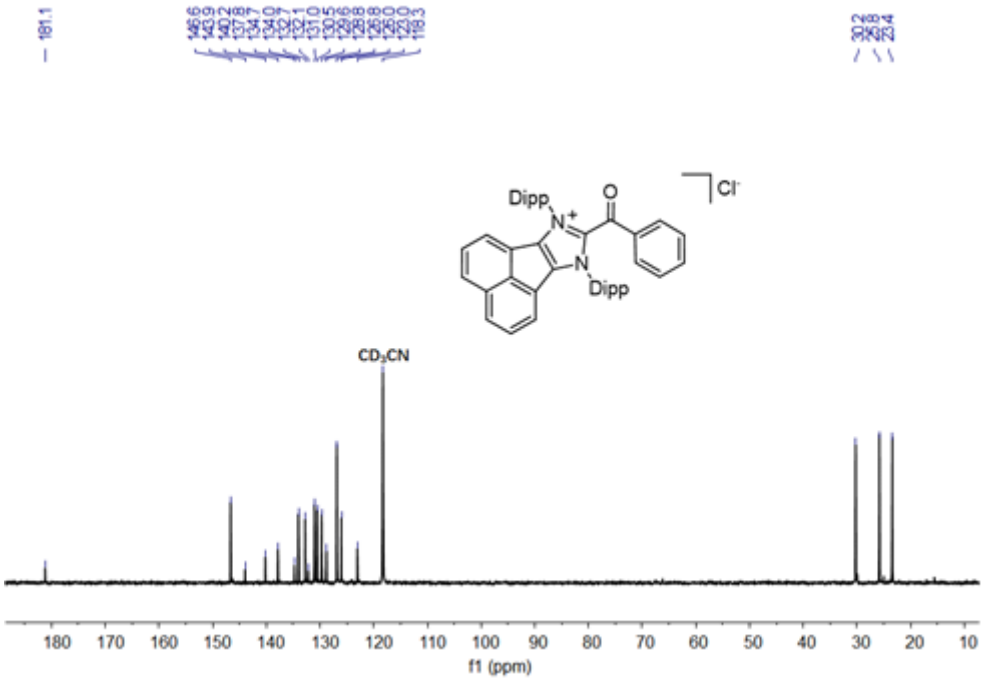


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3CN) of **2a**.

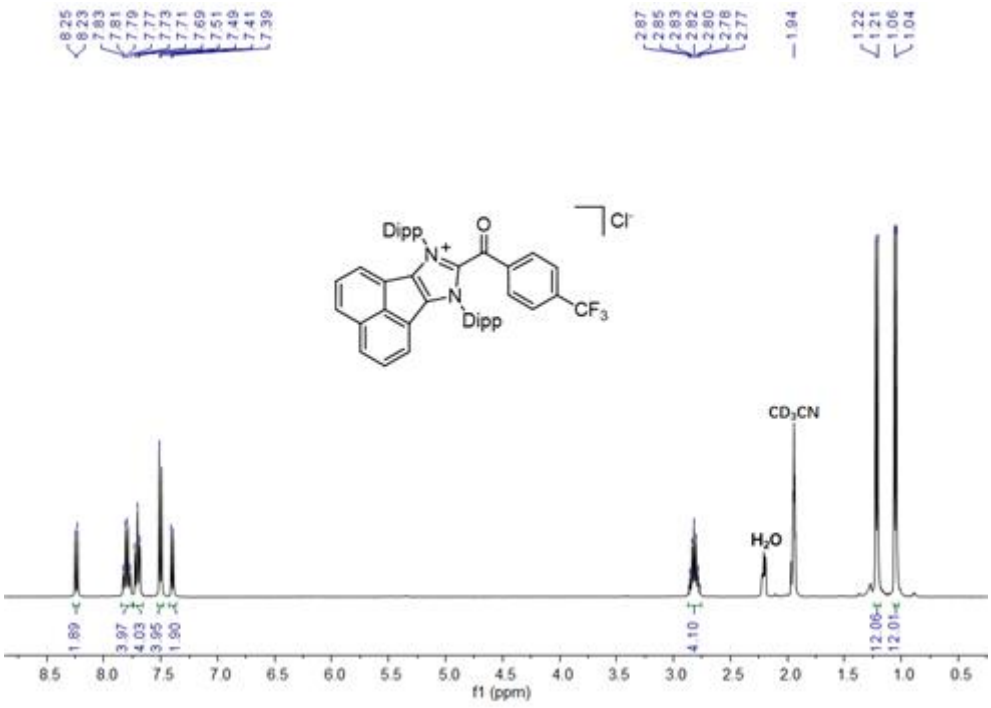


Figure S3. ^{1}H NMR spectrum (400 MHz, CD_3CN) of **2b**.

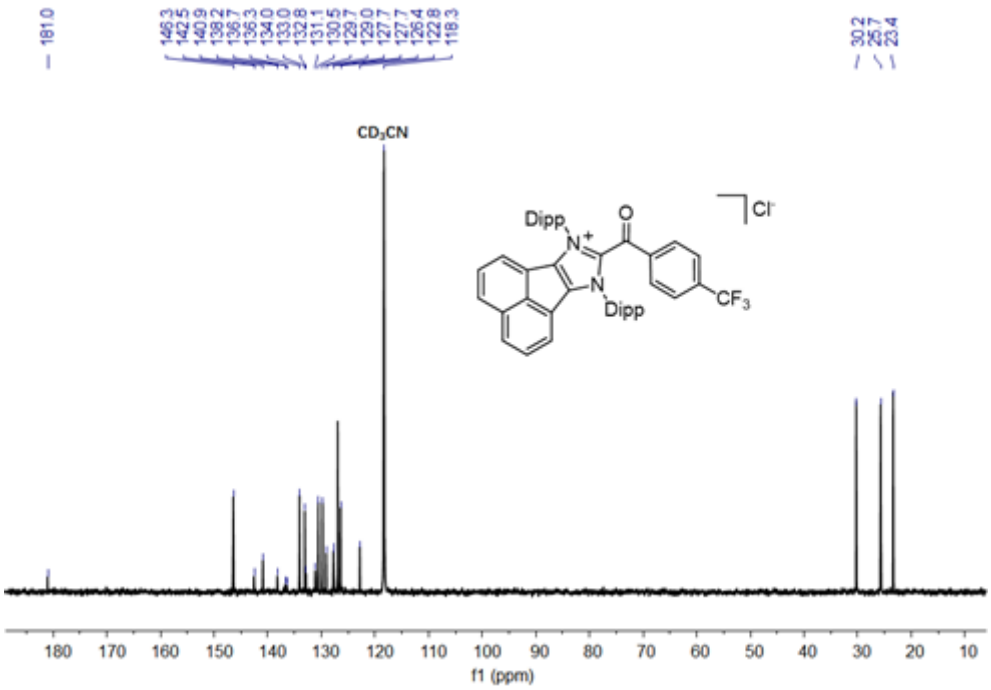


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3CN) of **2b**.

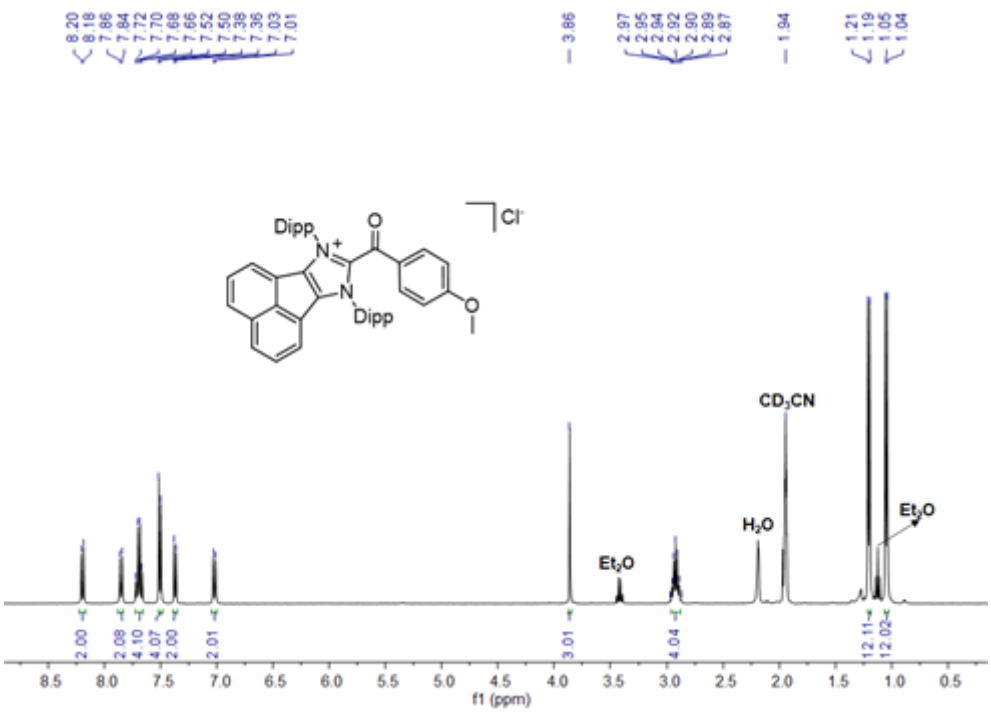


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_3CN) of **2c**.

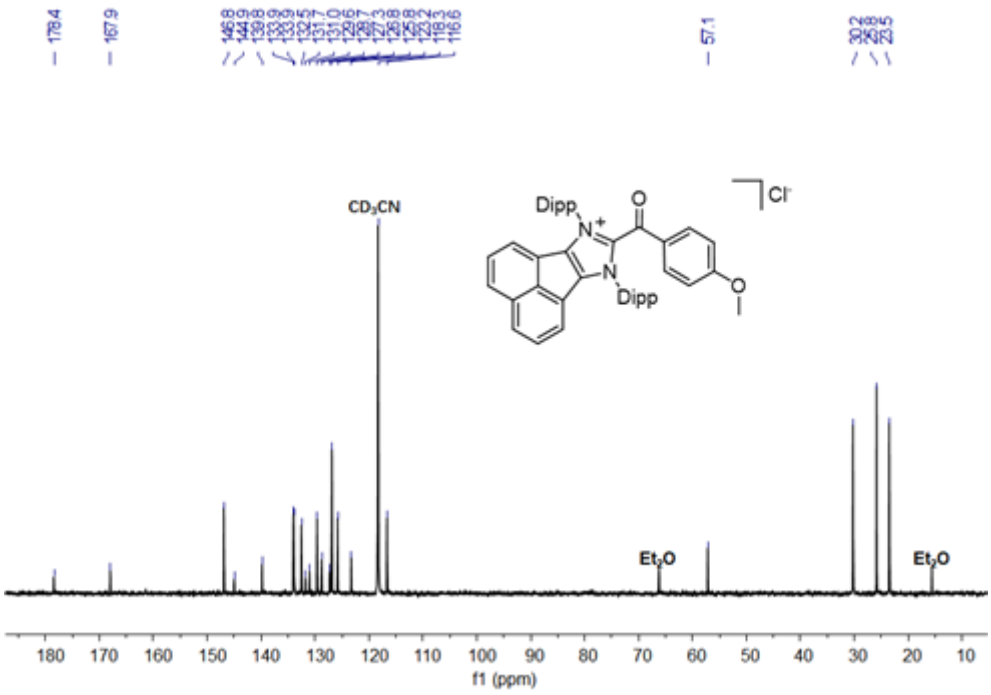


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3CN) of **2c**.

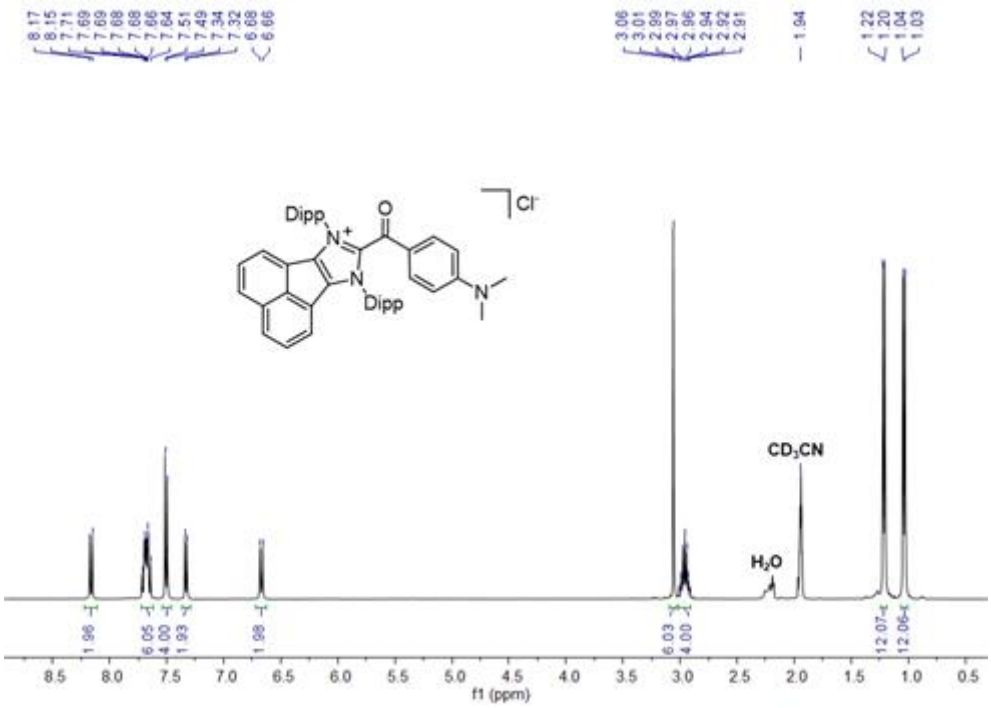


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_3CN) of **2d**.

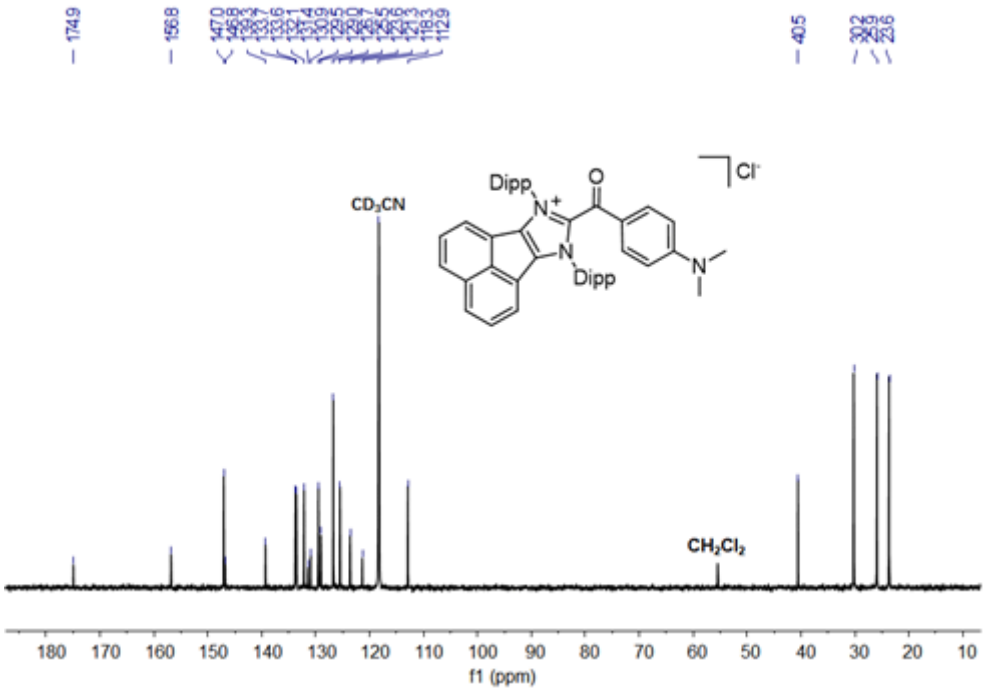


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3CN) of **2d**.

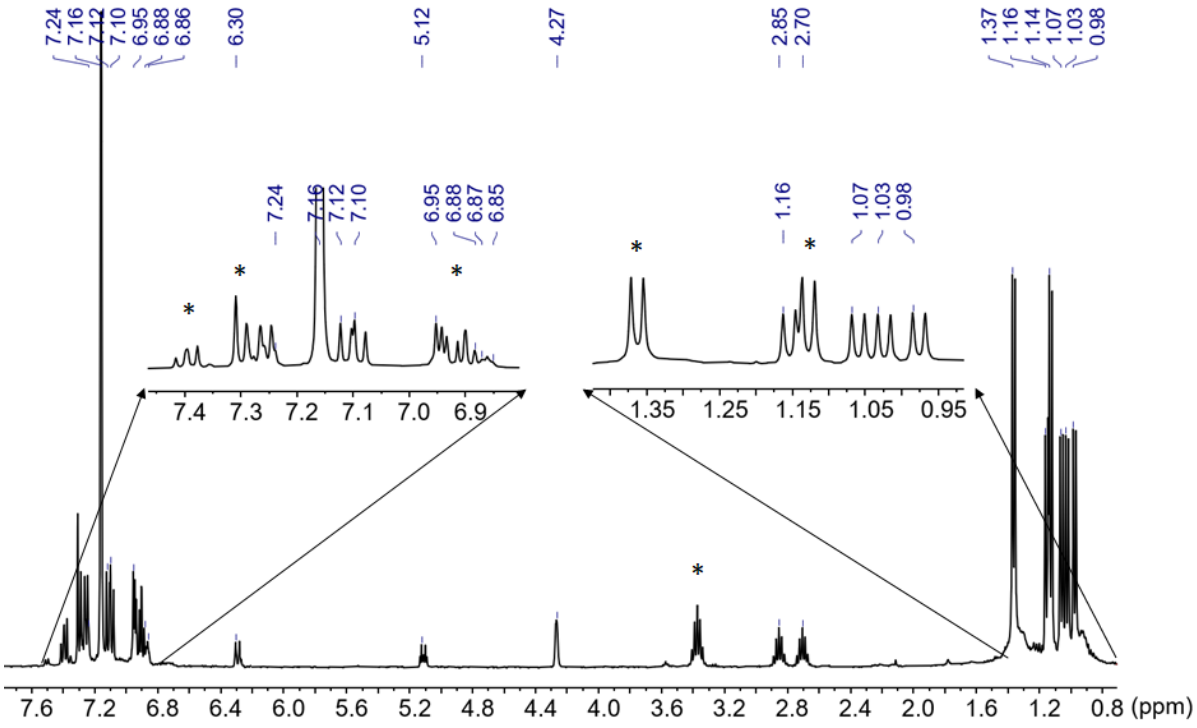


Figure S9. ^{1}H NMR spectrum (400 MHz, C_6D_6) of $[(\mathbf{4a})K]_2(Et_2O)_2$. * free carbene IPr(BIAN).

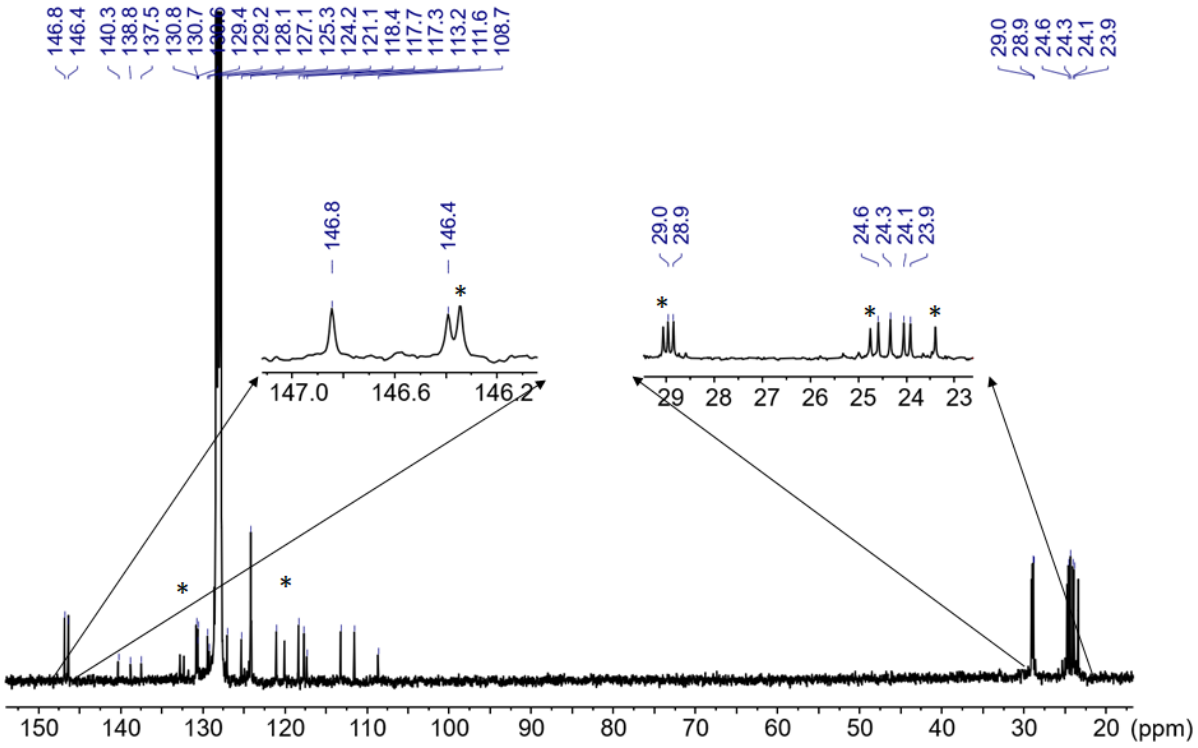


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, C_6D_6) of $[(\mathbf{4a})K]_2(Et_2O)_2$. * free carbene IPr(BIAN).

3. HRMS spectra

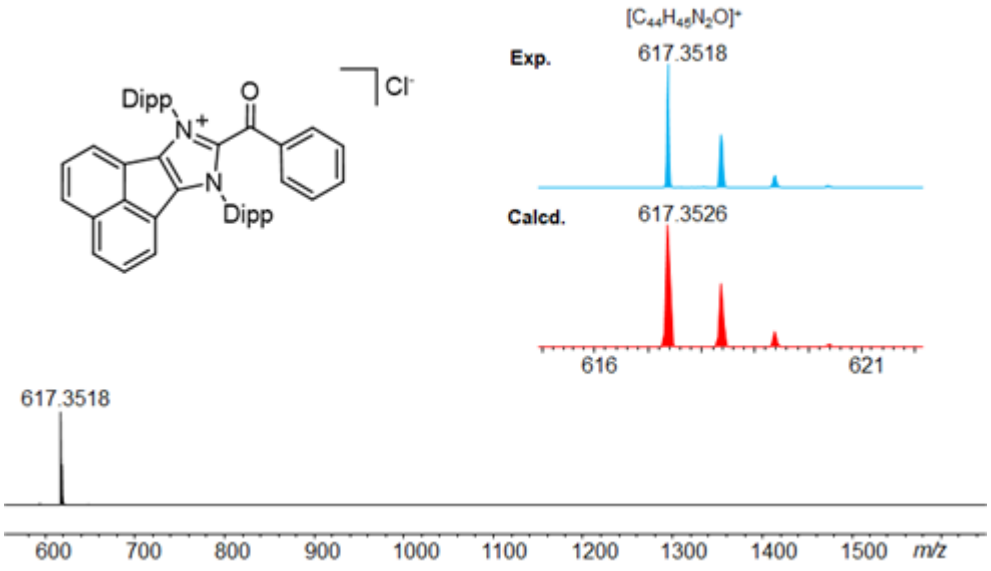


Figure S11. The HRMS spectrum of **2a**, inset experimental for (blue) and calculated (red) isotope distributions for peak corresponding to $[C_{44}H_{45}N_2O]^+$.

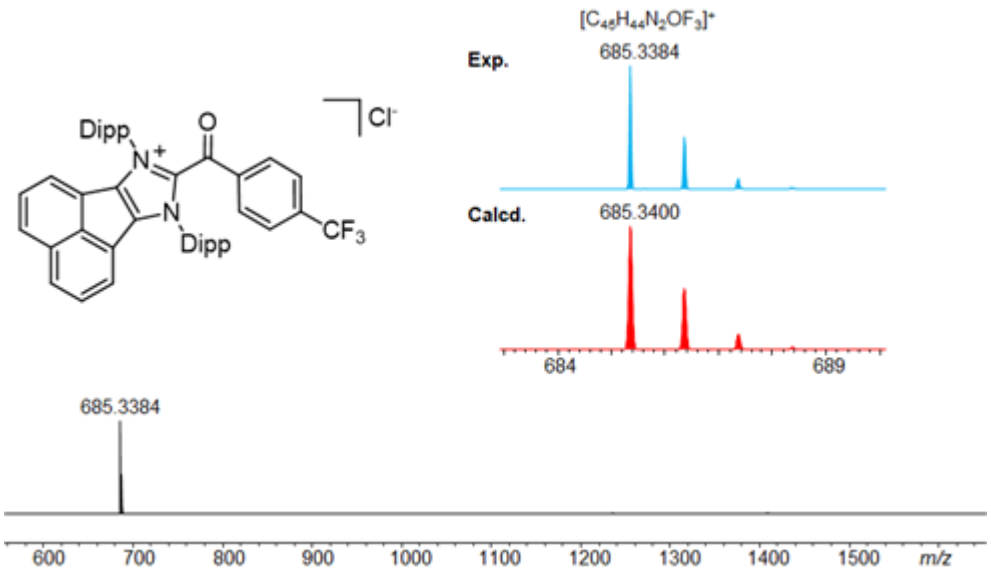


Figure S12. The HRMS spectrum of **2b**, inset experimental for (blue) and calculated (red) isotope distributions for peak corresponding to $[C_{45}H_{44}N_2OF_3]^+$.

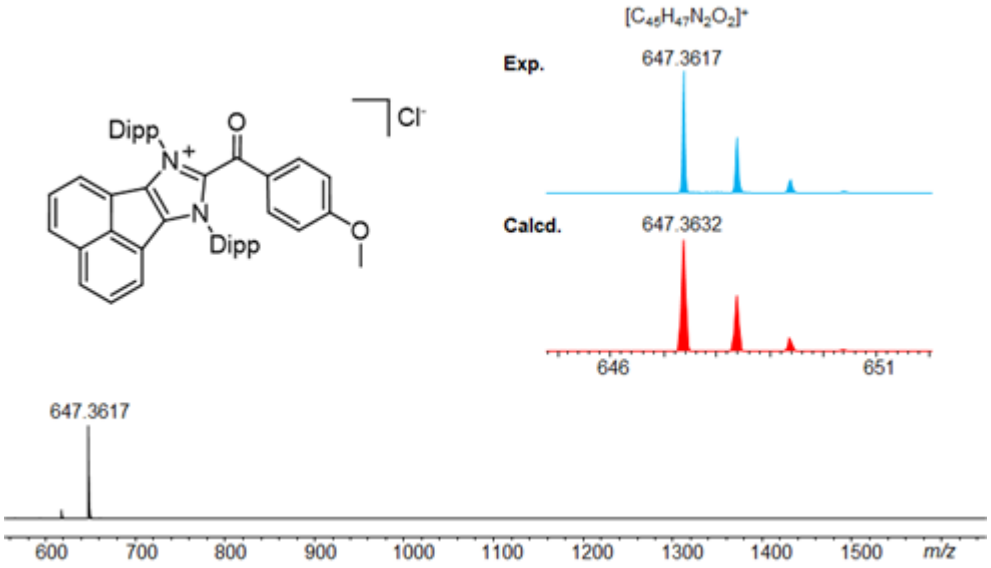


Figure S13. The HRMS spectrum of **2c**, inset experimental for (blue) and calculated (red) isotope distributions for peak corresponding to $[C_{45}H_{47}N_2O_2]^+$.

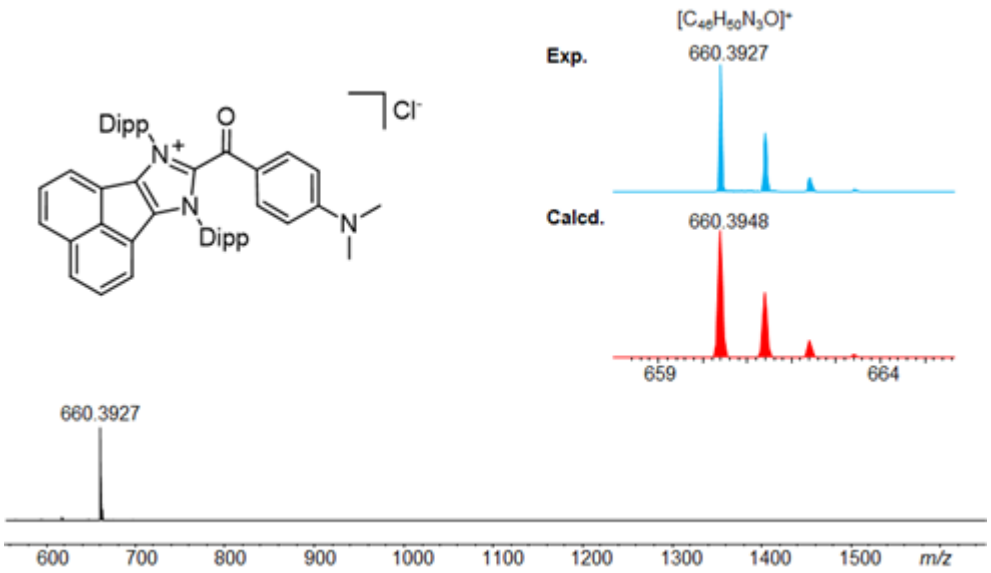


Figure S14. The HRMS spectrum of **2d**, inset experimental for (blue) and calculated (red) isotope distributions for peak corresponding to $[C_{46}H_{50}N_3O]^+$.

4. Cyclic voltammetry

Cyclic voltammetry (CV) experiments were carried out using a CHI660E electrochemical workstation (CH Instruments, Inc). All experiments were performed in an inert atmosphere of argon glove box at room temperature. A standard three-electrode cell configuration was employed using a glass carbon working electrode, a platinum counter electrode, and a silver wire serving as the reference electrode. The obtained voltammograms were referenced to the Fc^+/Fc (ferrocenium/ferrocene) redox couple as a standard.

5. X-ray crystallography

Diffraction data of compounds were collected with a Bruker APEX-II CCD diffractometer. Raw data collection and processing were performed with APEX III software package. The data were corrected for absorption using the SADABS program.[5] Using the program Olex2, the structures were solved with the olex2, solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization.[6,7] All hydrogen atoms were treated as idealized contributions, and non-hydrogen atoms were refined anisotropically.

Table S1. X-Ray crystallographic details of **2a** and **3a**.

	2a	**3a**
Empirical formula	$C_{44}H_{45}ClN_2O$	$C_{44}H_{45}N_2O$
Formula weight	653.27	617.82
Radiation / λ	Mo K_α / (0.71073 Å)	Mo K_α / (0.71073 Å)
Temperature/K	200.0	210.0
Crystal system	tetragonal	monoclinic
Space group	I_4/m	$P2_1/c$
a/Å	21.727(6)	8.829(3)
b/Å	21.727(6)	23.340(8)
c/Å	17.751(4)	17.872(6)
α/°	90	90
β/°	90	103.175(9)
γ/°	90	90
V/Å^3	8380(5)	3586(2)
Z	8	4
P calcg/cm^3	1.036	1.144
μ/mm^{-1}	0.123	0.068
F(000)	2784.0	1324.0
2Θ range for data collection/°	3.75 to 50.806	4.682 to 50
Index ranges	$-26 \le h \le 26$, $-26 \le k \le 26$, $-20 \le l \le 21$	$-10 \le h \le 10$, $-21 \le k \le 27$, $-20 \le l \le 21$
Independent reflections	3981 [R_{int} = 0.0905]	6225 [R_{int} = 0.0843]
Data/restraints/parameters	3981/0/239	6225/21/432
Goodness-of-fit on F^2	1.102	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1683	R_1 = 0.0818, wR_2 = 0.2111
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1784	R_1 = 0.1780, wR_2 = 0.2624
Largest diff. peak/hole / e Å^{-3}	0.23/-0.40	0.44/-0.27
CCDC	2215442	2215447

Table S2. X-Ray crystallographic details of **2b** and **3b**.

	2b	**3b**
Empirical formula	$C_{45}H_{44}ClF_3N_2O$	$C_{45}H_{44}F_3N_2O$
Formula weight	721.27	685.82
Radiation / λ	Mo K_α / (0.71073 Å)	Mo K_α / (0.71073 Å)
Temperature/K	190.0	210.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.4788(3)	8.8744(6)
b/Å	16.7969(5)	24.6056(16)
c/Å	20.4525(7)	18.0997(11)
α/°	90	90
β/°	98.9930(10)	103.757(2)
γ/°	90	90
V/Å^3	3894.9(2)	3838.9(4)
Z	4	4
P calcg/cm^3	1.230	1.187
μ/mm^{-1}	0.149	0.080
F(000)	1520.0	1452.0
2Θ range for data collection/°	3.592 to 52.712	4.726 to 52.706
Index ranges	$-14 \le h \le 13$, $-20 \le k \le 20$, $-25 \le l \le 25$	$-10 \le h \le 11$, $-30 \le k \le 30$, $-22 \le l \le 22$
Independent reflections	7935 [R_{int} = 0.0331]	7810 [R_{int} = 0.0412]
Data/restraints/parameters	7935/114/477	7810/0/468
Goodness-of-fit on F^2	1.049	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0763, wR_2 = 0.2177	R_1 = 0.0742, wR_2 = 0.2113
Final R indexes [all data]	R_1 = 0.0964, wR_2 = 0.2378	R_1 = 0.1128, wR_2 = 0.2414
Largest diff. peak/hole / e Å^{-3}	1.35/-0.78	0.45/-0.39
CCDC	2215443	2215448

Table S3. X-Ray crystallographic details of **2c** and **3c**.

	2c	**3c**
Empirical formula	$C_{45}H_{47}ClN_2O_2 \cdot CH_2Cl_2$	$C_{45}H_{47}N_2O_2$
Formula weight	768.22	647.84
Radiation / λ	Mo K_α / (0.71073 Å)	Mo K_α / (0.71073 Å)
Temperature/K	190.0	214.0
Crystal system	monoclinic	monoclinic
Space group	*C*2/*m*	$P2_1/c$
a/Å	13.1041(7)	8.8133(8)
b/Å	18.4405(9)	24.708(3)
c/Å	18.7136(8)	18.0295(19)
α/°	90	90
β/°	102.261(2)	103.983(3)
γ/°	90	90
V/Å^3	4418.9(4)	3809.8(7)
Z	4	4
P calcg/cm^3	1.219	1.129
μ/mm^{-1}	0.306	0.068
F(000)	1708.0	1388.0
2Θ range for data collection/°	3.872 to 52.752	4.762 to 50.638
Index ranges	$-14 \le h \le 16$, $-23 \le k \le 22$, $-23 \le l \le 23$	$-10 \le h \le 10$, $-29 \le k \le 25$, $-21 \le l \le 21$
Independent reflections	4633 [R_{int} = 0.0268]	6873 [R_{int} = 0.0764]
Data/restraints/parameters	4633/16/285	6873/0/451
Goodness-of-fit on F^2	1.058	1.020
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.0914, wR_2 = 0.2791	R_1 = 0.0712, wR_2 = 0.1668
Final *R* indexes [all data]	R_1 = 0.1038, wR_2 = 0.2948	R_1 = 0.1465, wR_2 = 0.2036
Largest diff. peak/hole / e Å^{-3}	1.12/-0.79	0.37/-0.31
CCDC	2215446	2215449

Table S4. X-Ray crystallographic details of **2d** and **3d**.

	2d	**3d**
Empirical formula	$C_{46}H_{50}ClN_3O \cdot 1.5Et_2O$	$C_{46}H_{50}N_3O$
Formula weight	897.52	660.89
Radiation / λ	Ga K_α / (1.34139 Å)	Ga K_α / (1.34139 Å)
Temperature/K	90	190.0
Crystal system	orthorhombic	triclinic
Space group	*Pbcn*	$P\bar{1}$
a/Å	18.5634(19)	8.7055(3)
b/Å	23.410(2)	9.3964(3)
c/Å	21.513(2)	23.6914(7)
α/°	90	87.6640(10)
β/°	90	82.0200(10)
γ/°	90	77.0010(10)
V/Å^3	9349.1(16)	1869.93(10)
Z	8	2
P calcg/cm^3	1.147	1.174
μ/mm^{-1}	0.680	0.344
F(000)	3480.0	710.0
2Θ range for data collection/°	6.382 to 108.442	8.99 to 118.406
Index ranges	$-20 \le h \le 21$, $-20 \le k \le 28$, $-23 \le l \le 25$	$-11 \le h \le 11$, $-11 \le k \le 12$, $-29 \le l \le 30$
Independent reflections	8260 [R_{int} = 0.0676]	8134 [R_{int} = 0.0429]
Data/restraints/parameters	8260/69/541	8134/0/461
Goodness-of-fit on F^2	1.052	1.069
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.0538, wR_2 = 0.1410	R_1 = 0.0440, wR_2 = 0.1112
Final *R* indexes [all data]	R_1 = 0.0637, wR_2 = 0.1491	R_1 = 0.0591, wR_2 = 0.1186
Largest diff. peak/hole / e Å^{-3}	0.40/-0.52	0.24/-0.20
CCDC	2215445	2215450

Table S5. X-Ray crystallographic details of $[(\mathbf{4a})K]_2(Et_2O)_2$.

	$[(\mathbf{4a})K]_2(Et_2O)_2$
Empirical formula	$C_{96}H_{110}K_2N_4O_4$
Formula weight	731.04
Radiation / λ	Mo K_α / (0.71073 Å)
Temperature/K	220
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	13.059(5)
b/Å	13.426(5)
c/Å	14.496(5)
α/°	65.992(9)
β/°	68.215(9)
γ/°	69.891(9)
V/Å^3	2099.4(13)
Z	2
P calcg/cm^3	1.156
μ/mm^{-1}	0.166
F(000)	784.0
2Θ range for data collection/°	4.02 to 49.796
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 16$
Independent reflections	7021 [R_{int} = 0.0905]
Data/restraints/parameters	7021/3/464
Goodness-of-fit on F^2	1.025
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0964, wR_2 = 0.2723
Final R indexes [all data]	R_1 = 0.1801, wR_2 = 0.3364
Largest diff. peak/hole / e Å^{-3}	0.34/-0.30
CCDC	2268433

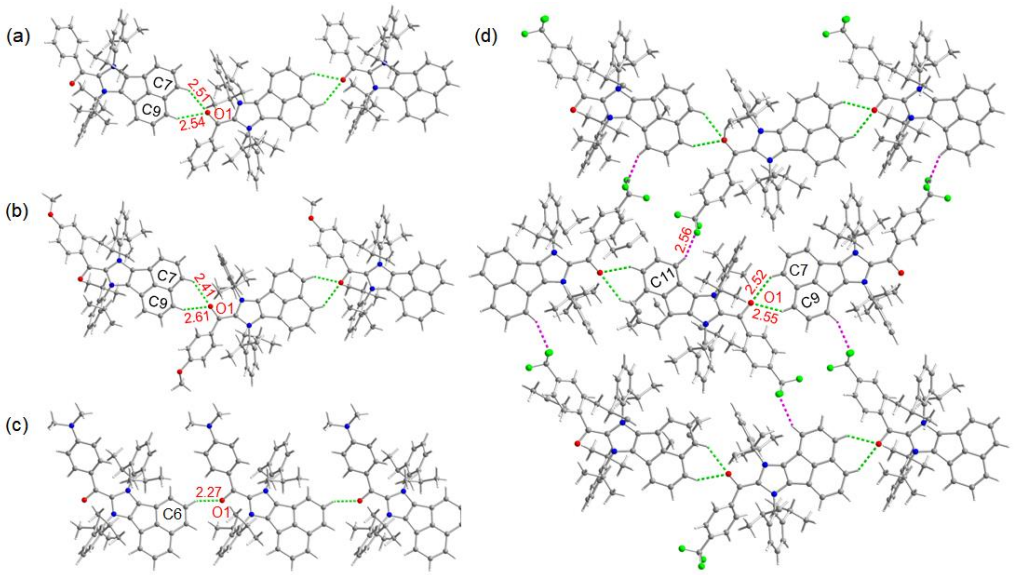


Figure S15. The packing structure of radicals **3a** (a), **3c** (b), **3d** (c), and **3b** (d). The green dashed line behalf C–H···O hydrogen bond, and the purple dashed line behalf C–H···F hydrogen. Color code: C, gray; N, blue; O, red; F, green; H, white.

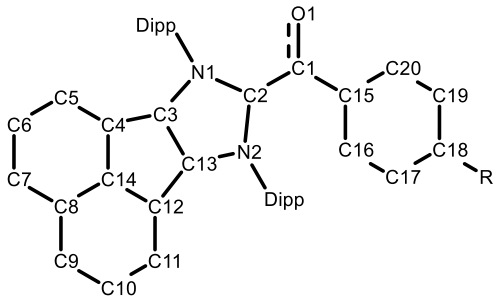


Table S6. Hydrogen bond lengths (Å) and angles (°) for **3a**–**d**.

	D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
3a	C7	H7	O1[1]	0.94	2.51	3.325(6)	144.8
	C9	H9	O1[2]	0.94	2.54	3.347(6)	143.9
[1]1-X, 1/2-Y, 1/2+Z							
3b	C7	H7	O1[1]	0.94	2.55	3.343(4)	141.8
	C9	H9	O1[1]	0.94	2.52	3.317(4)	142.5
	C11	H11	F1[2]	0.94	2.56	3.431(4)	153.8
[1]-1+X, 3/2-Y, 1/2+Z; [2]1-X, 1/2+Y, 3/2+Z							
3c	C7	H7	O1[1]	0.94	2.61	3.372(4)	138.3
	C9	H9	O1[1]	0.94	2.41	3.221(4)	144.9
[1]1-X, 1/2-Y, 1/2+Z							
3d	C6	H6	O1[1]	0.95	2.27	3.107(2)	146.3
[1]-1+X, 1+Y, +Z							

6. EPR spectra

The continuous wave (CW) EPR spectra were obtained using an X-band Bruker E500 spectrometer at room temperature. The microwave frequency was 9.8 GHz, and the modulation amplitude was 0.1 mT. Simulations of the EPR spectra have been performed with Easyspin v5.2.11.[8]

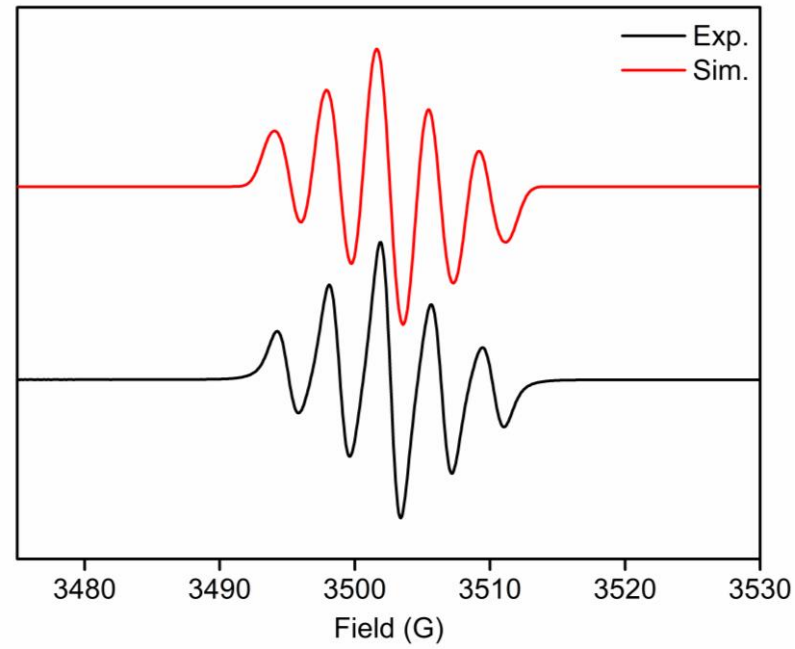


Figure S16. X-Band EPR spectrum of **3a** in THF. g = 2.0044, hyperfine coupling constants: $A_{iso}(^{14}N)$ = 3.82, 3.78 MHz, line broadening: 0.154.

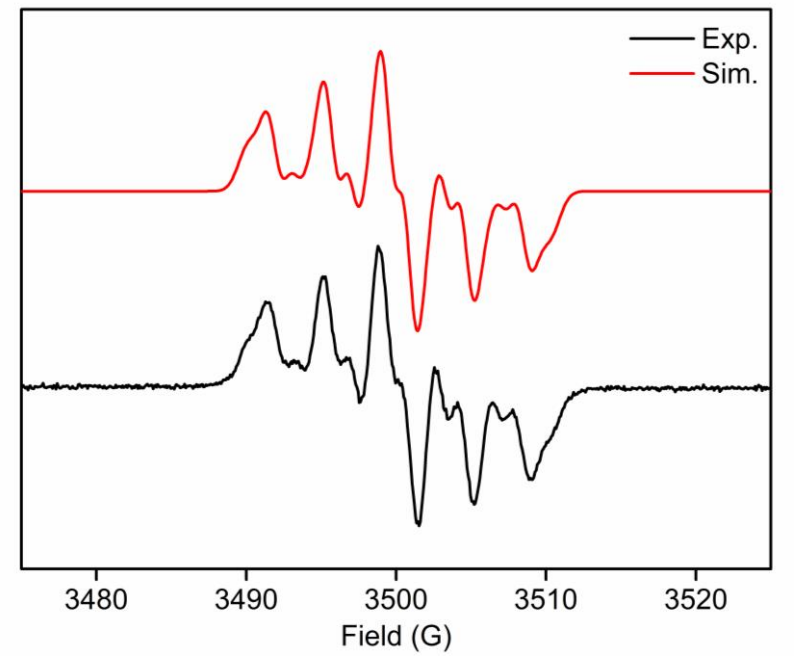


Figure S17. X-Band EPR spectrum of **3b** in THF. g = 2.0047, hyperfine coupling constants: $A_{iso}(^{14}N)$ = 3.80, 3.77 MHz, $A_{iso}(^{19}F)$ = 1.23 MHz, line broadening: 0.166.

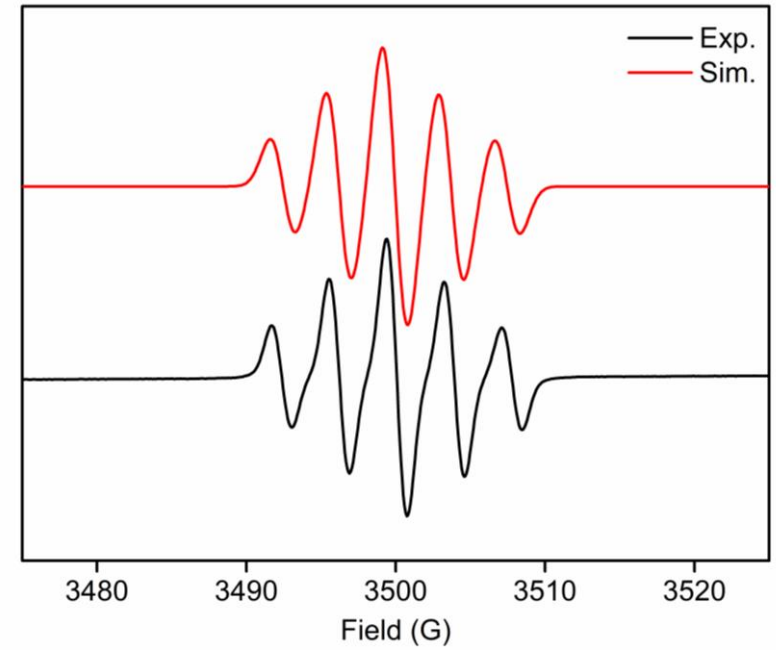


Figure S18. X-Band EPR spectrum of **3c** in THF. g = 2.0046, hyperfine coupling constants: $A_{iso}(^{14}N)$ = 3.83, 3.78 MHz, line broadening: 0.158.

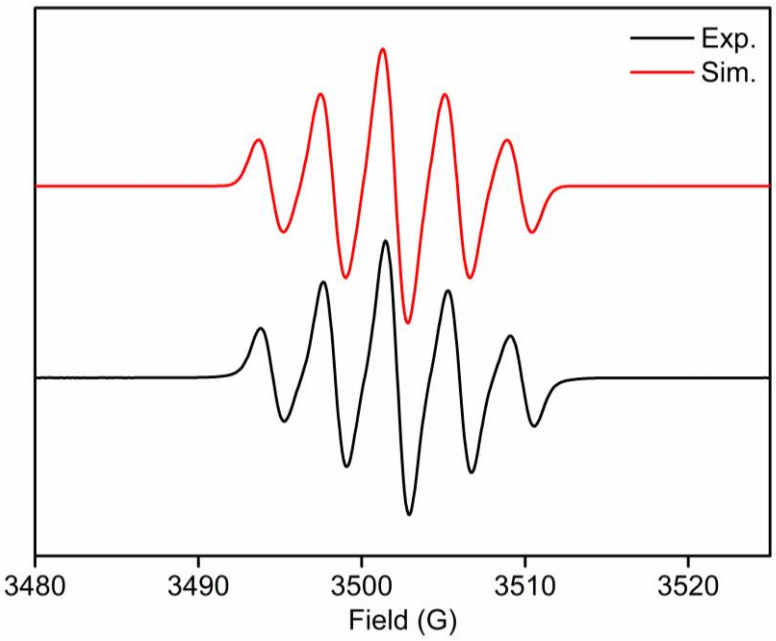


Figure S19. X-Band EPR spectrum of **3d** in THF. g = 2.0043, hyperfine coupling constants: $A_{iso}(^{14}N)$ = 3.85, 3.75 MHz, line broadening: 0.151.

7. Computational details

All calculations were performed with the Gaussian(R) 09 program optimizer.[9] The theoretical approach is based on the density functional theory (DFT) framework.[10,11] The geometry optimizations of radicals **3a**–**d** were calculated at the UB3LYP/6-311G** level of theory using the crystal structure coordinate of **3a**–**d**

as the starting model, respectively. The geometry optimizations of **4a**$^{-}$ were calculated at the B3LYP-D3-(BJ)/def2-SVP level of theory. Frequency analysis was performed to verify the stationary state geometry. In all cases no imaginary frequency was found. Wiberg bond indices (WBIs) were calculated from the optimized geometry with Löwdin orthogonalization method using Multiwfn. Time-dependent density functional theory (TD-DFT) was employed to calculate excitation energies. We used the functional B3LYP in combination the def2-TZVP basis sets. The solvent DMF was described in this case by the conductor-like polarizable continuum model, CPCM.

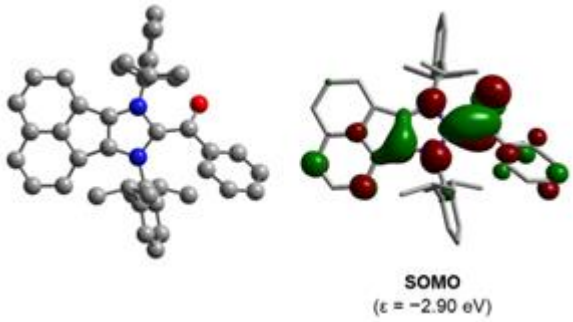


Figure S20. Optimized structure at the UB3LYP/6-311G** level of theory for **3a** (left) and the shape of SOMO and eigenvalues (eV) at the UB3LYP/6-311G** level of theory for **3a** (right). Hydrogen atoms have been omitted for clarity.

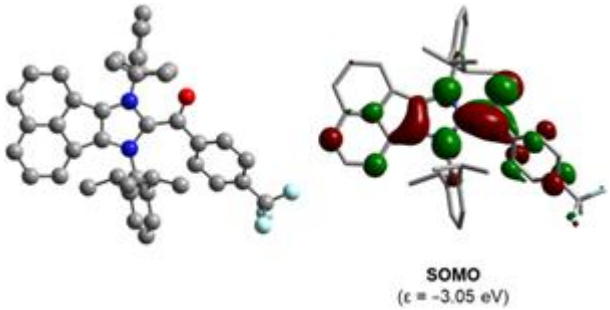


Figure S21. Optimized structure at the UB3LYP/6-311G** level of theory for **3b** (left) and the shape of SOMO and eigenvalues (eV) at the UB3LYP/6-311G** level of theory for **3b** (right). Hydrogen atoms have been omitted for clarity.

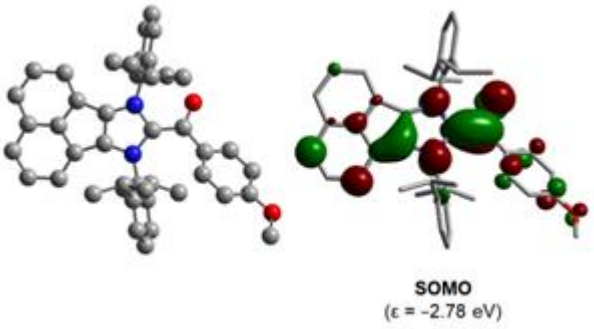


Figure S22. Optimized structure at the UB3LYP/6-311G** level of theory for **3c** (left) and the shape of SOMO and eigenvalues (eV) at the UB3LYP/6-311G** level of theory for **3c** (right). Hydrogen atoms have been omitted for clarity.

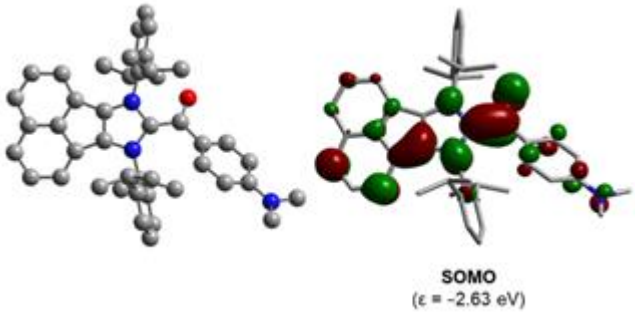


Figure S23. Optimized structure at the UB3LYP/6-311G** level of theory for **3d** (left) and the shape of SOMO and eigenvalues (eV) at the UB3LYP/6-311G** level of theory for **3d** (right). Hydrogen atoms have been omitted for clarity.

8. UV–vis spectra

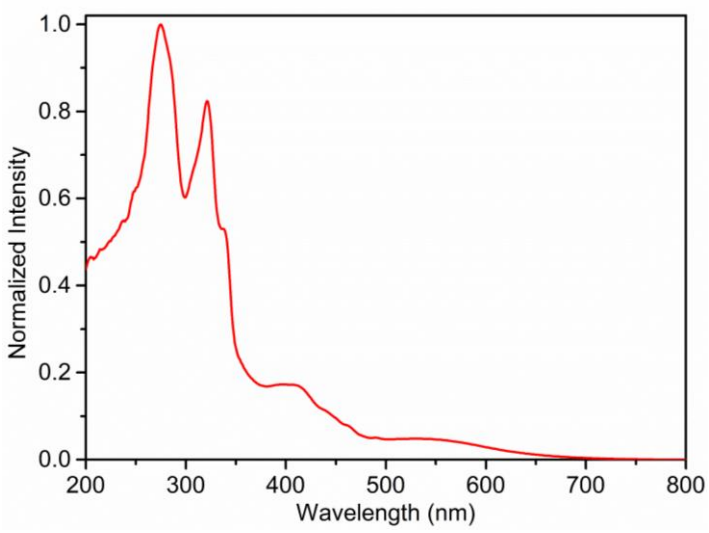


Figure S24. UV–vis spectrum of **3a** in DMF at room temperature (c = 10^{-5} M).

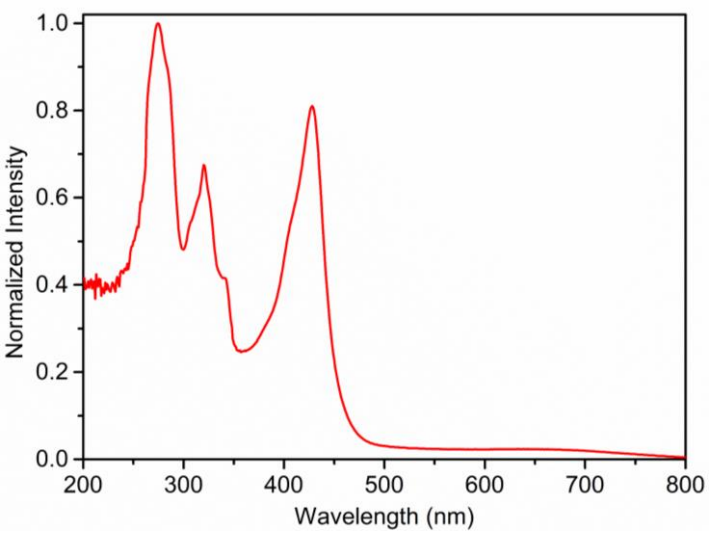


Figure S25. UV–vis spectrum of **3b** in DMF at room temperature (c = 10^{-5} M).

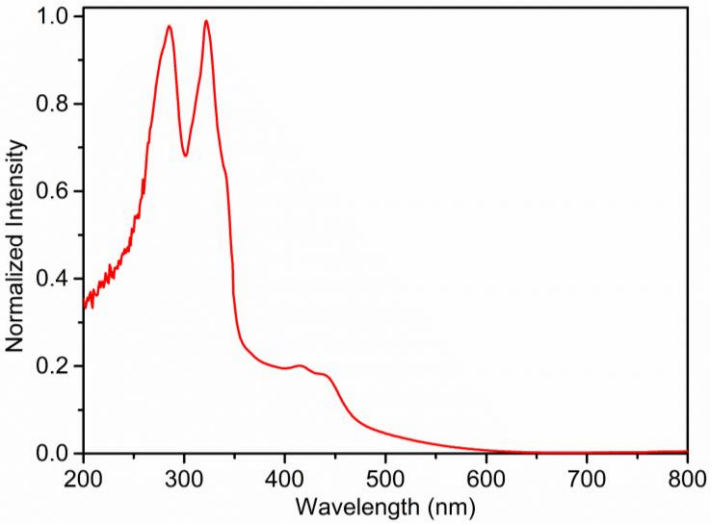


Figure S26. UV–vis spectrum of **3c** in DMF at room temperature (c = 10^{-5} M).

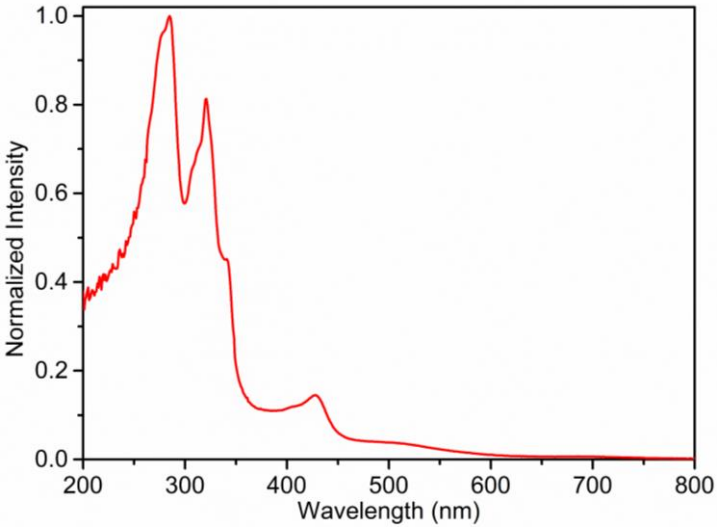


Figure S27. UV–vis spectrum of **3d** in DMF at room temperature (c = 10^{-5} M).

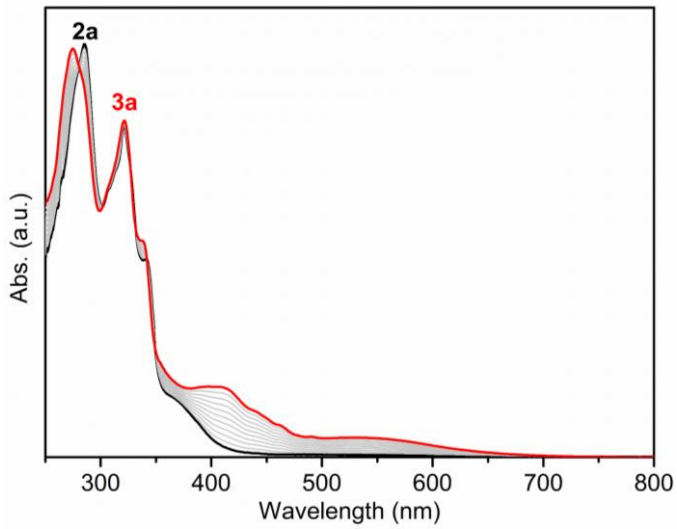


Figure S28. Spectroelectrochemistry of **2a** in DMF (c = 10^{-5} M). Experiment performed with Pt working electrode, Pt wire counter electrode and Ag wire reference electrode with 0.1 M NBu_4PF_6 electrolyte.

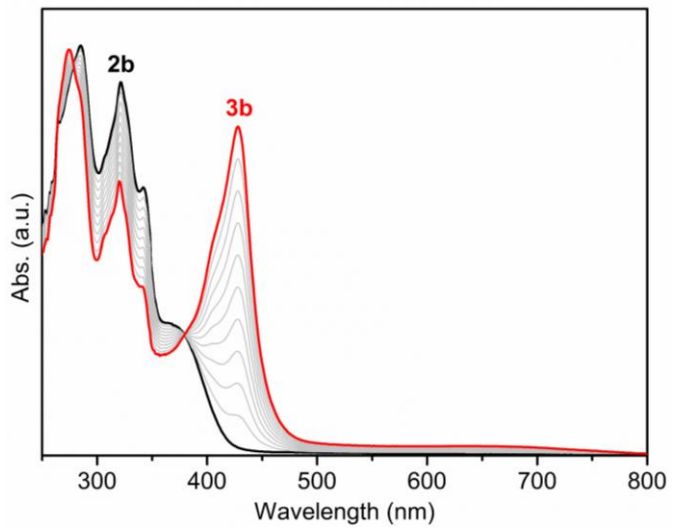


Figure S29. Spectroelectrochemistry of **2b** in DMF (c = 10^{-5} M). Experiment performed with Pt working electrode, Pt wire counter electrode and Ag wire reference electrode with 0.1 M NBu_4PF_6 electrolyte.

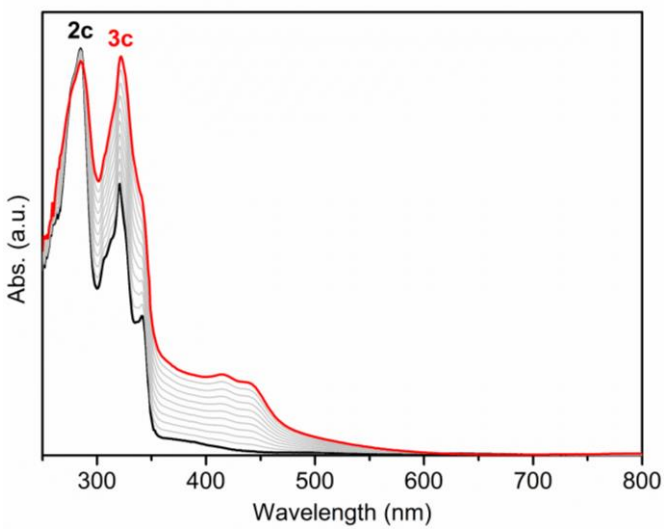


Figure S30. Spectroelectrochemistry of **2c** in DMF (c = 10^{-5} M). Experiment performed with Pt working electrode, Pt wire counter electrode and Ag wire reference electrode with 0.1 M NBu_4PF_6 electrolyte.

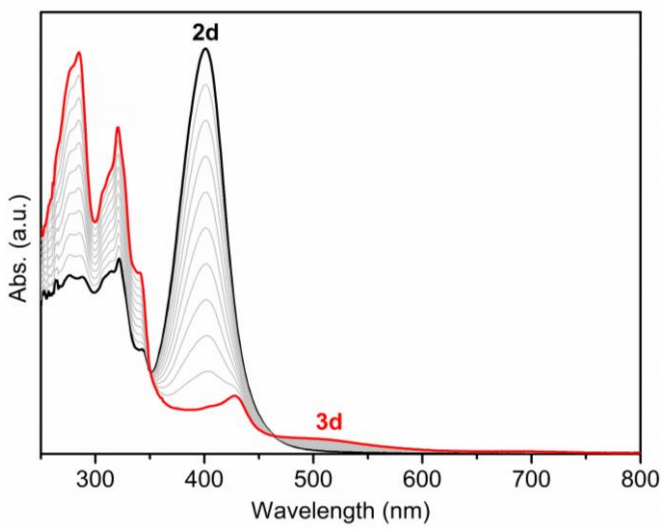


Figure S31. Spectroelectrochemistry of **2d** in DMF (c = 10^{-5} M). Experiment performed with Pt working electrode, Pt wire counter electrode and Ag wire reference electrode with 0.1 M NBu_4PF_6 electrolyte.

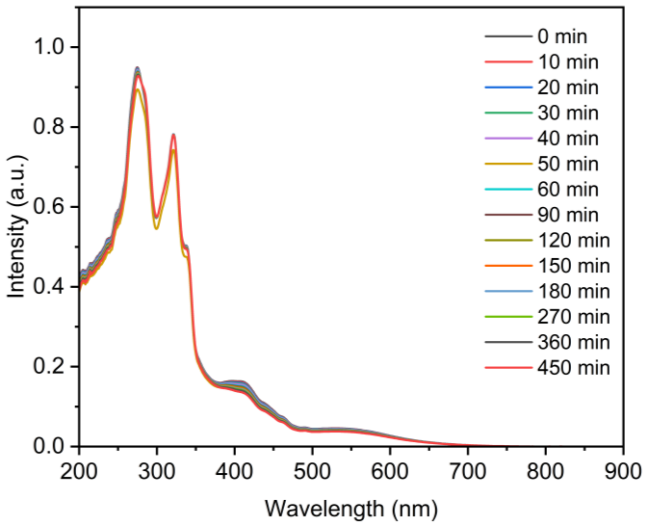


Figure S32. Decays of UV–vis spectra of **3a** (λ = 395 nm) in DMF (c = 10^{-5} M).

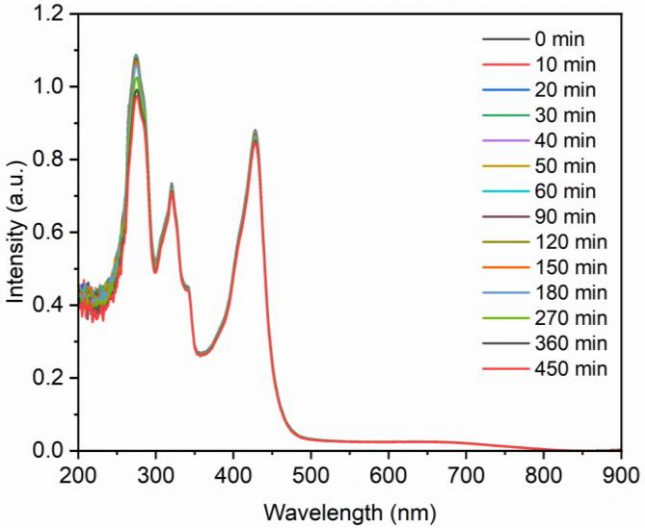


Figure S33. Decays of UV–vis spectra of **3b** (λ = 428 nm) in DMF (c = 10^{-5} M).

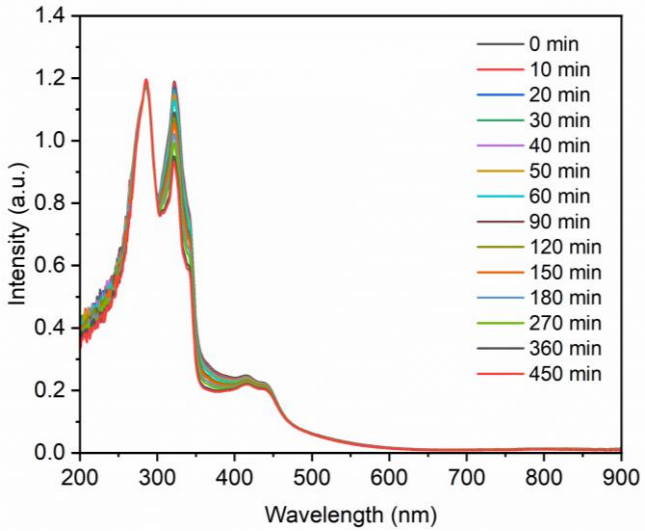


Figure S34. Decays of UV–vis spectra of **3c** (λ = 440 nm) in DMF (c = 10^{-5} M).

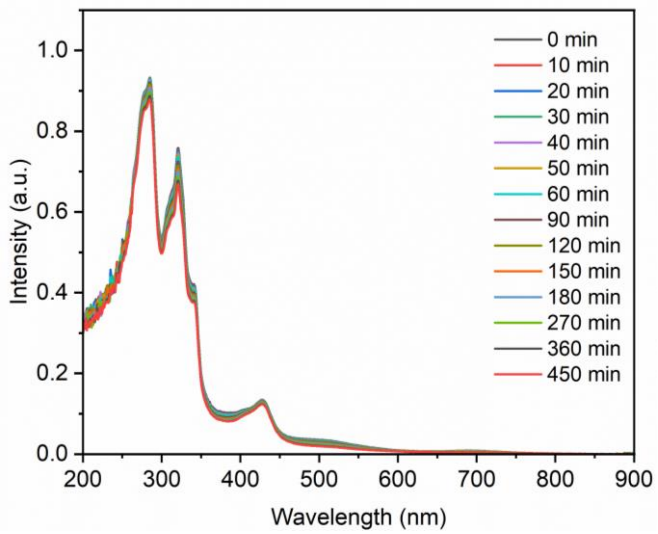


Figure S35. Decays of UV–vis spectra of **3d** (λ = 428 nm) in DMF (c = 10^{-5} M).

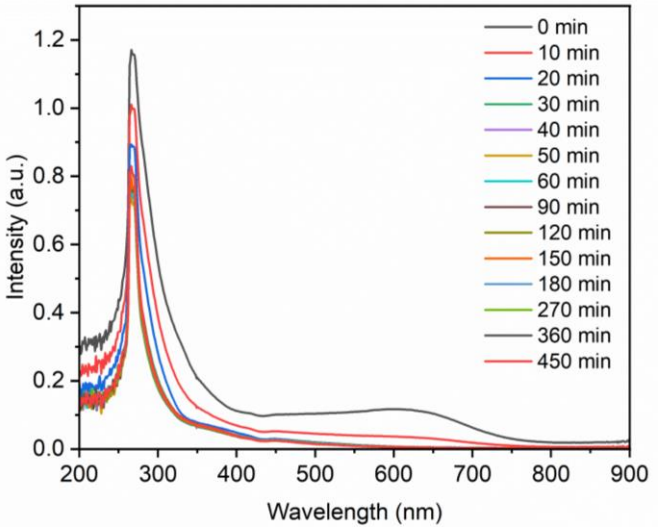


Figure S36. Decays of UV–vis spectra of **C** (λ = 600 nm) in DMF (c = 10^{-5} M).

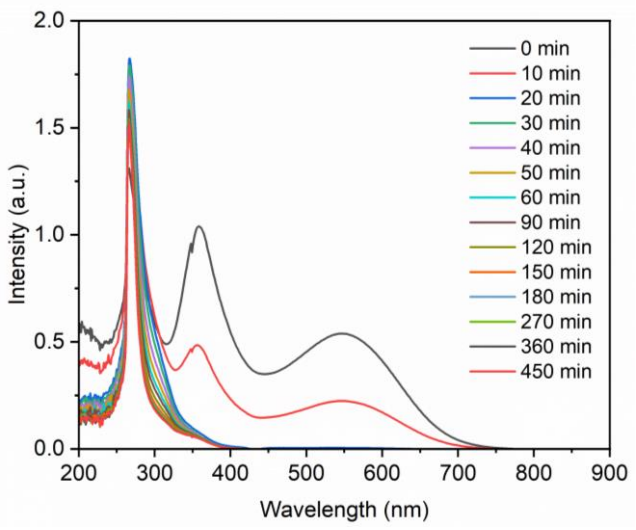


Figure S37. Decays of UV–vis spectra of **D** (λ = 545 nm) in DMF (c = 10^{-5} M).

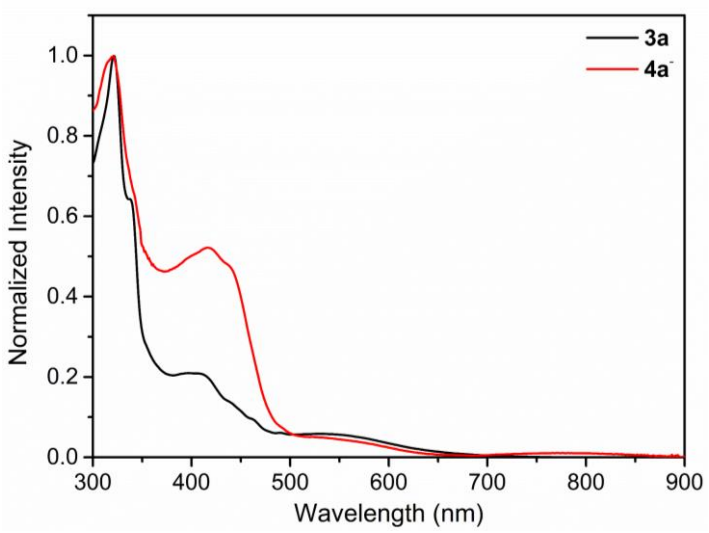


Figure S38. UV–vis spectra of **3a** and **4a**$^{-}$ in DMF at room temperature (c = 10^{-5} M).

9. TGA spectra

The TGA spectra were carried on the NETZSCH STA 449C microanalyzer from room temperature to 800°C at the heating rate of 10°C·min^{-1}. All samples for spectra were prepared under N_2 atmosphere.

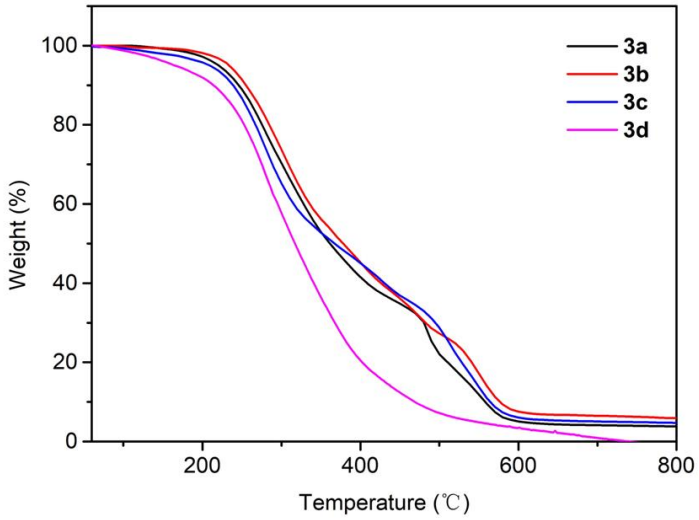


Figure S39. The TGA curve of **3a**–**d** under an N_2 atmosphere with the heating rate of 10°C min^{-1}.

10. Cartesian coordinates of the optimized geometries by DFT calculations

Table S7. Cartesians coordinates of calculated **3a** at the UB3LYP/6-311G** level of theory.

Atom	X	Y	Z
N	-0.74259	0.586759	0.001703
N	1.080687	-0.774961	0.081068
O	-0.369159	-3.05325	-0.643594
C	1.520419	0.534495	0.107839
C	2.761648	1.315341	0.118182
C	0.417076	1.383802	0.033169
C	2.304356	2.6736	0.002542
C	3.169101	3.783602	-0.056949
C	-2.065876	1.161994	-0.145026
C	-0.339594	-0.791449	0.007344
C	0.861958	2.76717	-0.07013
C	1.994447	-1.903475	0.195801
C	-2.683983	1.765989	0.990107
C	0.296396	4.035758	-0.239314
H	-0.784094	4.175023	-0.322848
C	2.553072	5.074252	-0.214758
H	3.176035	5.971643	-0.271408
C	4.130838	1.06937	0.19571
H	4.528087	0.055536	0.285687
C	-2.662809	1.19454	-1.435591
C	-1.05702	-2.020039	-0.23775
C	-2.522844	-2.179309	-0.047031
C	2.241647	-2.447982	1.482113
C	4.57322	3.502386	0.027811
H	5.292505	4.326458	-0.009548
C	1.163027	5.173579	-0.307615
H	0.707862	6.159646	-0.439158
C	-1.962698	0.625186	-2.674031
H	-1.141552	-0.029206	-2.332321
C	5.025724	2.185743	0.152506
H	6.100377	1.993448	0.21509
C	3.673548	-3.336569	-0.795865
H	4.220087	-3.69727	-1.672075

C	3.227183	-3.453301	1.589815
H	3.432172	-3.895918	2.568972
C	-3.923522	2.411785	0.793496
H	-4.417977	2.887234	1.645445
C	-2.058851	1.74708	2.393672
H	-1.19832	1.052753	2.368861
C	2.693042	-2.336919	-0.961885
C	-4.535213	2.446491	-0.468318
H	-5.499119	2.948136	-0.594716
C	3.943754	-3.889429	0.466213
H	4.706031	-4.667136	0.57088
C	-3.910516	1.840403	-1.568016
H	-4.390023	1.877609	-2.549664
C	-3.255851	-1.537333	0.977299
H	-2.737162	-0.855739	1.652754
C	1.458282	-2.013633	2.723485
H	0.789952	-1.182872	2.432125
C	2.364992	-1.812545	-2.362077
H	1.620546	-1.003071	-2.254247
C	-2.904484	-0.23881	-3.547816
H	-3.369858	-1.044157	-2.955992
H	-2.331498	-0.699694	-4.37145
H	-3.708377	0.366822	-4.003818
C	-3.192066	-3.131248	-0.860045
H	-2.606809	-3.665017	-1.612897
C	-4.623122	-1.80168	1.160213
H	-5.171223	-1.298538	1.962939
C	-1.333323	1.77418	-3.509134
H	-2.115912	2.463455	-3.875288
H	-0.800987	1.363586	-4.385575
H	-0.61472	2.360605	-2.911179
C	3.604226	-1.217829	-3.07604
H	4.049668	-0.392538	-2.494158
H	3.317744	-0.823872	-4.067474
H	4.384083	-1.984529	-3.235869
C	-4.558834	-3.390242	-0.682614
H	-5.061306	-4.119834	-1.325152

C	-5.28434	-2.722083	0.325437
H	-6.349394	-2.928084	0.467053
C	2.390087	-1.490737	3.845901
H	3.071552	-2.283584	4.203466
H	1.793401	-1.147786	4.710029
H	3.006483	-0.64527	3.494404
C	-3.047922	1.246509	3.480221
H	-3.891174	1.948485	3.607437
H	-2.528088	1.17514	4.451932
H	-3.467045	0.254833	3.244353
C	1.707662	-2.933113	-3.211333
H	2.416513	-3.76329	-3.384586
H	1.4026	-2.536321	-4.196867
H	0.822935	-3.327764	-2.686539
C	0.560012	-3.172232	3.232272
H	-0.097225	-3.541089	2.427718
H	-0.068071	-2.83192	4.075134
H	1.173328	-4.020175	3.587288
C	-1.526812	3.147565	2.803682
H	-0.760113	3.51746	2.105531
H	-1.079385	3.102559	3.812731
H	-2.352152	3.88247	2.831396

E (UB3LYP/6-311G**) = -1887.81543602 Hartree

Table S8. Cartesians coordinates of calculated **3b** at the UB3LYP/6-311G** level of theory.

Atom	X	Y	Z
N	-0.172358	0.850867	-0.0076
N	-1.474344	-0.996478	0.09243
C	-1.509084	1.24601	-0.013332
C	-3.711353	0.466681	0.057246
C	-2.014263	-2.341814	0.189707
C	-3.69254	1.893638	-0.074284
C	-2.354146	2.424047	-0.136396
C	-2.29377	0.106183	0.071237
C	0.90099	1.815133	-0.084549
C	-4.853837	2.682035	-0.154168

O	0.580929	-2.746184	-0.388394
C	-0.127512	-0.571138	0.040078
C	-2.203132	3.799256	-0.311718
H	-1.214807	4.26249	-0.385974
C	1.215478	2.573551	1.077271
C	-4.662232	4.094009	-0.3203
H	-5.530554	4.757444	-0.391634
C	-4.936568	-0.184968	0.128987
H	-5.000999	-1.272174	0.23039
C	-2.545756	-2.937814	-0.980333
C	-2.12212	-2.939872	1.467037
C	-6.101413	1.985496	-0.075245
H	-7.040012	2.54816	-0.128224
C	-3.373555	4.613865	-0.400355
H	-3.241815	5.692302	-0.53682
C	1.538096	2.035306	-1.332183
F	7.379873	-1.888386	-0.203051
C	-6.127895	0.59973	0.064322
H	-7.092951	0.08643	0.122973
C	-2.786198	-4.177824	1.549751
H	-2.873832	-4.670793	2.523689
C	2.211422	3.560718	0.954187
H	2.4778	4.162113	1.829968
F	7.14413	-0.275537	1.274812
F	7.086578	0.178035	-0.868631
C	-3.204831	-4.171365	-0.836106
H	-3.613959	-4.663183	-1.724972
C	2.390959	-1.244491	-0.061859
C	0.932435	-1.545147	-0.137361
C	-3.331239	-4.787041	0.414892
H	-3.847598	-5.748776	0.503035
C	2.869291	3.784113	-0.260032
H	3.64522	4.553787	-0.328332
C	2.987038	-0.313788	0.815035
H	2.357922	0.278776	1.4789
C	2.532853	3.028608	-1.388201
H	3.045019	3.218943	-2.336361

C	0.532695	2.363917	2.433263
H	-0.170956	1.518776	2.335234
C	-2.348355	-2.333889	-2.369009
H	-1.917197	-1.325218	-2.243182
C	3.246185	-2.060811	-0.844616
H	2.788235	-2.824616	-1.47861
C	4.375417	-0.161692	0.876219
H	4.817688	0.557266	1.571279
C	5.207309	-0.950491	0.063076
C	1.125872	1.29186	-2.602025
H	0.521404	0.418044	-2.304286
C	4.631926	-1.907931	-0.79561
H	5.27717	-2.539159	-1.413467
C	-1.496581	-2.324706	2.715781
H	-1.126259	-1.318407	2.45117
C	6.696583	-0.739182	0.070953
C	-3.672339	-2.173402	-3.14398
H	-4.151082	-3.148984	-3.342
H	-3.484521	-1.695739	-4.121704
H	-4.393225	-1.547169	-2.591169
C	-0.285308	3.606305	2.853928
H	0.36925	4.486119	2.988103
H	-0.793606	3.418334	3.816046
H	-1.053731	3.862384	2.107503
C	2.330803	0.759789	-3.404197
H	2.949689	1.578848	-3.811153
H	1.973321	0.164482	-4.262347
H	2.975432	0.116298	-2.783734
C	0.234232	2.199432	-3.482112
H	-0.660968	2.542247	-2.935829
H	-0.100334	1.653311	-4.381767
H	0.790652	3.093798	-3.815826
C	1.538367	2.006233	3.552245
H	2.107998	1.088797	3.330806
H	0.998681	1.844088	4.501683
H	2.265154	2.820692	3.719503
C	-2.515579	-2.151589	3.86134

H	-3.3717	-1.528989	3.549362
H	-2.036126	-1.666121	4.729633
H	-2.912528	-3.123211	4.205059
C	-0.275861	-3.161227	3.163123
H	-0.5881	-4.167747	3.494985
H	0.241123	-2.672952	4.008532
H	0.437582	-3.285281	2.332302
C	-1.323921	-3.173699	-3.166074
H	-0.383122	-3.264457	-2.599465
H	-1.115459	-2.700994	-4.142909
H	-1.711037	-4.19043	-3.359015

E (UB3LYP/6-311G**) = -2224.40443854 Hartree

Table S9. Cartesians coordinates of calculated **3c** at the UB3LYP/6-311G** level of theory.

Atom	X	Y	Z
N	1.219827	-0.935471	0.100603
N	-0.23959	0.788245	-0.027131
O	-0.659115	-2.865289	-0.405018
C	3.184069	2.124597	-0.033299
C	4.277821	3.007998	-0.097141
C	1.878026	-2.22763	0.196907
C	1.062079	1.30287	-0.006419
C	1.939561	0.229673	0.095608
C	3.323079	0.706599	0.104233
C	1.804094	2.541125	-0.118922
C	-1.386756	1.659067	-0.112371
C	-0.156537	-0.633846	0.018573
O	-6.813279	-1.558031	-0.138473
C	2.020428	-2.823952	1.471583
C	1.544192	3.904621	-0.298364
H	0.522267	4.284475	-0.389128
C	2.484435	-2.757917	-0.968143
C	4.597828	0.156056	0.197772
H	4.7495	-0.9222	0.303496
C	3.972557	4.400512	-0.26911
H	4.783631	5.133684	-0.329097

C	2.644	4.809815	-0.369138
H	2.42617	5.874019	-0.509846
C	-1.121713	-1.701292	-0.173295
C	-1.771762	2.38766	1.047405
C	2.801563	-3.991394	1.55705
H	2.922114	-4.482288	2.528701
C	5.574885	2.416306	0.003726
H	6.464423	3.055131	-0.036254
C	-2.028681	1.833837	-1.365095
C	5.717952	1.035627	0.148851
H	6.722524	0.607138	0.224068
C	-2.602731	-1.527952	-0.137237
C	3.259013	-3.922195	-0.821064
H	3.731889	-4.363059	-1.705069
C	-2.833975	3.302107	0.91626
H	-3.152522	3.880112	1.790558
C	3.423746	-4.53337	0.427657
H	4.031722	-5.439775	0.518439
C	-3.089348	2.755835	-1.430776
H	-3.601104	2.913982	-2.385268
C	-3.307265	-0.664535	0.72112
H	-2.759076	-0.009831	1.399659
C	-3.489669	3.484856	-0.305902
H	-4.313883	4.202068	-0.383213
C	-5.443163	-1.498312	-0.080158
C	2.248967	-2.163908	-2.355477
H	1.72977	-1.197939	-2.228162
C	-1.090922	2.219431	2.409544
H	-0.329365	1.426066	2.313655
C	-3.364254	-2.41229	-0.945131
H	-2.826031	-3.125049	-1.576109
C	-1.557098	1.117492	-2.629586
H	-0.899529	0.286039	-2.323421
C	1.313835	-2.284144	2.711968
H	0.850243	-1.317736	2.446407
C	-4.709373	-0.638602	0.758046
H	-5.211924	0.043771	1.448126

C	-4.755582	-2.391472	-0.93183
H	-5.341023	-3.06421	-1.566017
C	3.560488	-1.883121	-3.116719
H	4.218413	-1.199835	-2.553296
H	3.340035	-1.417131	-4.093314
H	4.123656	-2.812022	-3.316353
C	-2.717706	0.505191	-3.440022
H	-3.318261	-0.18431	-2.824759
H	-2.314508	-0.061071	-4.297757
H	-3.389988	1.280265	-3.848917
C	-0.718274	2.078109	-3.505029
H	-1.329545	2.930814	-3.85203
H	-0.337068	1.550252	-4.397094
H	0.144894	2.483699	-2.950573
C	0.172734	-3.240649	3.128688
H	-0.511698	-3.421786	2.284123
H	-0.402057	-2.814527	3.970379
H	0.575485	-4.216502	3.454582
C	-7.544196	-0.679905	0.71558
H	-8.606146	-0.879354	0.510753
H	-7.320981	0.381873	0.496168
H	-7.333446	-0.88036	1.783638
C	2.286561	-2.020635	3.879894
H	2.766741	-2.951846	4.229174
H	1.743162	-1.588809	4.738964
H	3.085125	-1.316562	3.589456
C	1.309436	-3.085758	-3.166486
H	1.787952	-4.061889	-3.364384
H	1.065447	-2.625528	-4.141068
H	0.377086	-3.266013	-2.607389
C	-2.08242	1.783788	3.512985
H	-2.86306	2.546988	3.680028
H	-1.544047	1.647228	4.467312
H	-2.586636	0.832839	3.273826
C	-0.364923	3.512123	2.846462
H	0.392365	3.824102	2.10996
H	0.143977	3.352915	3.813542

H	-1.079215	4.344813	2.977916

E (UB3LYP/6-311G**) = -2002.33369468 Hartree

Table S10. Cartesians coordinates of calculated **3d** at the UB3LYP/6-311G** level of theory.

Atom	X	Y	Z
O	0.706817	-2.74855	0.461776
N	-0.010082	0.848427	0.048928
N	-1.319961	-0.986806	-0.092709
N	6.768074	-0.816279	-0.101378
C	-2.136268	0.111643	-0.090315
C	-2.194144	2.423797	0.146927
C	-1.351603	1.257131	0.025859
C	1.065218	1.803446	0.160846
C	-3.553897	0.469202	-0.105799
C	-3.534293	1.892108	0.046318
C	2.530564	-1.26957	0.101185
C	0.022626	-0.573355	-0.005202
C	1.689366	1.996941	1.419779
C	-1.855782	-2.33195	-0.221998
C	-2.407033	-2.949868	0.926758
C	1.394956	2.589772	-0.978541
C	1.07613	-1.562657	0.188511
C	-1.936941	-2.905797	-1.511871
C	3.131803	-0.338373	-0.769172
H	2.503765	0.269488	-1.42141
C	-4.778066	-0.187696	-0.215022
H	-4.83555	-1.273476	-0.335267
C	-4.700621	2.679454	0.11154
C	-2.054146	3.80503	0.347954
H	-1.06997	4.270249	0.456779
C	3.400406	-2.092821	0.856619
H	2.95413	-2.863584	1.491713
C	-2.24978	-2.36425	2.327984
H	-1.804474	-1.358852	2.228835
C	-3.055693	-4.184115	0.747741
H	-3.480449	-4.692735	1.619728
C	4.516988	-0.19461	-0.85754

H	4.922438	0.529525	-1.567478
C	-4.516523	4.090749	0.302512
H	-5.387392	4.751568	0.364628
C	-3.226868	4.609919	0.420298
H	-3.102285	5.686969	0.577349
C	0.730768	2.409734	-2.347745
H	0.026676	1.562456	-2.276795
C	4.78478	-1.954196	0.794252
H	5.406323	-2.6135	1.404698
C	1.261738	1.227706	2.668728
H	0.654818	0.364971	2.345858
C	-2.592784	-4.14559	-1.629569
H	-2.662138	-4.619758	-2.614302
C	5.387086	-0.983276	-0.056294
C	-3.15444	-4.778447	-0.516149
H	-3.664181	-5.740955	-0.631145
C	-5.940639	1.980523	-0.005081
H	-6.881501	2.541198	0.034952
C	2.387379	3.575425	-0.821441
H	2.661539	4.197967	-1.680153
C	-1.300053	-2.260745	-2.739958
H	-0.926121	-1.2641	-2.446745
C	7.62867	-1.781728	0.568477
H	7.407892	-1.821762	1.65054
H	8.676906	-1.467593	0.454688
H	7.526529	-2.809318	0.160153
C	-5.9668	0.592505	-0.165352
H	-6.93179	0.082886	-0.252971
C	2.682267	2.989381	1.510695
H	3.180414	3.160189	2.47028
C	3.030279	3.772643	0.405183
H	3.801303	4.544631	0.501576
C	1.75349	2.076933	-3.459065
H	2.481093	2.896417	-3.597665
H	1.228499	1.934597	-4.420033
H	2.32122	1.155726	-3.247778
C	-1.264236	-3.222801	3.153169

H	-1.667763	-4.237698	3.320982
H	-1.089191	-2.762127	4.14228
H	-0.303489	-3.315294	2.621717
C	2.457247	0.669952	3.46752
H	3.101026	0.036218	2.835933
H	2.089998	0.058094	4.309975
H	3.078106	1.476374	3.896817
C	-3.600171	-2.19798	3.055516
H	-4.292624	-1.557517	2.483381
H	-3.443779	-1.733326	4.045056
H	-4.095917	-3.170942	3.223706
C	-0.08319	3.659479	-2.753599
H	-0.859564	3.89996	-2.01038
H	-0.580766	3.489292	-3.724757
H	0.572551	4.541929	-2.864372
C	7.352667	0.040343	-1.123172
H	7.162383	-0.324045	-2.155106
H	8.441112	0.090455	-0.970325
H	6.957055	1.06929	-1.046821
C	-0.081224	-3.089284	-3.20636
H	0.634053	-3.233603	-2.380342
H	0.43648	-2.582204	-4.040284
H	-0.394488	-4.087532	-3.561693
C	-2.313644	-2.051894	-3.884485
H	-2.712441	-3.012465	-4.256268
H	-1.829313	-1.543526	-4.736924
H	-3.168249	-1.435208	-3.557564
C	0.366535	2.120583	3.559878
H	0.92377	3.005774	3.916276
H	0.021791	1.557609	4.44538
H	-0.521925	2.477912	3.012103

E (UB3LYP/6-311G**) = -2021.87373474 Hartree

Table S11. Cartesians coordinates of calculated **4a**$^{-}$ at the B3LYP-D3-(BJ)/def2-SVP level of theory.

Atom	X	Y	Z
O	-0.37926000	-3.06484400	-0.55305900

N	1.10346900	-0.81624100	-0.01049700
N	-0.70549700	0.59006600	-0.03066900
C	-0.34979500	-0.80895600	-0.01874400
C	-2.40138300	1.69432600	1.35522200
C	-1.98632700	1.22183900	0.08892500
C	-2.75562000	1.43784400	-1.07347900
C	-3.95483000	2.14905600	-0.94439900
H	-4.56353400	2.33149800	-1.82550000
C	-4.37966100	2.62768700	0.29204000
H	-5.31405100	3.17923200	0.36982600
C	-3.60867000	2.40071700	1.42868400
H	-3.94706800	2.77920900	2.39020200
C	-2.53940700	-2.12514000	-0.37133200
C	-3.46959200	-1.50829600	0.48556200
H	-3.11717600	-0.83302100	1.25374600
C	-4.83721500	-1.76937700	0.38884100
H	-5.52362700	-1.27303800	1.07268100
C	-5.32284100	-2.67439900	-0.55723600
H	-6.38823500	-2.88339000	-0.62844200
C	-4.40886500	-3.33031000	-1.39297400
H	-4.76545100	-4.05490000	-2.12370200
C	-3.04638600	-3.07258300	-1.29060400
H	-2.32594400	-3.60357100	-1.90387300
C	0.44315600	1.33541700	-0.09869700
C	2.27447700	2.67751400	-0.13145500
C	0.85200700	2.74635600	-0.14204300
C	1.54644000	0.51775700	-0.08395100
C	-1.05434200	-1.98883700	-0.31719900
C	3.90926200	-3.16801700	-0.60271700
H	4.61721000	-3.41606000	-1.38951000
C	3.10498000	3.80060200	-0.15591900
C	2.74220700	1.31153700	-0.08174800
C	4.12610400	1.11894900	-0.02796700
H	4.55472400	0.12369800	0.03206300
C	4.97944300	2.25404600	-0.04895500

H	6.05367600	2.07934800	-0.01051800
C	2.91661300	-2.21425700	-0.84837000
C	3.04237300	-3.56483100	1.60461500
H	3.08677100	-4.10394500	2.54870900
C	1.99726400	-1.90536200	0.18805900
C	1.04742500	-2.33290900	2.53748000
H	0.40817500	-1.50531800	2.22016900
C	3.98343800	-3.83935800	0.61670100
H	4.75858700	-4.58368400	0.78735900
C	2.44960700	5.06362900	-0.20862700
H	3.04487200	5.97507400	-0.22978800
C	4.52045600	3.56067700	-0.11544000
H	5.21642500	4.39588100	-0.13031700
C	0.24136100	3.98707000	-0.19675500
H	-0.83997200	4.09097900	-0.21028000
C	2.72146800	-1.65346800	-2.25569500
H	2.16732500	-0.71533100	-2.17187600
C	2.04972800	-2.59615600	1.42075500
C	-1.58202800	1.46466600	2.62452900
H	-0.70926800	0.86437600	2.35417700
C	-2.36924300	0.67585800	3.68994300
H	-2.69635500	-0.29835300	3.31360900
H	-1.73691400	0.50065600	4.56894600
H	-3.25849700	1.22440900	4.02509200
C	1.06453000	5.14513700	-0.23046800
H	0.58771400	6.12178900	-0.27160200
C	-2.28479900	0.95522300	-2.44193800
H	-1.50007000	0.21254200	-2.27359100
C	-1.06776500	2.79234700	3.21606500
H	-1.89886000	3.43580900	3.53278300
H	-0.44308000	2.59795200	4.09654900
H	-0.46672600	3.34679500	2.48971300
C	-3.40021100	0.26149800	-3.24422900
H	-4.19885600	0.95954400	-3.52698500
H	-2.98495200	-0.14922100	-4.17256800

H	-3.84399000	-0.56236000	-2.67847000
C	4.02677100	-1.33560000	-3.00205900
H	4.62293700	-2.23572200	-3.19925900
H	3.79783900	-0.88357000	-3.97551200
H	4.64850300	-0.62886400	-2.44079500
C	1.83746300	-2.63355800	-3.05764800
H	0.93170300	-2.87283600	-2.48866000
H	1.55878400	-2.19913000	-4.02796300
H	2.37864900	-3.57012500	-3.25012100
C	1.73187100	-1.90819100	3.85011000
H	2.35816800	-1.02058300	3.70274000
H	0.98029400	-1.67214600	4.61528400
H	2.37105800	-2.70409000	4.25305300
C	0.12918500	-3.55473500	2.74077600
H	0.69659800	-4.41827600	3.11391500
H	-0.65758600	-3.33166200	3.47431200
H	-0.33272400	-3.82749800	1.78718400
C	-1.67229300	2.11749700	-3.25044500
H	-0.84051700	2.58573400	-2.71464600
H	-1.29385500	1.75376900	-4.21383100
H	-2.42255900	2.89291600	-3.45497800

E (B3LYP-D3-(BJ)/def2-SVP) = -1888.522639 Hartree

11. Abstracted results of TD-DFT calculations

Table S12. UB3LYP/def2-TZVP computed transitions for **3a** with oscillator strengths (*f*) greater than 0.01.

166A is SOMO

	$\lambda_{(nm)}$	*f*	Assignment	
1	561.78	0.0094	165A -> 167A	0.83865
			165B -> 166B	0.24599
2	423.61	0.1804	156B -> 167B	-0.32715
			164B -> 167B	0.79924
			165B -> 167B	0.28542
3	362.69	0.0135	162A -> 173A	0.38482
			165A -> 172A	-0.24902
			162B -> 172B	0.33699
			162B -> 173B	-0.22238
			164B -> 171B	0.22555
			165B -> 167B	0.25273
4	359.69	0.0509	161A -> 171A	0.25752
			166A -> 171A	0.21376
			160B -> 170B	-0.24323

			165B -> 167B	0.53450
5	359.05	0.0339	160A -> 170A	-0.25874
			161A -> 171A	-0.28322
			157B -> 169B	0.22707
			160B -> 170B	0.29466
			165B -> 167B	0.39126
6	349.08	0.0517	158A -> 167A	0.22862
			166A -> 172A	0.72153
			158B -> 166B	0.21265
			165B -> 167B	-0.32621
7	340.63	0.1743	166A -> 171A	0.45797
			166A -> 172A	-0.43750
			166A -> 174A	-0.20386
			165B -> 167B	-0.36872
8	301.16	0.1947	163A -> 167A	0.68233
			163B -> 166B	-0.64419
9	283.99	0.0317	158A -> 167A	0.35153
			163A -> 168A	0.29415
			166A -> 175A	0.41843
			166A -> 180A	0.34919
			158B -> 166B	-0.32746
			163B -> 167B	0.22011
10	276.46	0.0666	158A -> 167A	0.34590
			164A -> 167A	-0.21546
			158B -> 166B	-0.46205
			163B -> 168B	0.57305
11	274.00	0.0409	159A -> 174A	0.27758
			166A -> 175A	0.24677
			159B -> 174B	-0.28508
			161B -> 167B	0.45070
			162B -> 167B	-0.20698

Table S13. UB3LYP/def2-TZVP computed transitions for **3b** with oscillator strengths (*f*) greater than 0.01.

182A is SOMO

	$\lambda_{(nm)}$	*f*	Assignment	
1	694.63	0.0198	180A -> 183A	0.25824
			182A -> 183A	0.92907
			181B -> 182B	0.19219
2	432.54	0.3427	172B -> 183B	0.32338
			180B -> 183B	0.81579
3	348.48	0.1518	172A -> 184A	-0.20769
			174A -> 184A	-0.23682
			172B -> 183B	-0.20148
			176B -> 183B	-0.21699
			176B -> 184B	0.20573
			181B -> 183B	0.34881
4	300.90	0.2227	179A -> 183A	0.67313
			179B -> 182B	-0.64545
5	278.61	0.0169	175A -> 185A	0.40004
			182A -> 191A	-0.24243
			175B -> 184B	0.22397
			175B -> 185B	-0.25034
			175B -> 186B	0.22303

			179B -> 182B	0.23156
			181B -> 185B	-0.20625
6	275.73	0.0530	175A -> 183A	-0.29829
			180A -> 183A	0.22727
			175B -> 182B	0.40272
			179B -> 184B	0.29269
			179B -> 185B	-0.38032
			179B -> 186B	0.32635
7	274.23	0.0261	177A -> 186A	-0.31838
			182A -> 191A	0.47963
			182A -> 193A	0.20054
			177B -> 185B	0.21475
			177B -> 186B	0.27747
8	273.68	0.0108	177A -> 186A	0.42353
			177A -> 187A	0.24678
			182A -> 191A	0.32015
			177B -> 186B	-0.39001
			177B -> 187B	-0.22895
9	261.6	0.0610	181A -> 184A	0.20270
			182A -> 193A	0.43957
			182A -> 198A	-0.24210
			182A -> 201A	-0.29131

Table S14. UB3LYP/def2-TZVP computed transitions for **3c** with oscillator strengths (*f*) greater than 0.01. 174A is SOMO

	$\lambda_{(nm)}$	*f*	Assignment	
1	536.16	0.0075	170A -> 175A	-0.28725
			171A -> 175A	0.56414
			170B -> 174B	0.59395
			171B -> 174B	0.25872
2	422.71	0.1882	164B -> 175B	-0.38540
			170B -> 175B	-0.24177
			172B -> 175B	0.51065
			173B -> 175B	0.31814
3	364.96	0.0234	169A -> 181A	0.21996
			169B -> 180B	0.28466
			171B -> 175B	-0.22433
			173B -> 175B	0.40885
4	361.43	0.0355	169B -> 180B	-0.26241
			171B -> 175B	-0.22564
			171B -> 179B	-0.22644
			173B -> 175B	0.53065
5	352.04	0.0701	174A -> 178A	0.29705
			174A -> 180A	0.68818
			172B -> 175B	0.20836
			173B -> 175B	-0.31949
6	346.02	0.0639	174A -> 178A	-0.32592
			174A -> 180A	0.45884
			174A -> 181A	-0.40475
			174A -> 182A	0.38026
			172B -> 175B	-0.20436
7	343.07	0.2351	174A -> 178A	-0.29878
			174A -> 179A	0.20974
			174A -> 180A	-0.31458
			174A -> 181A	-0.32503

			174A -> 182A	0.44981
			172B -> 175B	0.28106
			173B -> 175B	-0.36742
8	300.99	0.1808	170A -> 175A	-0.29681
			171A -> 175A	0.60916
			170B -> 174B	-0.57920
			171B -> 174B	-0.27513
9	276.80	0.0705	166A -> 175A	0.36291
			166B -> 174B	-0.48228
			170B -> 176B	0.51887
			171B -> 176B	0.22475

Table S15. UB3LYP/def2-TZVP computed transitions for **3d** with oscillator strengths (*f*) greater than 0.01.

178A is SOMO

	$\lambda_{(nm)}$	*f*	Assignment	
1	515.92	0.0100	174A -> 179A	0.59890
			175A -> 179A	-0.21382
			174B -> 178B	0.64070
2	426.52	0.1915	168B -> 179B	-0.35143
			176B -> 179B	0.66752
			177B -> 179B	-0.45510
3	372.94	0.0290	177A -> 183A	0.21734
			178A -> 180A	-0.25015
			178A -> 183A	0.37064
			175B -> 179B	0.39491
			177B -> 179B	0.34772
			177B -> 186B	0.29298
4	356.75	0.0837	178A -> 182A	0.56680
			178A -> 184A	-0.29612
			178A -> 186A	-0.20584
			176B -> 179B	-0.47761
5	350.87	0.1979	177A -> 186A	-0.24135
			178A -> 184A	0.33952
			178A -> 186A	0.57044
			176B -> 179B	-0.54366
			177B -> 185B	0.20422
6	348.17	0.0884	170A -> 179A	0.55243
			175A -> 179A	0.21114
			178A -> 185A	0.23439
			178A -> 186A	-0.33075
			170B -> 178B	0.45604
			176B -> 179B	-0.29418
7	347.16	0.1187	170A -> 179A	0.42896
			178A -> 182A	0.35196
			178A -> 185A	-0.22954
			178A -> 186A	0.35065
			170B -> 178B	0.44969
			176B -> 179B	0.37717
8	301.17	0.1854	174A -> 179A	0.62583
			175A -> 179A	-0.24145
			174B -> 178B	-0.61733
9	281.20	0.0825	170A -> 179A	-0.43763
			174A -> 180A	-0.22386

			177A -> 179A	0.60354
			170B -> 178B	0.47443
10	273.18	0.0235	171A -> 186A	0.26337
			177A -> 179A	0.27997
			177A -> 183A	0.22942
			177A -> 185A	-0.26280
			171B -> 185B	-0.26778
			172B -> 185B	0.22288
			174B -> 180B	0.20349
			177B -> 186B	0.25931

Table S16. B3LYP/def2-TZVP computed transitions for **4a**$^{-}$ with oscillator strengths (*f*) greater than 0.01. 166 is HOMO

	$\lambda_{(nm)}$	*f*	Assignment	
1	771.51	0.0194	166 ->168	0.69963
2	546.25	0.1778	166 ->169	0.63787
			166 ->171	0.25073
3	513.04	0.0690	166 ->168	-0.39738
			166 ->169	-0.20341
			166 ->170	0.22255
			166 ->171	0.48474
4	450.44	0.01122	166 ->172	0.45657
			166 ->173	-0.45549
5	442.77	0.0223	166 ->172	0.48309
			166 ->173	0.46919
6	423.18	0.1410	166 ->174	0.66156
7	393.85	0.0245	164 ->167	0.64981
8	291.06	0.3684	163 ->167	-0.22934
			166 ->176	0.53345
			166 ->177	-0.27618
9	284.58	0.1272	157 ->167	-0.25427
			166 ->176	0.25625
			166 ->177	0.46034
			166 ->178	0.22247
10	281.14	0.0913	157 ->167	0.49076
			163 ->168	-0.21746
			166 ->177	0.28262
11	271.06	0.1256	165 ->171	0.28047
			166 ->178	0.54095
12	269.94	0.0190	165 ->171	0.51862
			166 ->178	-0.28654
13	244.57	0.0116	156 ->170	0.21978
			158 ->170	0.20093
			159 ->167	0.21794
			159 ->169	0.28367
14	232.42	0.0105	166 ->179	-0.26833
			166 ->183	0.45926
			166 ->184	-0.24252

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