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SUPPORTING INFORMATION FOR

Poly(trifluoromethyl)azulenes: structures and acceptor properties

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Table of Contents

Experimental

General information: All reagents and solvents were reagent grade or better. ACS Grade dichloromethane (Fisher Scientific), HPLC Grade acetonitrile (Fisher Scientific), ACS Grade hexanes (Fisher Scientific), sodium thiosulfate crystals (Mallinckrodt), trifluoromethyl iodide (Synquest Labs), chloroform-D (Cambridge Isotopes Laboratories), and hexafluorobenzene (Oakwood Products) were used as received. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPDA UV detector set to 300 or 275 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with semipreparative 10 mm I.D. × 250 nm COSMOSIL Buckyprep column (Nacalai Tesque, Inc.) or analytical 4.6 mm I.D. × 150 nm FluoroFlash PF-C8 100 Å 5 μm column (Fluorous Technologies, Inc.). The atmospheric-pressure chemical ionization (APCI) mass spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (acetonitrile carrier solvent, 0.3 $mL \cdot min^{-1}$ flow rate, analyte samples injected as solutions in dichloromethane or acetonitrile). All NMR spectra were recorded on Varian INOVA 400 instrument in $CDCl_3$ solution. The ^1H and ^{19}F frequencies were 400 and 376 MHz, respectively. The ^{19}F chemical shifts were determined using hexafluorobenzene as an internal standard (δ −164.9). The ^1H chemical shifts were determined using the resonance of the residual $CHCl_3$ in $CDCl_3$ as an internal standard (δ 7.26). UV-vis absorption spectra were recorded by using a Cary 500 spectrophotometer with a resolution of 1 nm. Cyclic voltammetry measurements were carried out on PAR 263 potentiostat/galvanostat in anaerobic conditions using 0.1 M $N(n\mathrm{Bu})_4ClO_4$ in dimethoxyethane; platinum working and counter electrodes; silver wire quasi-reference electrode; 500 $mV \cdot s^{-1}$; ferrocene internal standard. X-ray diffraction data for a single crystal of AZUL-4-1 were recorded by using a Bruker Kappa APEX II CCD diffractometer at Colorado State University.

Trifluoromethylation of azulene: Azulene$(CF_3)_n$ was prepared according a modified literature procedure. Azulene (50 mg, 0.39 mmol, blue solid) was placed into a glass ampoule (327 mL) and the ampoule was cooled with liquid nitrogen and evacuated using a vacuum line equipped with a pressure gauge and a calibrated volume (51.7 mL). Using the calibrated volume and pressure gauge, CF_3I gas was measured (11.7 mmol, 30 equiv.), and then the measured CF_3I gas was condensed into the cooled ampoule containing azulene. The ampoule was then flame-sealed and warmed to room temperature. **DANGER! High pressure can be generated within the ampoule leading to explosive ampoule failure. The maximum pressure inside the ampoule at high temperature has to be calculated using ideal gas law. Depending on the size and wall thickness of the ampoule the maximum allowable pressure changes, so a conservative limit of 2-3 bar must be set. The burst pressure for the glass ampoule is largely determined by the quality of the seal, so care must be taken during the sealing step. Use shields and personal protection at all times. Only experienced personnel must perform these operations.** The sealed ampoule was then placed in a heating furnace and heated at 10 °C min^{-1} to 300 °C. When the formation of purple iodine gas was observed at 285 °C, the ampoule was heated for another 15 min. up to 300 °C before cooling to room temperature. After cooling to room temperature, the ampoule was cooled in liquid nitrogen and opened (lower than ambient pressure inside). Excess CF_3I gas was boiled off upon warming to room temperature and then the soluble products were dissolved in dichloromethane. The purple dichloromethane solution was washed twice with a saturated sodium thiosulfate solution (aq) to remove I_2 until color was no longer observed in the aqueous layer. The dichloromethane was removed by rotovap and the remaining solid was dissolved and filtered in acetonitrile (purple solution) for HPLC separation as described below. Care must be taken when rotovapping the crude mixture since some of the products are rather volatile. Total conversion of azulene to isolated products = 25 mol%.

HPLC purifications of azulene$(CF_3)_n$:

The first HPLC separation of the azulene$(CF_3)_n$ crude samples was done using semipreparative COSMOSIL Buckyprep HPLC column, acetonitrile eluent, flow rate of 5.0 mL·min^{-1}, 300 nm detection. Three different fractions 4.3–5.0 min (**I**), 5.0–5.8 min (**II**), and 5.9–6.7 min (**III**) were isolated for further separation using analytical FluoroFlash column, flow rate of 2.0 mL·min^{-1}. Second stage separation of **I** (acetonitrile/H_2O = 90:10, 300 nm detection) resulted in two more fractions: 3.4–5 min. (**IV**) and 5.9–7.3 min (**AZUL-4-1**). Fraction **IV** was further separated (acetonitrile/H_2O = 60:40, 275 nm detection) and resulted in two fractions: 20–21.6 min (**AZUL-3-2**) and 21.6–24.0 min (**AZUL-3-1**). Second stage separation of **II** (acetonitrile/H_2O = 80:20, 275 nm detection) resulted in one predominant fraction collected from 4.0–6.4 min (**AZUL-3-3**). Second stage separation of **III** (acetonitrile/H_2O = 95:5, 300 nm detection) resulted in two more fractions: 3.3–4.6 min (**V**) and 4.6–6.0 min (**AZUL-5-1**). Fraction **V** was further separated (acetonitrile/H_2O = 80:20, 300 nm detection) and resulted in two fractions: 6.8–7.8 min (**AZUL-4-3**) and 7.8–9.4 min (**AZUL-4-2**). The HPLC solvent mixtures could not easily be removed by rotovap due to the volatility of the compounds. Acetonitrile/H_2O mixtures were cooled in a freezer until purple acetonitrile solutions remained on top of colorless $H_2O_{(s)}$. The acetonitrile solutions were decanted from $H_2O_{(s)}$ and carefully rotovapped until a concentrated purple solution remained. Dichloromethane was then added to the purple solution and all of the solvent was dried down in air.

AZUL-5-1, 1,2,3,5,7-azulene$(CF_3)_5$: Purple solid. Co-crystals of AZUL-5-1/pyrene (dark red-purple rods) were grown from the slow evaporation of a dichloromethane solution (AZUL-5-1:pyrene = 1:1) at 2 °C. 16.6 mg, 9.0 mol% yield based on azulene. ^{19}F NMR: δ −54.35 (q, J = 12.3 Hz, 2CF_3, $CF_3^{1,3}$); −58.02 (sept, J = 12.0 Hz, 1CF_3, CF_3^{2}); −65.46 (s, 2CF_3, $CF_3^{5,7}$). ^{1}H NMR: δ 9.50 (s, 2H, $H^{4,8}$); 8.63 (s, 1H, H^{6}). UV-vis (hexane, λ_{nm} (log ε)): 276 (4.40), 282 (4.43), 299 (3.46), 327 (3.32), 338 (3.45), 353 (3.28), 536 (2.36), 570 (2.33), 632 (1.88). NI-APCI mass spec: 468.41 *m*/*z*. Calc. 468.00.

AZUL-4-1, 1,3,5,7-azulene$(CF_3)_4$: Purple solid. Single crystals (purple plates) were grown by the slow evaporation from a dichloromethane solution. 14.7 mg, 9.5 mol% yield based on azulene. ^{19}F NMR: δ −58.41 (s, 2CF_3, $CF_3^{1,3}$); −65.19 (s, 2CF_3, $CF_3^{5,7}$). ^{1}H NMR: δ 9.12 (s, 2H, $H^{4,8}$); 8.51 (s, 1H, $H^{2 \text{ or } 6}$); 8.49 (s, 1H, $H^{2 \text{ or } 6}$). UV-vis (hexane, λ_{nm} (log ε)): 273 (4.13), 281 (4.15), 301 (3.41), 330 (3.12), 342 (3.28), 359 (3.29), 532 (2.01), 574 (1.94), 629 (1.60). NI-APCI mass spec: 400.40 *m*/*z*. Calc: 400.01.

AZUL-4-2, 1,2,3,5-azulene$(CF_3)_4$: Purple solid. Single crystals (thin purple plates) were grown by the slow evaporation from a dichloromethane solution. 4.6 mg, 3.1 mol% yield based on azulene. ^{19}F NMR: δ −54.02 (q, J = 12.3 Hz, 1CF_3, $CF_3^{1 \text{ or } 3}$); −54.07 (q, J = 11.8 Hz, 1CF_3, $CF_3^{1 \text{ or } 3}$); −57.71 (sept, J = 12.0 Hz, 1CF_3, CF_3^{2}); −65.20 (s, 1CF_3, CF_3^{5}). ^{1}H NMR: δ 9.41 (s, 1H, H^{4}); 9.28 (d, $^{3}J_{HH}$ = 10.6 Hz, 1H, H^{8}); 8.41 (d, $^{3}J_{HH}$ = 10.6 Hz, 1H, H^{6}); 7.90 (t, $^{3}J_{HH}$ = 10.4 Hz, 1H, H^{7}). UV-vis (hexane, λ_{nm} (log ε)): 276 (3.59), 281 (3.58), 321 (2.67), 334 (2.72), 348 (2.49), 531 (1.71), 562 (1.69), 613 (1.39). NI-APCI mass spec: 400.40 *m*/*z*. Calc: 400.01.

AZUL-4-3, 1,2,3,6-azulene$(CF_3)_4$: Purple solid. 1.1 mg, 0.7 mol% yield based on azulene. ^{19}F NMR: δ −54.06 (q, J = 11.8 Hz, 2CF_3, $CF_3^{1,3}$); −57.82 (sept, J = 12.0 Hz, 1CF_3, CF_3^{2}); −66.46 (s, 1CF_3, CF_3^{6}). ^{1}H

NMR: δ 9.28 (d, ${}^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}$); 8.05 (d, ${}^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}$). UV-vis (hexane, λ_{nm} (log ε)): 259 (3.21), 275 (3.44), 283 (3.39), 331 (2.58), 344 (2.25), 503 (1.72), 552 (1.79), 583 (1.78), 664 (1.54). NI-APCI mass spec: 400.40 *m*/*z*. Calc: 400.01.

AZUL-3-1, 1,3,5-azulene(CF_3)$_3$: Purple solid. 2.1 mg, 1.6 mol% yield based on azulene. ^{19}F NMR: δ −58.17 (s, 1CF$_3$, $CF_3^{1\text{ or }3}$); −58.21 (s, 1CF$_3$, $CF_3^{1\text{ or }3}$); −64.89 (s, 1CF$_3$, CF_3^{5}). ^{1}H NMR: δ 9.03 (s, 1H, H^4); 8.91 (d, ${}^3J_{HH}$ = 9.8 Hz, 1H, H^8); 8.37 (s, 1H, H^2); 8.27 (d, ${}^3J_{HH}$ = 10.6 Hz, 1H, H^6); 7.77 (t, ${}^3J_{HH}$ = 10.4 Hz, 1H, H^7). UV-vis (hexane, λ_{nm} (log ε)): 276 (4.40), 281 (4.39), 297 (3.54), 330 (3.37), 338 (3.46), 354 (3.43), 533 (2.32), 569 (2.28), 620 (1.91). NI-APCI mass spec: 332.40 *m*/*z*. calc: 332.02.

AZUL-3-2, 1,3,6-azulene(CF_3)$_3$: Purple solid. 0.8 mg, 0.6 mol% yield based on azulene. ^{19}F NMR: δ −58.21 (s, 2CF$_3$, $CF_3^{1,3}$); −65.98 (s, 1CF$_3$, CF_3^{6}). ^{1}H NMR: δ 8.90 (d, ${}^3J_{HH}$ = 10.2 Hz, 2H, $H^{4,8}$); 8.40 (s, 1H, H^2); 7.95 (d, ${}^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}$). UV-vis (hexane, λ_{nm} (log ε)): 275 (3.95), 280 (3.95), 312 (2.81), 320 (2.91), 327 (3.00), 334 (3.05), 350 (2.87), 555 (2.06), 595 (2.00), 653 (1.62). NI-APCI mass spec: 332.40 *m*/*z*. calc: 332.02.

AZUL-3-3, 1,2,3-azulene(CF_3)$_3$: Pink solid. 0.7 mg, 0.5 mol% yield based on azulene. ^{19}F NMR: δ −53.71 (q, *J* = 11.8 Hz, 2CF$_3$, $CF_3^{1,3}$); −57.38 (sept, *J* = 12.0, 1CF$_3$, CF_3^{2}). ^{1}H NMR: δ 9.17 (d, ${}^3J_{HH}$ = 10.2 Hz, 2H, $H^{4,8}$); 8.17 (t, ${}^3J_{HH}$ = 10.0 Hz, 1H, H^6); 7.81 (t, ${}^3J_{HH}$ = 10.4 Hz, 2H, $H^{5,7}$). UV-vis (hexane, λ_{nm} (log ε)): 275 (3.91), 284 (3.90), 310 (2.94), 329 (3.06), 341 (2.66), 522 (2.14), 555 (2.15), 601 (1.82). NI-APCI mass spec: 332.27 *m*/*z*. calc: 332.02.

X-ray diffraction study

The diffraction-quality single crystals of 1,2,3,5-azulene(CF_3)$_4$ were mounted in a paratone oil onglass fiber rods glued to a small copper wire. X-ray diffraction data were collected at ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sector 15-B at the Advanced Photon Source (Argonne National Laboratory). The data sets were collected at 100(2) K using a diamond (111) crystal monochromator, a wavelength of 0.41328 Å and a Bruker CCD detector. The structure was solved using direct methods and refined (on *F*2, using all data) by a full-matrix, weighted least squares process. Standard Bruker control and integration software (APEX II) was employed,[1] and Bruker SHELXTL software[2] was used for structure solution, refinement, and graphics.

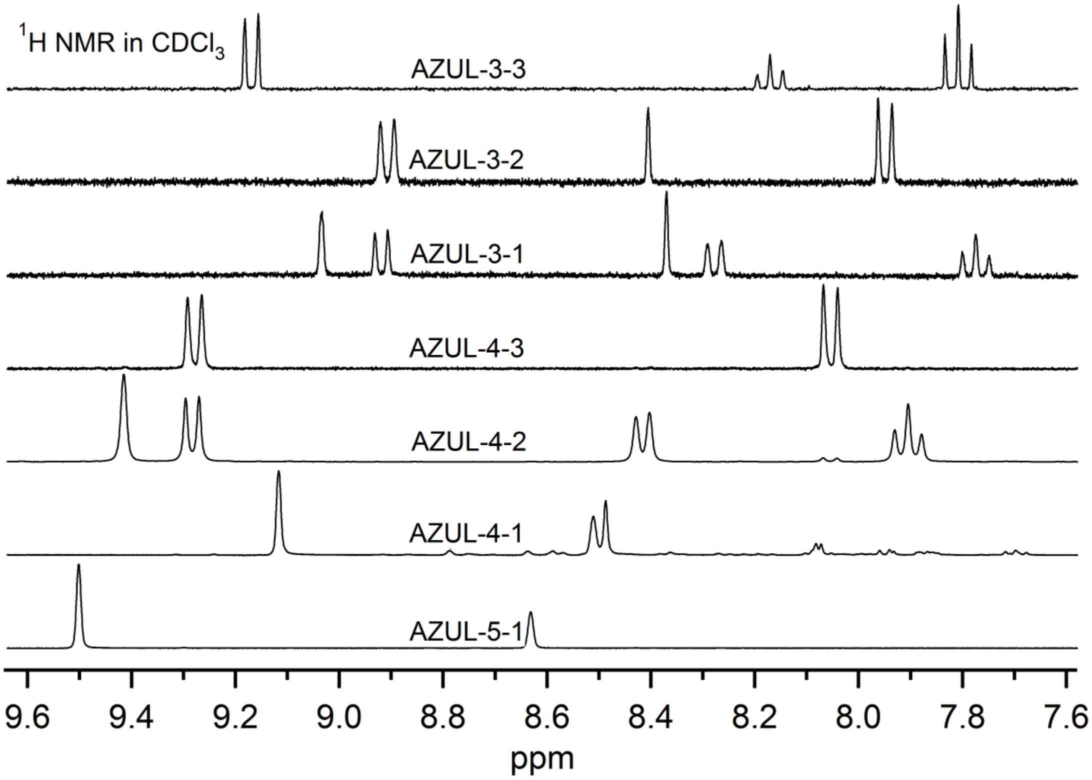
Data for 1,3,5,7-azulene(CF_3)$_4$ and 1,2,3,5,7-azulene(CF_3)$_5$/pyrene were collected using a Bruker Kappa APEX II CCD diffractometer employing Mo Kα radiation and a graphite monochromator. Unit cell parameters were obtained from least-squares fits to the angular coordinates of all reflections, and intensities were integrated from a series of frames (*ω* and *ϕ* rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied using SCALE.[3] The structures were solved using direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process. Standard Bruker control and integration software (APEX II) was employed,[1] and Bruker SHELXTL software was used for structure solution, refinement, and molecular graphics.[2]

Crystal data for AZUL-4-1: $C_{14}H_4F_{12}$, M = 400.17, triclinic, a = 8.9064(4) Å, b = 9.5245(4) Å, c = 13.4137(6) Å, α = 105.240(2)°, β = 101.240(2)°, γ = 101.091(2)°, V = 1040.70(8) Å^3, T = 120(2) K, space group P-1, Z = 3, μ(MoKα) = 0.225 mm^{-1}, 22507 reflections measured, 5131independent reflections (R_{int}

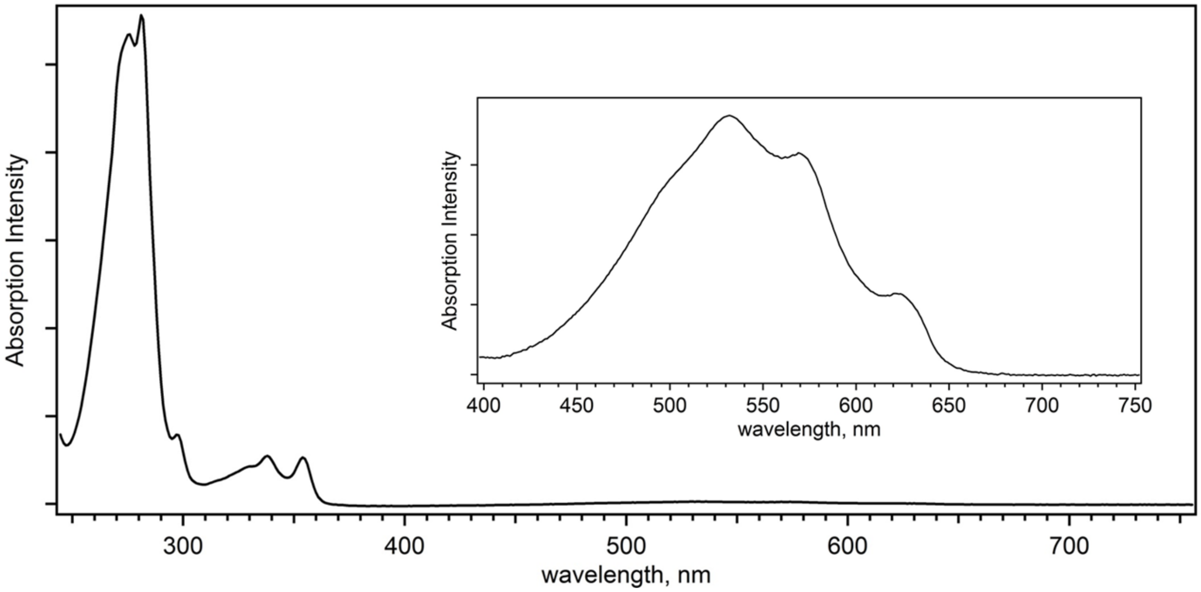
= 0.0268). The final R_1 values were 0.0497 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1173 ($I > 2\sigma(I)$). The final R_1 values were 0.0667 (all data). The final $wR(F^2)$ values were 0.1283 (all data). The goodness of fit on F^2 was 1.045. CCDC number CCDC 980904.

Crystal data for AZUL-4-2: $C_{14}H_4F_{12}$, M = 400.17, monoclinic, a = 4.8939(3) Å, b = 32.3450(18) Å, c = 8.6013(5) Å, α = 90°, β = 94.4396(11)°, γ = 90°, V = 1357.44(14) Å^3, T = 100(2) K, space group Cc, Z = 4, synchrotron radiation at ChemMatCARS Sector 15-B at the Advanced Photon Source at Argonne National Laboratory (diamond (111) crystal monochromator μ(diamond (111)) = 0.073 mm^{-1}; λ=0.41328 Å). 17319 reflections measured, 4394 independent reflections (R_{int} = 0.0457). The final R_1 values were 0.0369 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0963 ($I > 2\sigma(I)$). The final R_1 values were 0.0499 (all data). The final $wR(F^2)$ values were 0.1226 (all data). The goodness of fit on F^2 was 1.194. CCDC number CCDC 980900.

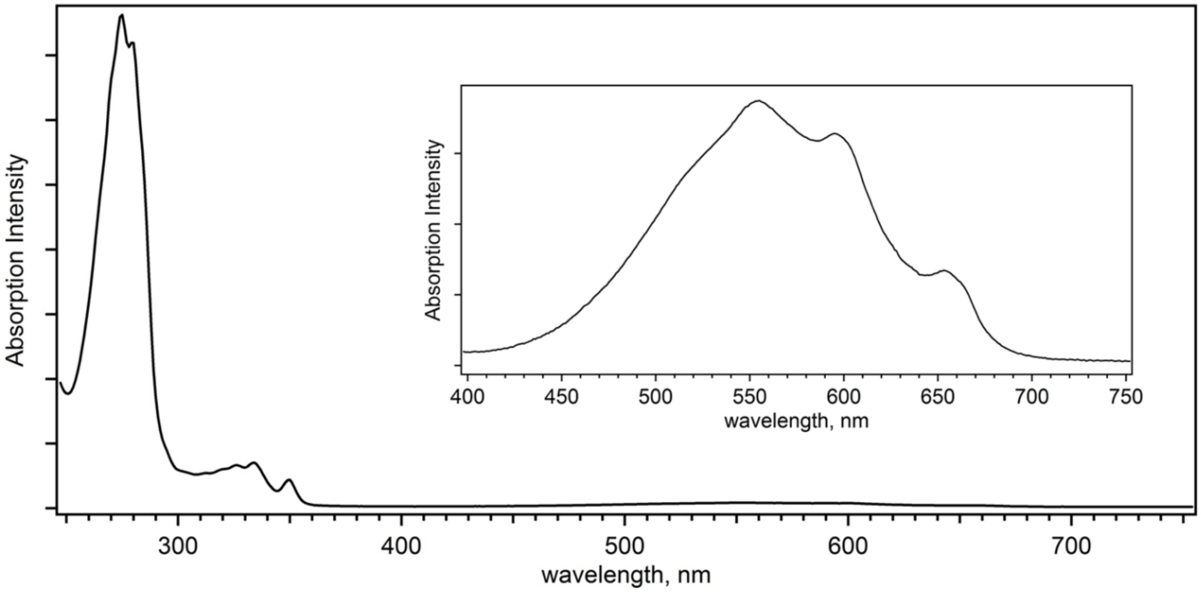
Crystal data for AZUL-5-1/pyrene: $C_{31}H_{13}F_{15}$, M = 670.41, monoclinic, a = 7.2226(7) Å, b = 16.1783(17) Å, c = 21.334(2) Å, α = 90°, β = 92.461(5)°, γ = 90°, V = 2490.6(4) Å^3, T = 120(2) K, space group $P21/n$, Z = 4, μ(MoKα) = 0.183 mm^{-1}, 59030 reflections measured, 7578 independent reflections (R_{int} = 0.0293). The final R_1 values were 0.0396 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1056 ($I > 2\sigma(I)$). The final R_1 values were 0.0441 (all data). The final $wR(F^2)$ values were 0.1095 (all data). The goodness of fit on F^2 was 1.024. CCDC number CCDC 980901.



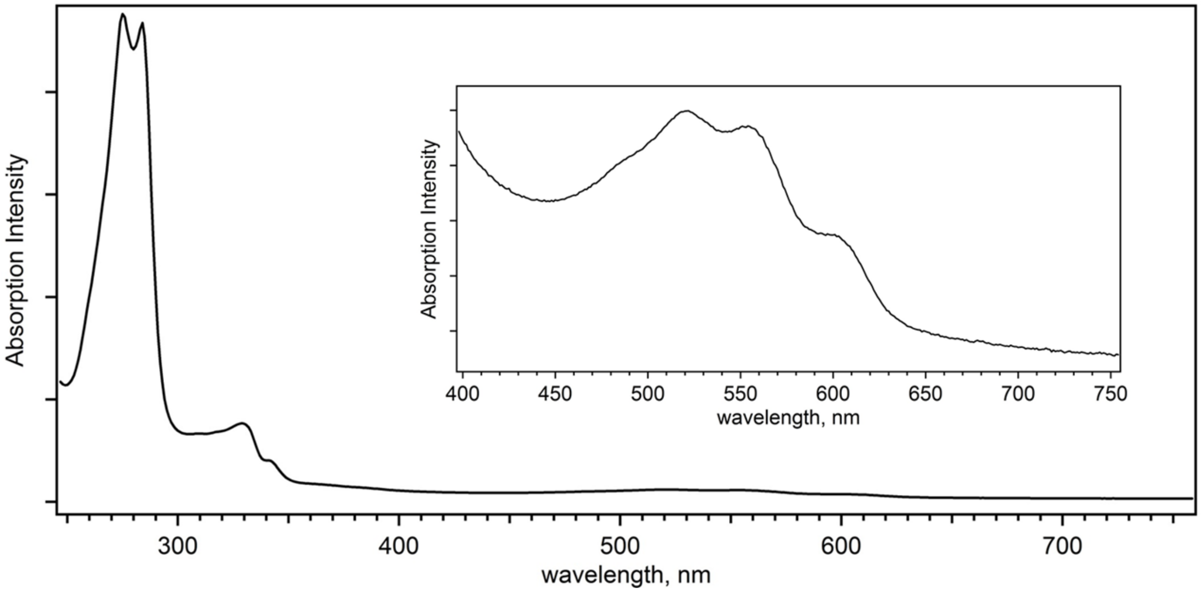
SI-1. Proton NMR of the seven azulene derivatives in CDCl$_3$. Some residual solvents are present (acetonitrile, water, dichloromethane, toluene, hexane), which cannot be easily removed due to the volatility of the compounds, and may cause different chemical shifts. AZUL-4-2 contains a 3% impurity of AZUL-4-3. AZUL-4-1 contains ca 5% impurities of other AZUL(CF$_3$)$_4$ derivatives.



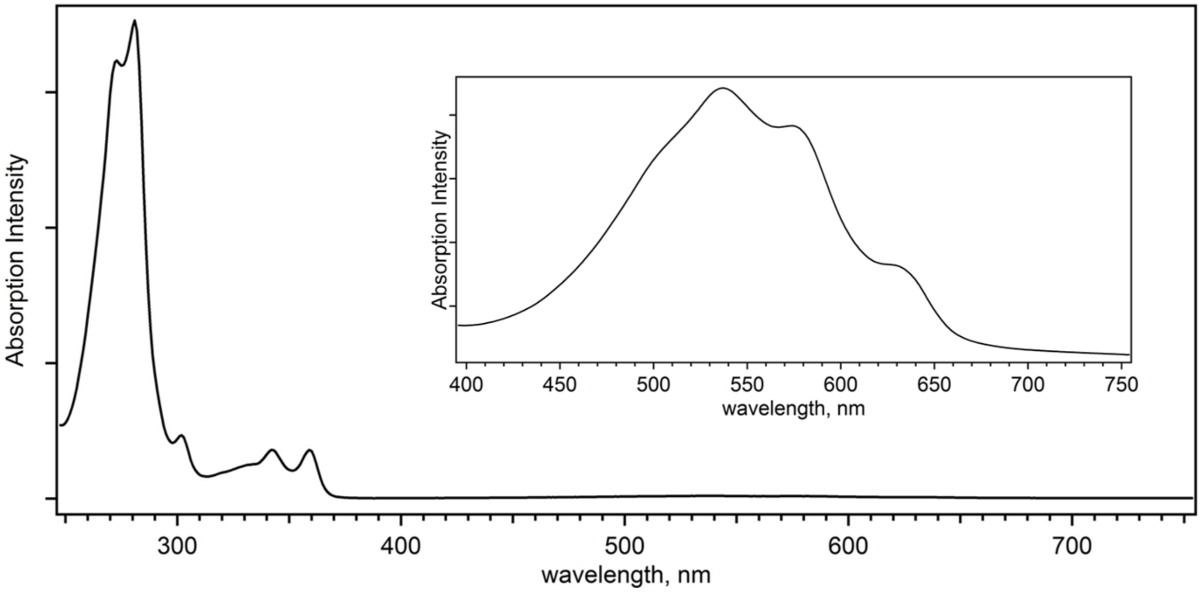
SI-2. UV-vis of AZUL-3-1 in hexanes. The inset shows a zoomed in view of the S_1 band.



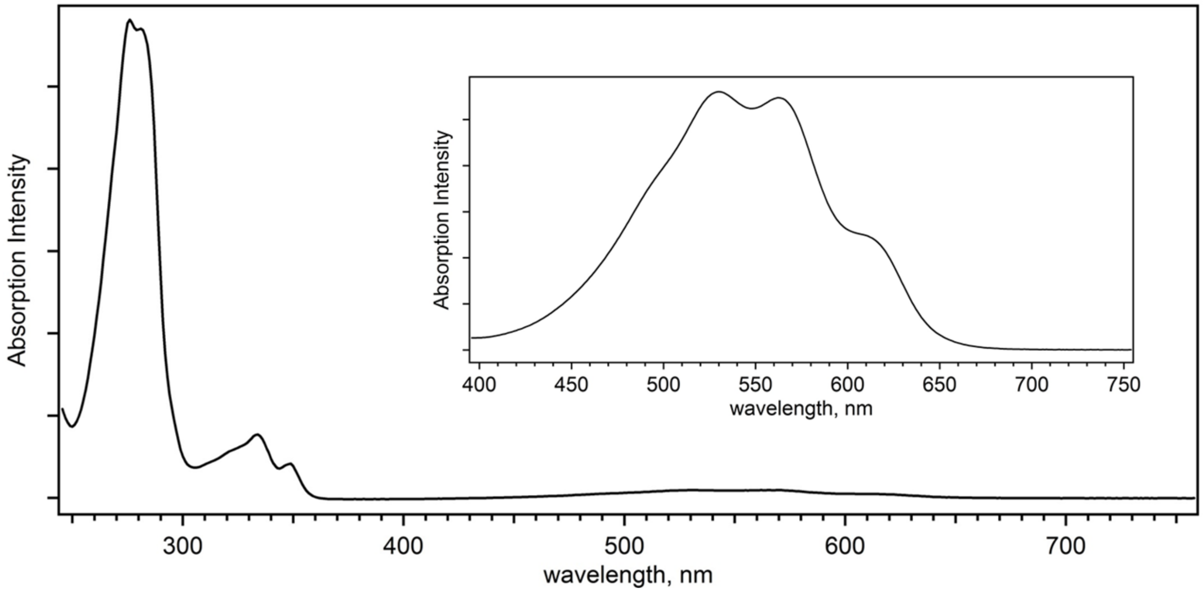
SI-3. UV-vis of AZUL-3-2 in hexanes. The inset shows a zoomed in view of the S_1 band.



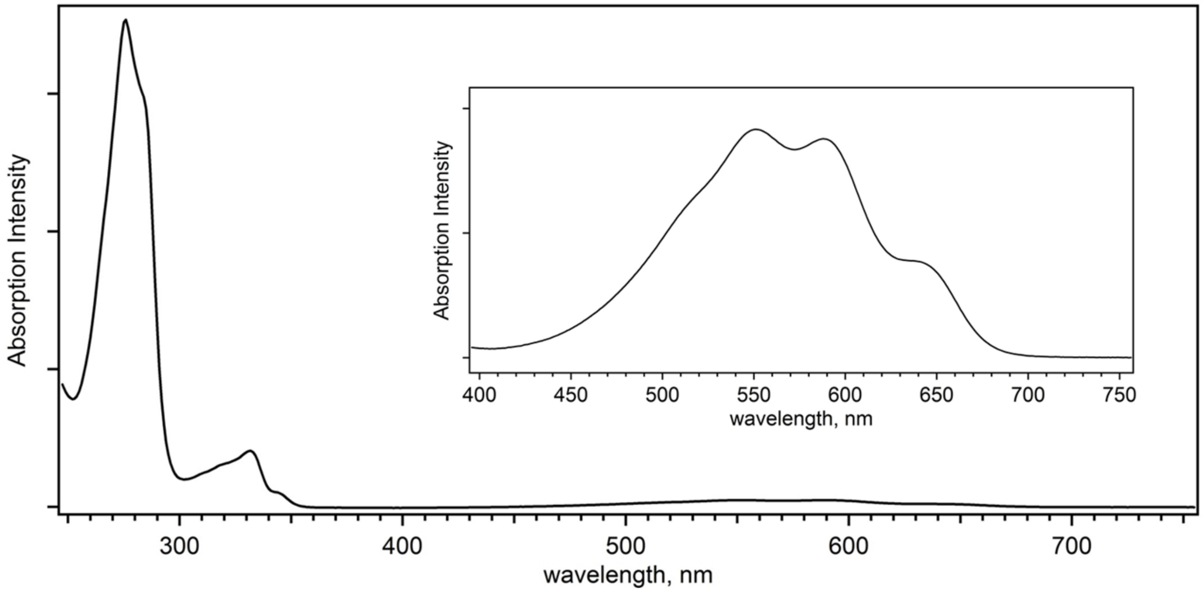
SI-4. UV-vis of AZUL-3-3 in hexanes. The inset shows a zoomed in view of the S_1 band.



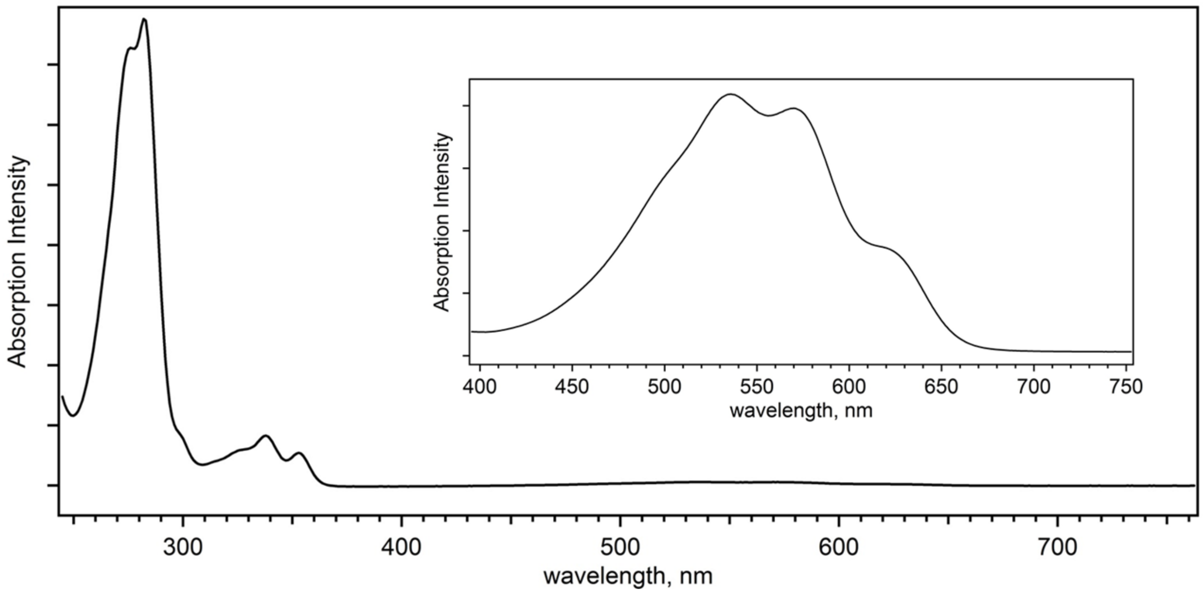
SI-5. UV-vis of AZUL-4-1 in hexanes. The inset shows a zoomed in view of the S_1 band.



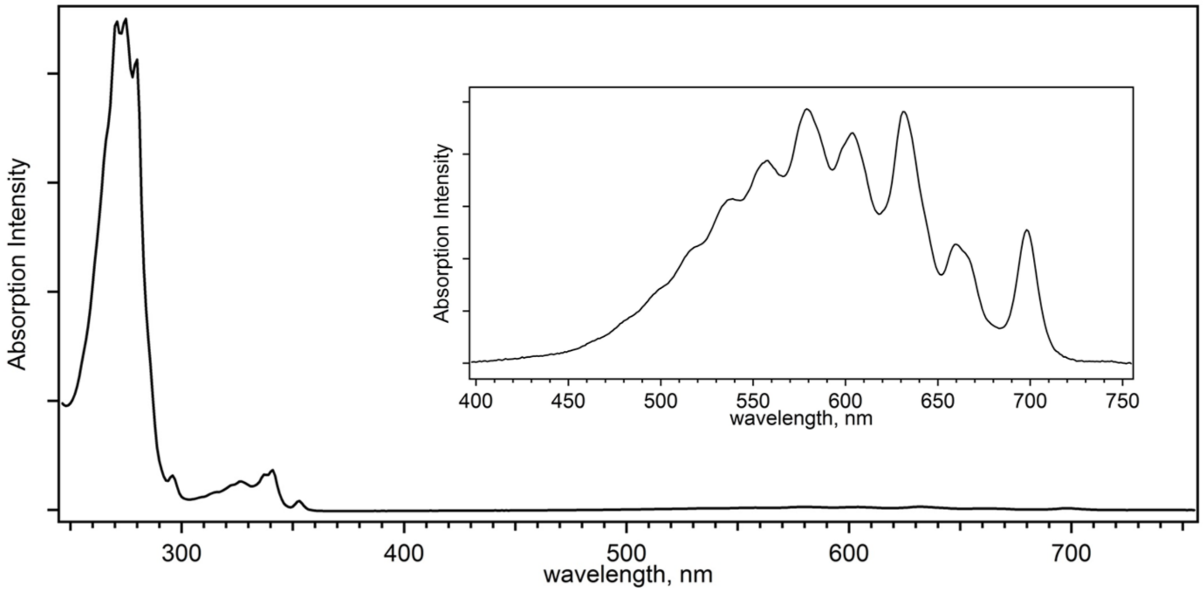
SI-6. UV-vis of AZUL-4-2 in hexanes. The inset shows a zoomed in view of the S_1 band.



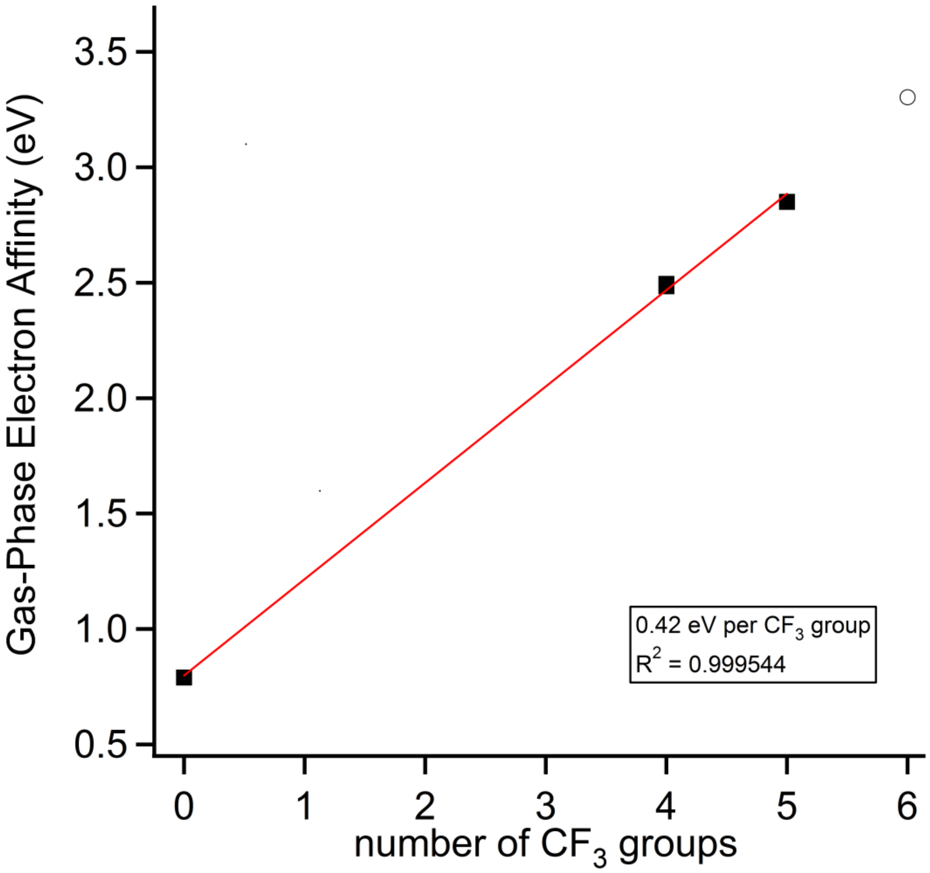
SI-7. UV-vis of AZUL-4-3 in hexanes. The inset shows a zoomed in view of the S_1 band.



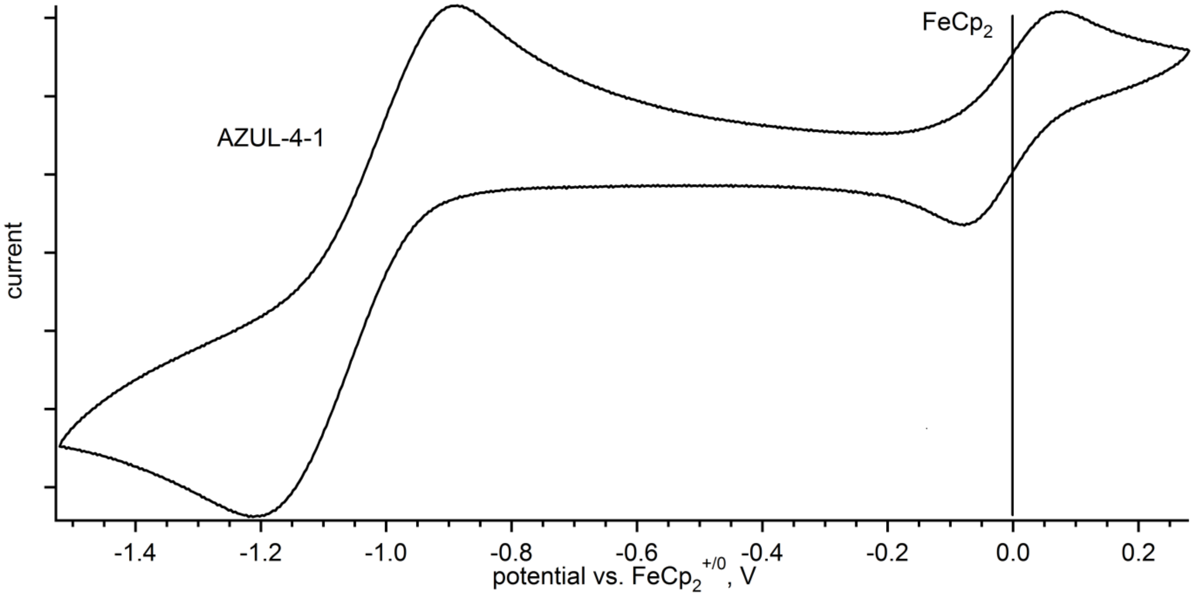
SI-8. UV-vis of AZUL-5-1 in hexanes. The inset shows a zoomed in view of the S_1 band.



SI-9. UV-vis of azulene in hexanes. The inset shows a zoomed in view of the S_1 band.



SI-10. Plot of the experimentally measured gas-phase EA values of AZUL, AZUL-4-1, AZUL-4-2, and AZUL-5-1 (black squares) including extrapolation to the estimated EA value for the experimentally observed azulene$(CF_3)_6$.



SI-11. Cyclic voltammogram (0.1 м N(nBu)$_4$ClO$_4$ in dimethoxyethane, 500 mV·s^{-1}) of AZUL-4-1 with FeCp$_2$(+/0) internal standard.

References

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2 G. M. Sheldrick, *Crystallography Software Package SHELXTL, v. 6.12 UNIX*, 2001.
3 G. M. Sheldrick, *SADABS - A program for area detector absorption corrections*, 2004.