1,3-Di(2-pyrrolyl)azulene: An Efficient Luminescent Probe for Fluoride

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Photo-induced Energy Transfer (PET) based chemosensing is a very elegant way for reporting the presence of an analyte in solution. This method was successfully applied to the detection of many cationic species in solutions and already appears in interesting commercial applications. In this paper we report on the preparation and host–guest chemistry of 1,3-di(2-pyrrolyl)azulene (**5**), a new azulene-based selective PET-like chemosensor that turns fluorescent upon binding the fluoride anion.

Introduction

Halides, especially fluoride, chloride and iodide, are of biological relevance. They play important roles in the formation and prevention of severe diseases such as cancer,[1] cystic fibrosis,[2] caries[3] and osteoporosis.[4] Their bio-relevance raises a need for a better understanding of the host–guest chemistry of such ions, especially in polar and aqueous media. From the practical point of view, there is also a need for new, simple, efficient and selective methods for the detection of such ions in solutions.

Of particular interest would be systems that can recognize a target anion in solution and signal its presence through an easy-to-detect optical signature, such as a color change or increase in the luminescence of the sensing moiety. In the past few years, different groups have proposed a wide range of anion binding systems based on guanidinium derivatives,[5] oligoamines,[6] sapphyrins,[7] calixpyrroles,[8] cyclopyrroles,[9] quinoxalines-pyrroles,[10] etc.[11,12] Introduced by the group of Sessler, the quinoxaline-pyrrole systems are of particular interest since they present a general approach to efficient anion binders which are coupled to moieties that respond to the presence of some anions by a color change.[10]

These systems have been shown to be both effective and specific. A very elegant way that was developed for reporting the presence of cations is the Photo-induced Energy Transfer (PET) signaling approach, first proposed by Weller[13] and brought to perfection by De Silva[14] and others.[15] This method was successfully applied to the detection of many cationic species in solutions and already appears in interesting commercial applications. PET chemosensors consist of a luminescent species attached to a recognition group. In the unbound dark state, the binding group quenches the excited state of the luminescent part, usually by its lone pair electrons of the unoccupied metal binding site. Upon binding, the metal ion is attached to the recognition group through the lone pair electrons. Consequently, the binding group can no longer serve as an efficient quencher and the luminescence is regained, thus signaling the capture of the guest. The use of such approach to signal the binding of an anion is not straightforward since anions are usually coordinated by efficient hydrogen donors. These usually do not decrease their tendency to quench the excited state of the luminophore upon binding.[16] One possible approach to the preparation of a PET-like chemosensor for anions is to couple an efficient anion receptor to a luminescent moiety in such a way that binding of an anion forces the receptor out of the plane of the luminescent group and by that decreases its electronic coupling with the luminescent moiety. In such a system the fluorescence is expected to increase upon binding of the target anion.

In this paper we report on the preparation, crystal structure characterization and anion binding properties of an azulene-based selective chemosensor that turns fluorescent upon binding the fluoride ion. Azulene was chosen as the luminophore due to its exceptionally short-lived emission from S_2. The very short fluorescence lifetime of the new azulene derivative, $\tau = 50 \pm 5$ ps and $\tau = <30$ ps in dichloromethane and DMSO, respectively, excludes the interference of any diffusion-controlled process between the azulene derivative and unbound species in solution.

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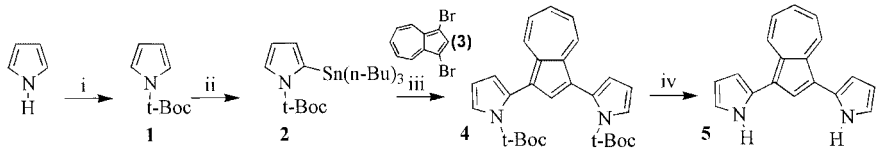


Scheme 1. i) $(Boc)_2O$, CH_3CN, room temp., >95%; ii) *N*-lithium-2,2,6,6-tetramethylpiperidine, –70 °C, 1.3 equiv. $(Bu)_3SnCl$, THF, –70 °C to room temp., 70%; iii) 1,3-dibromoazulene (0.5 equiv.), $[Pd(PPh_3)_4]$ (catalytic amount), toluene, 1 M aq. Na_2CO_3, 42%; iv) solid-state thermally induced decarboxylation: 230 °C, 30 min 10^{-3} Torr, >98% yield.

Results and Discussion

1,3-Di(2-pyrrolyl)azulene (**5**) was prepared according to Scheme 1. Pyrrole was *N*-protected using di-*tert*-butyl dicarbonate, $(Boc)_2O$, to yield *tert*-butyl pyrrole-1-carboxylate (**1**). This product was then lithiated at the 2 position and reacted with tri-*n*-butylstannyl chloride to yield *N*-(*tert*-butoxycarbonyl)-2-(trimethylstannyl)pyrrole (**2**). Reaction between one equivalent of 1,3-dibromoazulene (**3**) and two equivalents of **2** afforded 1,3-bis[*N*-(*tert*-butoxycarbonyl)-2-pyrrolyl]azulene (**4**). The later product was deprotected by heating under reduced pressure to yield 1,3-bis(2-pyrrolyl)-azulene (**5**).

The molecular structure of **5** in the crystal state is depicted in Figure 1. The packing motif of the molecules in the crystal is presented in Figure 2. As can be appreciated from the structure, the planes of the two pyrrole rings are slightly tilted with respect to the plane of the azulene moiety, $\theta_{C1-C2-C7-N1} = 29.1°$. Consequently, the two acidic protons of the pyrrole rings are pointing to the same direction. The molecules are arranged in a herring bone motif, in which each molecule points two acidic protons of its pyrrole rings towards the electron-rich cyclopentadienyl moiety of its neighbor, thus forming H–π bonded dimers, d_{H11-C2} = 2.608 Å, $\alpha_{N1-H11-C2}$ = 156.70°, d_{H11-C3} = 2.698 Å, $\alpha_{N1-H11-C3}$ = 168.76°, emphasizing its ability to bind electron rich moieties.

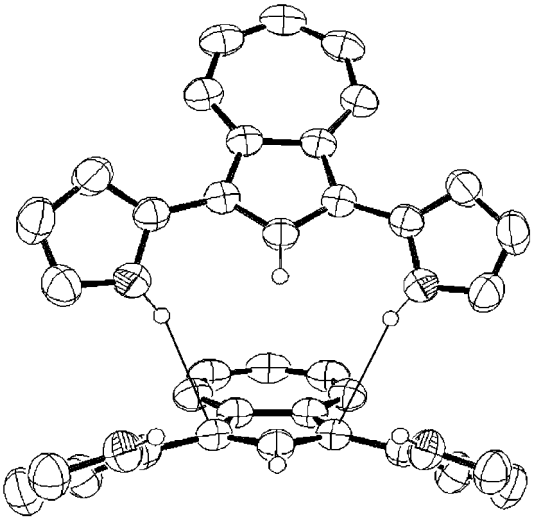


Figure 2. Top and side view of the dimeric form, **5**–**5**, in the crystal.

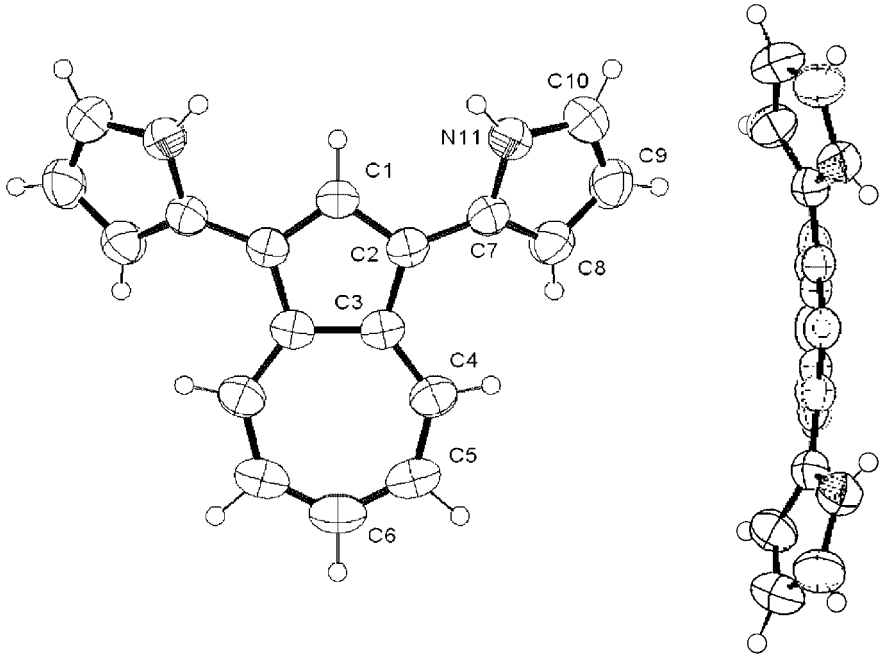


Figure 1. Top and side view of the molecular structure of **5** in the crystal.

In DMSO solutions,[17] **5** is deep green and emits mainly from the S_2 excited state. The absorption spectrum of **5** in DMSO is sensitive to the presence of different anions, especially fluoride, Figure 3.

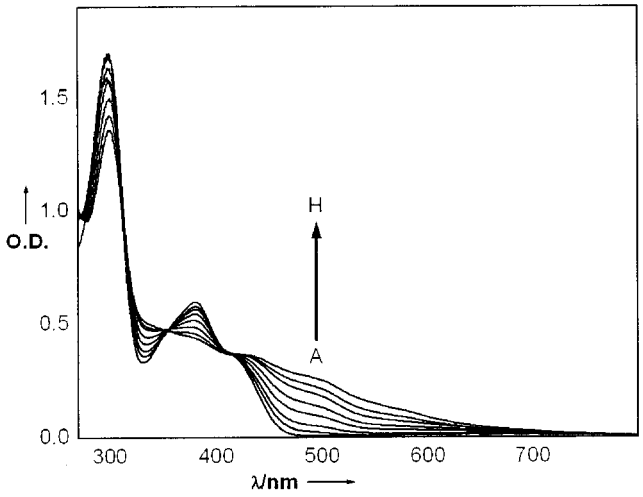


Figure 3. The absorption spectra of 1.45×10^{-5} M 1,3-di(2-pyrrolyl)-azulene (**5**) in a mixture of 0.1% water in DMSO in the presence of different concentrations of tetrabutylammonium fluoride (TBAF): **a**) 0 M; **b**) 6.09×10^{-4} M; **c**) 8.1×10^{-4} M; **d**) 1.08×10^{-3} M; **e**) 1.47×10^{-3} M; **f**) 2.0×10^{-3} M; **g**) 2.46×10^{-3} M; **h**) 2.97×10^{-3} M.

Addition of increasing amounts of fluoride to a solution of **5** leads to the formation of at least two types of complexes, one being the 1:1 complex, as evident from the two isosbestic points and the other being a different type of a 1:1 complex or a complex of a higher stoichiometry, presumably a 1:2 complex. In the regime in which the first complex is dominant, the changes in the absorption spectrum are moderate; while in the regime in which the second complex is dominant, two new absorption bands appear in the visible, rendering the solution dark violet.

The association constants of the first complex between the different tetrabutylammonium halide salts and **5** were extracted from the association-induced changes in its absorption spectrum using the Benessi–Hildebrand equation, assuming a 1:1 complex, Table 1.[18] Almost identical values were obtained from the association-induced fluorescence in the case of the fluoride ion. Table 1 clearly indicates that **5** appears to be a selective host for fluoride even in wet DMSO solutions.[17] Addition of higher amounts of fluoride to a DMSO solution of **5** results in the appearance of a dark violet colour, while in the presence of the other halides and other anions the change in colour is negligible. This is in accordance with earlier reports by Sessler and Anzenbacher on dipyrrolylquinoxaline derivatives, showing that his approach is a general one.[10]

The effect of the fluoride ion on the emission spectrum of **5** in DMSO is even more dramatic, Figure 4. In the 1:1 regime, addition of tetrabutylammonium fluoride to a DMSO solution of **5** results in a more than ten-fold increase in the quantum yield for fluorescence from the S_2 state. Being an electro-inert anion, it is highly unlikely that fluoride participates in any charge/energy transfer processes with **5**.

Table 1. 1:1 Association constants between the different tetrabutylammonium salts and **5**.

Anion salt	K_{ass} (DCM)	K_{ass} (DMSO)
$(Bu)_4N^+F^-$	11000	>1000
$(Bu)_4N^+Cl^-$	110	<20
$(Bu)_4N^+Br^-$	100	<20
$(Bu)_4N^+I^-$	50	<20
$(Bu)_4N^+$ *p*-toluenesulfonate	<20	<20
$(Bu)_4N^+BF_4^-$	<20	<20
$(Bu)_4N^+PF_6^-$	<20	<20

The increase in the fluorescence quantum yield upon complexation with the fluoride ion most likely originates from changes in the degree of conjugation between the electron-rich pyrrole rings and the azulene skeleton, Scheme 2. It is anticipated that upon binding the fluoride ion, the pyrrolyl–azulene interplanar angle changes, thus altering the nature of the excited state and increasing the tendency of the molecule to emit light.

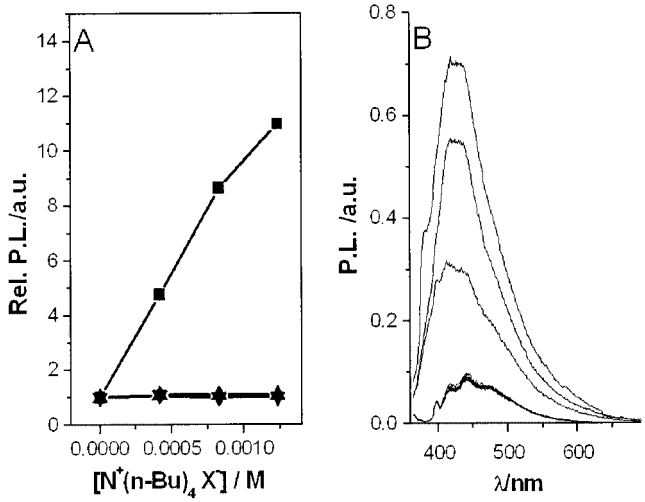
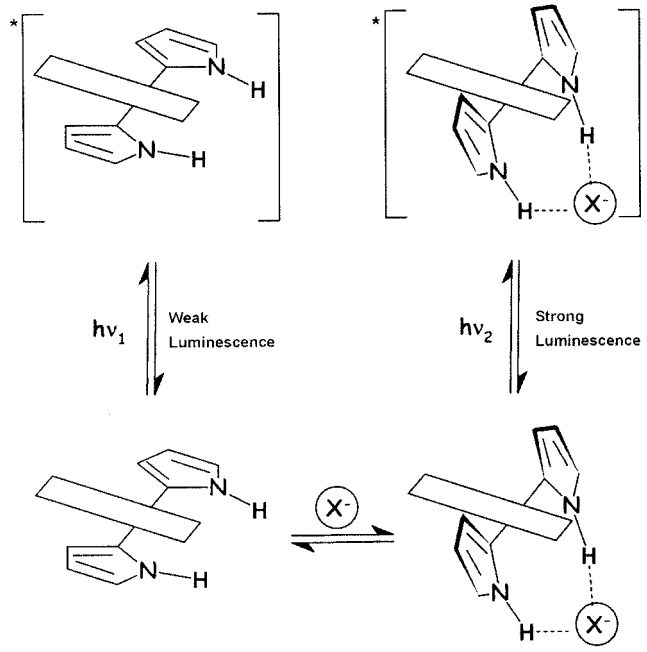


Figure 4. Relative luminescence intensity (A) and respective emission spectra (B) of 1.45×10^{-5} M 1,3-di(2-pyrrolyl)azulene (**5**), in a mixture of 0.1% water in DMSO in the presence of different concentrations of tetrabutylammonium halides (λ_{ex} = 355 nm): ■, [TBAF] = 0 M; 4.15×10^{-4} M; 8.26×10^{-4} M; 1.23×10^{-3} M; ▲, [TBACl] = 0 M; 4.15×10^{-4} M; 8.26×10^{-4} M; 1.23×10^{-3} M; ▼, [TBABr] = 0 M; 4.15×10^{-4} M; 8.26×10^{-4} M; 1.23×10^{-3} M; ◀, [TBAI] = 0 M; 4.15×10^{-4} M; 8.26×10^{-4} M; 1.23×10^{-3} M.

A further support for the suggested mechanism comes from the fact that the increase in luminescence is much smaller in dichloromethane. The proposed mechanism is expected to be highly sensitive to the solvent and nature of the luminophore since it depends on the change of molecular conformation upon binding the anion, in contrast with true PET systems that are expected to be largely solvent insensitive.

In the last years there is a debate in the literature regarding the origins of the interaction between the fluoride ion and different hydrogen donor systems.[19]

Three basic mechanisms may be involved in the interaction between pyrrole containing systems (especially when coupled to other aromatic systems) and anions. The first



Scheme 2.

possible mechanism is the formation of a complex between the pyrrole and the anion, acting as a hydrogen donor and as a hydrogen acceptor, respectively. This type of complexes is found in many X-ray structures that have been published in the last decade, mostly by the groups of Sessler and Gale.[12,20] Most published work assume this type of interaction to be the dominant one when pyrrole and anions are reacted. The second possible mechanism is an acid–base type of interaction in which the fluoride anion acts as a surprisingly strong base, capable of deprotonating some rather weak acids such as urea and pyrrole derivatives. Most systems that were shown to undergo acid–base chemistry with fluoride are electronically coupled to strong electron withdrawing systems.[19] The third possible mechanism is the formation of a charge transfer complex between the anion and the π-system, as was theoretically postulated for some fluoride-aromatic systems and is often found in crystal structures.[21]

The first process we observe for **5** at low concentrations of fluoride has only a minor effect on the absorption spectrum of the dipyrrolylazulene chromophore. We believe it to be due to hydrogen-bond type association between the chromophore and the fluoride anion. In contrast to the rather small effect this complex has on the absorption spectrum, we observe a strong increase of luminescence, probably due to changes in the electronic coupling between the azulene and pyrrole rings that affect the efficiency of luminescence. For the first process, we could exclude the two other types of interactions as responsible for this effect. Strong bases such as NEt_3, TBAOH, NaH (probably transformed into NaOH in solution) and KOH failed to reproduce the same effect. This is therefore not an acid–base process. Chloride was found to have an almost identical effect on the luminescence but at much higher concentrations, as reflected from its much lower association constant. As a π-donor or π-acceptor, we would expect a dramatic difference between fluoride and chloride since they possess very different electron affinities and thus very different π-donor/acceptor character.

The second process between **5** and fluoride occurs upon addition of higher concentrations of the anion. At these fluoride concentrations, a new absorption band is introduced to the visible region. Similar behavior was observed by others and was attributed to either complexation[10] or acid–base chemistry.[19] Again, the second possibility was excluded showing that strong bases such as amines and KOH failed to reproduce the effect at similar concentrations. It is therefore concluded that the second process is not an acid–base process. Owing to the strong effect it has on the absorption spectrum, we estimate the second process to at least involve some kind of strong π-interaction between the aromatic host and fluoride.

Conclusions

In conclusion, 1,3-di(2-pyrrolyl)azulene is an example for a new class of PET-like fluorescent anion receptors that, at least in DMSO solutions, allows for the detection of fluoride anion either by a colour change or by turning "on" its fluorescence emission. We are currently exploring the possibility of applying the PET-like fluorescent anion receptor approach to podant and macrocyclic pyrrole-based systems. Additionally, we are in a process of uncovering the factors that control the nature of the effect of anion binding on the luminescence since binding of fluoride to very similar systems, 1,3-di(2-pyrrolyl)azulene and 1,4-di(2-pyrrolyl)-quinoxaline produce quite the opposite effect (turning the fluorescence "ON" and "OFF", respectively).

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker AC-200F spectrometer. Mass spectra were recorded with a triple quadrupole TSQ-70 spectrometer (Finnigan MAT). Melting points were recorded with a PL-DSC (Polymer Laboratories) machine. Absorption and emission spectra were recorded with a Shimadzu UV-1601 spectrometer and a Perkin–Elmer LS 50 luminescence spectrometer, respectively. Single-crystal X-ray diffraction data was collected with a Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107Å).

All optical measurements were performed in analytical grade solvents. The effect of residual water in the solvents and materials was tested and found to be negligible. All the ammonium salts were kept under argon throughout the experiment. All reagents and solvents were used as received unless noted. Anhydrous solvents were obtained using standard methods.

***tert*-Butyl Pyrrole-1-carboxylate (1):** Di-*tert*-butyl dicarbonate, $(Boc)_2O$, (7.8 g, 35.7 mmol) and 4-(dimethylamino)pyridine, DMAP, (0.5 g, 4.49 mmol) were added to pyrrole (2.0 g, 29.8 mmol) in acetonitrile (30 mL) under argon. After the addition was completed, the mixture was stirred at room temperature for two hours. Evaporation of the solvent and subsequent column

chromatography (Al_2O_3, hexane), afforded 4.73 g (95% yield) of **1** as a colorless liquid. MS (CI): *m*/*z* = 168 [M^+]. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.22 (m, 2 H), 6.20 (m, 2 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 149, 120, 112, 83, 27 ppm.

***N*-(*tert*-Butoxycarbonyl)-2-(trimethylstannyl)pyrrole (2):** A 250-mL three-necked flask equipped with magnetic stirrer, a thermometer, a dropping funnel and nitrogen gas inlet was charged with dry THF (40 mL) and 2,2,6,6-tetramethylpiperidine (2.79 g, 19.75 mmol). The mixture was cooled to –78 °C and 18 mL of a 1.6 N solution of *n*BuLi (21.5 mmol) in hexane is added slowly so that the temperature of the mixture always remained below –65 °C. The mixture was stirred for 10 min at –75 °C, then warmed to 0 °C and stirred for additional 10 min. At this point, the mixture was cooled again to –75 °C and a solution of *tert*-butyl pyrrole-1-carboxylate (**1**, 3 g, 17.94 mmol) in dry THF (40 mL) was added while keeping the temperature below –65 °C. The mixture was stirred for additional 90 min while keeping the temperature below –65 °C. A solution of Bu_3SnCl (7.5 mL, 23.32 mmol) in dry THF (40 mL) was added dropwise to the reaction mixture while keeping the temperature below –65 °C. The reaction was stirred for 40 min at –75 °C and additional 40 min at 0 °C and then for 12 h at room temperature. After removal of the THF under reduced pressure, water (50 mL) and diethyl ether (50 mL) were added to the crude and the aqueous phase was extracted with three portions of diethyl ether. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Column chromatography (Al_2O_3, hexane) of the resulting oil afforded 6.18 g (75% yield) of **2** as a yellow liquid. MS (CI): *m*/*z* = 456 [M^+]. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.49 (m, 1 H), 6.58 (m, 1 H), 6.38 (m, 1 H), 1.84–1.60 (m, 12 H), 1.57–1.35 (m, 8 H), 1.12 (m, 4 H) 1.03 (m, 12 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 134, 123.1, 122.8, 112.7, 82.8, 29.19, 27.9, 27.3, 13.6, 11.0 ppm.

1,3-Dibromoazulene (3): *N*-Bromosuccinimide (1.78 g, 10.0 mmol) was added to azulene (0.5 g, 3.9 mmol) in hexane (20 mL) at 0 °C. After the addition was completed, the mixture was warmed to room temperature and then stirred overnight. Evaporation of the solvent and subsequent column chromatography (250 g SiO_2: hexane) followed by recrystallization from hexane afforded 1 g (89% yield) of **3** as dark green needles. M.p. 76–77 °C. MS(CI): *m*/*z* = 286 [M^+]. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.26 (d, 2 H), 7.73 (s, 1 H), 7.66 (t, 1 H), 7.26 (m, 2 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 140, 138, 136, 133, 124, 102 ppm.

1,3-Bis[*N*-(*tert*-butoxycarbonyl)-2-pyrrolyl]azulene (4): *N*-(*tert*-Butoxycarbonyl)-2-(trimethylstannyl)pyrrole (**2**) (0.29 g, 0.88 mmol), 1,3-dibromoazulene (0.1 g,.35 mmol) and a catalytic amount of tetrakis(triphenylphosphane)palladium(0) were dissolved in a mixture of toluene (10 mL) and a 1 M aqueous solution of sodium carbonate (10 mL). The mixture was stirred at 110 C for 72 h. After cooling, the resulting solution was extracted with diethyl ether. The combined organic layers were washed with water and dried with sodium sulfate. Evaporation of the solvent and subsequent column chromatography (Al_2O_3, hexane), afforded 0.36 g (42% yield) of **4** as a dark green viscous liquid. MS (CI): *m*/*z* = 458.1 [M^+]. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.26 (d, 2 H), 7.73 (s, 1 H), 7.66 (t, 1 H), 7.26 (m, 2 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 140, 138, 136, 123, 122, 115, 110, 83, 27 ppm.

1,3-Di(2-pyrrolyl)azulene (5): Thermolysis of 1,3-bis[*N*-(*tert*-butoxycarbonyl)-2-pyrrolyl]azulene (0.36 g) at 190 °C under reduced pressure (10^{-5} Torr, 30 min) afforded 0.185 g (98% yield) of 1,3-di(2-pyrrolyl)azulene (**5**), as dark green crystals. M.p. 162 °C. MS (CI): *m*/*z* = 258.1 [M^+]. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.54 (d, 2 H), 8.38 (br. s, N–H, 2 H), 7.89 (s, 1 H), 7.52 (t, 1 H), 7.03 (t, 2 H), 6.93 (m, 2 H), 6.47 (m, 2 H), 6.4 (m, 2 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 139, 136, 135, 132, 128, 123, 122, 118, 109, 107 ppm.

X-ray Crystallographic Study. Crystallographic Data for 5: $C_{18}H_{14}N_2$ (358.31), a = 7.0230(2) Å, b = 21.5150(3) Å, c = 8.8670(9) Å, Z = 4, $d_{calcd.}$ = 1.281 g·cm^{-3}, V = 1339.80(14) Å^3, orthorhombic, space group *Pnma*. Data for a crystal of dimensions of 0.33 × 0.30 × 0.12 mm was collected at 293(2) K on a Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). Data collection was performed using ω and φ scans. Data processing was performed using SHELXL-97 and SHELXS-97. R_1 = 0.0328 for 868 independent reflections with $I > 2\sigma(I)$.

CCDC-220679 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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