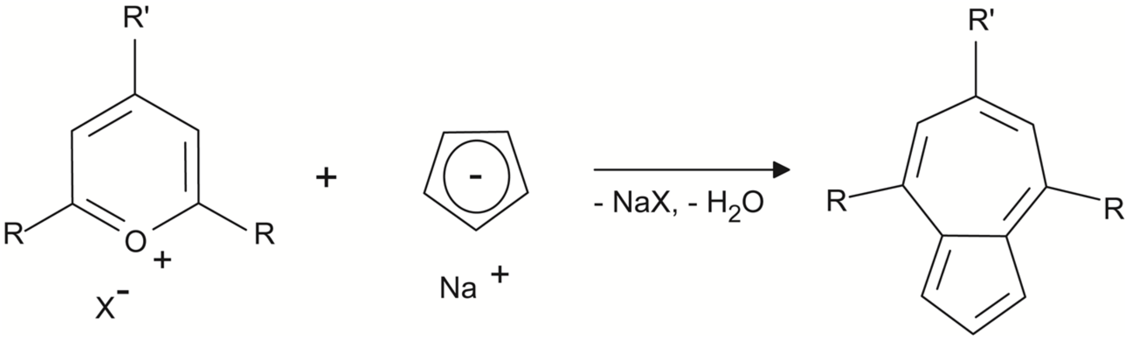
SUPPORTING INFORMATION

Synthesis of azulene derivatives A2-A4

^{1}H-NMR spectra were recorded on a Bruker DPX 300 Avance spectrometer operating at 300 MHz using the residual chloroform signal at 7.26 ppm for calibrating the chemical shifts. MALDI-Tof mass spectra were accumulated usually with 100 laser pulses at 20 kV acceleration voltage on a Applied Biosystems Voyager Instrument. UV-Vis spectra and fluorescence spectra were recorded on Varian Cary 500 and Eclipse instruments, respectively. Column chromatography was performed on silica gel (0.040-0.063 mm). Analytical thin-layer chromatography was performed on ready-made plates from Macherey Nagel.

Azulene **A1** was purchased Sigma-Aldrich (99%, A97203) while azulenes **A2**, **A3** and **A4** were synthesized from the corresponding pyrylium salts (Py) using Klaus Hafner’s reaction with sodium cyclopentadienide as depicted in Scheme 1:[1]



Scheme S1. **A2** R = R’ = CH$_3$; **A3** R = CH$_3$, R’ = C$_6$H$_5$; **A4** R = -(CH$_2$)$_{14}$CH$_3$, R’ = C$_6$H$_5$

4,6,8-Trimethylazulene (**A2**) was prepared in 35 % yield from 2,4,6-trimethylpyrylium tetrafluoroborate and a sodium cyclopentadienide solution in THF according to the established literature procedure.[1]

4,8-Dimethyl-6-phenylazulene (**A3**) was prepared analogously by slowly adding at room temperature under nitrogen atmosphere to 17.3 mL THF solution of sodium cyclopentadienide (2.86 g, 32.56 mmol) the solid 2,6-dimethyl-4-phenylpyrylium sulfoacetate[2] (5.0 g, 15.43 mmol). The temperature was maintained between 45 – 50 °C by cooling with a water bath. Care must be taken because a too rapid addition can lead to a sudden temperature increase while cooling with ice can inhibit the reaction and accumulation of reactants which upon warming may start again to react violently. After completion of the pyrylium salt addition, the mixture is stirred for 20 min and then quenched with water. The mixture is extracted three times with *n*-hexane and the combined *n*-hexane layers are washed three times with water, then dried over anhydrous CaCl$_2$ and evaporated in vacuum. The residue which weighed 2.85 g was separated on a silica gel column eluted with a 2 : 1 (v : v) mixture of dichloromethane / *n*-hexane. The eluted azulenic fractions were combined, concentrated and passed again on a second chromatographic column which was eluted this time with a 1 : 2 (v : v) mixture of dichloromethane / *n*-hexane affording 1.47 g of pure **A3** (45 % yield). R$_f$ (CH$_2$Cl$_2$ / n-hexane, 1:2) = 0.63.

^{1}H-NMR (300 MHz, CDCl$_3$) 7.78-7.70 (t, 1H), 7.67-7.64 (m, 3H), 7.52-7.48 (m, 5H), 7.35 (s, 2H, 5,7-H$_2$), 3.00 (s, 6H, Me$_2$).
MALDI-ToF: 231.85 [M]$^+$ (100 %); C$_{18}$H$_{16}$ requires 232.125.

4,8-Dipentadecyl-6-phenylazulene (**A4**) was analogously prepared by adding 500 mg of 2,6-dipentadecyl-4-phenyl pyrylium (**Py4**, 0.753 mmol) to 140 mg sodium cyclopentadienide (1.588 mmol) in dry THF. Column chromatography over silica gel eluted with a mixture of 1 : 4 (v : v) mixture of dichloromethane / *n*-hexane afforded 150 mg of pure azulene (32 % yield). R$_f$ (CH$_2$Cl$_2$ / n-hexane, 1:4) = 0.64.

^{1}H-NMR (300 MHz, CDCl$_3$) 7.45 (t, 1H, J = 4 Hz), 7.65-7.61 (m, 3H), 7.52-7.42 (m, 5H), 7.31 (s, 2H, 5,7-H$_2$), 3.25 (dd, 4H, 1’-CH$_2$), 1.85 (quintet, 4H, 2’-CH$_2$), 1.48 (quintet, 4H, 3’-CH$_2$), 1.29 (sharp m, 22H, CH$_2$), 0.88 (t, 6H, 15’-CH$_3$).
MALDI-ToF: 624.79 [M]$^+$; C$_{46}$H$_{72}$ requires 624.563.

The precursor pyrylium salt **Py4** was prepared by diacylating α-methylstyrene (11.66 g, 12.83 mL, 98 mmol) with palmitoyl chloride (54.36 g, 60 mL, 197 mmol) in the presence of SnCl$_4$ (32.76 g, 14.77 mL, 125 mmol). Thus under cooling with an ice-water bath, the Perrier complex was first formed by adding SnCl$_4$ to palmitoyl chloride under efficient stirring. Under cooling with water, α-methylstyrene was added slowly dropwise and the mixture was left to stir at room temperature for 42 hrs after which is was stirred at 40 °C for 6 hrs. Evolution of HCl accompanies the progression of the reaction. The reaction mixture was decomposed by pouring over crushed ice (ca. 100 g) with 2 mL HCl (36 %). The aqueous layer containing the pyrylium salt was extracted three times with diethyl ether and then treated under stirring with 40 % aqueous HBF$_4$. After stirring for an additional 20 min and cooling, the pyrylium salt **Py4** crystallized and was filtered and dried giving 8.57 g of pure product (13.1 % yield).

^{1}H-NMR (300 MHz, CDCl$_3$) 8.10-8.05 (m and s, 4H, 2’,6’-H$_2$ and 3,5-H$_2$), 7.65-7.61 (m, 1H, 4’-H), 7.60-7.55 (t, 2H, 3’,5’-

H_2), 3.25 (t, 4H, 1'-CH_2), 1.90 (broad quintet, 4H, 2"-CH_2), 1.48 (m, 4H, 3"-CH_2), 1.29 (sharp m, 22H, CH_2), 0.88 (t, 6H, 15"-CH_3).

MALDI-ToF: 576.98 $[M]^+$; $C_{41}H_{69}OBF_4$ requires 577.535 for the pyrylium cation.

Calculation of the azulene spectra

The optical spectra were calculated using several methods based on both molecular orbital (MO) formalism and density functional theory (DFT). For the smallest **A1** molecule the influence of basis sets was examined considering three Dunning's aug-cc-pVXZ basis sets where X=D, T, Q. From the MO-based methods the CI singles corrected for connected double excitations CIS/CIS(D)[3] method the Algebraic Diagrammatic Construction (ADC(2))[4,5] and the approximate coupled-cluster singles-and-doubles model CC2 [6] were chosen. As to DFT approach, TDDFT and Tamm-Dancoff (TDA-TDDFT) approximations were applied using several functionals: B3LYP, CAM-B3LYP, and ω-B97-XD.[7,8] For the calculations the programs Turbomole 6.4[9] and Gaussian 09[10] were utilized. Detailed information on this part can be obtained upon request from the authors.

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