3-Pyrenylacrylates: Synthetic, Photophysical, Theoretical and Electrochemical Investigations

Sebastian Reimann[a,b,e], Muhammad Sharif[a,b,c,e], Kai Wittler[d], Leif R. Knöpke[a],
Annette-E. Surkus[a], Christian Roth[d], Ralf Ludwig[a,d], and Peter Langer[a,b]

[a] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059
    Rostock, Germany
[b] Institut für Chemie, Abteilung Organische Chemie, Universität Rostock, Albert-Einstein-Str.
    3a, 18059 Rostock, Germany
[c] Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad,
    Pakistan
[d] Institut für Chemie, Abteilung Physikalische Chemie, Universität Rostock, Dr. Lorenz Weg 1,
    18059 Rostock, Germany
[e] Equal contribution of these co-authors

Reprint requests to P. Langer. Fax: +49-381-498-6410. E-mail: peter.langer@uni-rostock.de

The Mizoroki-Heck coupling of 1-bromopyrene with acrylates provides a convenient access to a variety of 3-pyrenylacrylates in very good yields (up to 93 %). Their photophysical properties combined with solvatochromic effects were studied. In addition, electrochemical oxidation potentials were determined by DPV (differential pulse voltammetry) measurements. The fine structure of the absorbance spectra obtained from photophysical measurements are compared with the results of theoretical calculations performed by time dependent TD-B3LYP methods using the 6-31G* basis set.

Key words: Arenes, Polycycles, Pyrene, Density Functional Calculations, Electrochemistry, UV/Vis
          Spectroscopy

Introduction

Pyrene is a thoroughly investigated and important organic chromophore. Its photophysical properties [1 – 5] and its supramolecular chemistry [4 – 9] have been widely studied. Structural modifications [10] allow for many applications, which include the development of fluorescent dyes [11], molecular electronics [2, 12], optical sensors [13], field-effect transistors [13] and photovoltaic cells [14, 15]. A wide range of fabrication techniques in combination with modern synthetic methods allow for the development of new materials which meet special demands and applications. Vinylated pyrene derivatives are monomers for the synthesis of specific polymers containing a pyrene fluorophore attached to the polymer backbone [16 – 19]. Pyrene acrylic acid (PAA) and its methyl ester have been synthesized previously by Knoevenagel condensation (Doebner modification) starting from 1-pyrene carboxaldehyde. They were used as probes to monitor polymerization and surface properties by spectroscopic methods [20]. PAA was applied as an excellent label for tagging polyelectrolytes with a fluorescence probe by copolymerization [21]. The synthesis and photophysical properties of 1-ethynylpyrenes and 1-arylpyrenes have been previously studied as well. They were prepared by Sonogashira and Suzuki-Miyaura cross-coupling reactions of halogenated pyrenes and characterized with regard to their absorption and emission spectral properties [2, 3, 22]. In this respect, the fluorescence properties of the parent pyrenes are well known to be characterized by long excited-state lifetimes and distinct solvatochromic shifts. For example, Marder *et al.* recently reported the unique range of photophysical and structural properties of 2- and 2,7-pyrene deriva-
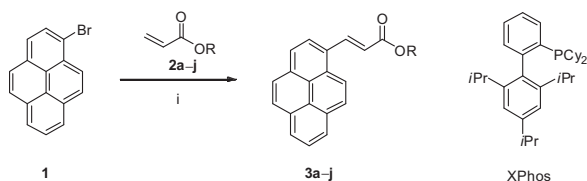
Scheme 1. Synthesis of **3a–j**. Conditions: (i) **1** (1.0 equiv.), **2a–j** (1.2 equiv.), K$_2$CO$_3$ (2.0 equiv.), Pd(OAc)$_2$ (5 mol-%), XPhos (10 mol-%), DMF, 60 °C, 6 h.

Table 1. Synthesis of **3a–j**.

2, 3	R	Yield of **3** (%)[a]
a	Me	90
b	Et	87
c	*n*Bu	84
d	*i*Bu	86
e	*t*Bu	93
f	*n*Hex	80
g	*i*Oct	79
h	2-ethylhexyl	88
i	(CH$_2$)$_2$CF$_3$	83
j	(CH$_2$)$_2$OH	74

[a] Yields of isolated products.

tives which differ from those of the more traditional 1-substituted pyrene derivatives by high fluorescence quantum yields and long fluorescence lifetimes [23].

Recently, we have reported the synthesis of 1-(arylalkenyl)pyrenes by application of the Mizoroki-Heck coupling reaction. Selected alkenylpyrenes, containing electron donor or electron acceptor substituents, were studied regarding their absorption, emission, and electrochemical properties. The fine structure of the absorption spectra was compared with the electronic states derived from theoretical calculations [24]. As an extension of our previous work [24] we herein report the synthesis of a set of 3-pyrenylacrylates and their photophysical and solvatochromic properties (Scheme 1) [25]. In addition, DPV measurements were carried out to determine the potential values. For a better understanding of the electronic situation of the molecules, calculations were carried out using the B3LYP TD-DFT method with a 6-31G* basis set. We studied in detail the physical properties of one derivative, *e. g.* (*E*)-*iso*-butyl 3-(pyren-3-yl)acrylate. Since no dramatic changes within the series of different esters in their general properties were observed, we compared the data of this example with those of a series of 1-(arylalkenyl)pyrenes which were recently prepared by us [24].

Results and Discussion

Synthesis

The Mizoroki-Heck reaction of 1-bromopyrene **1** with acrylates **2a–j** (1.2 equiv.) afforded the 3-pyrenylacrylates in good to very good yields (Scheme 1, Table 1). The reaction conditions were thoroughly optimized. The best yields were obtained when the reaction was carried out using Pd(OAc)$_2$ (5 mol-%), the biarylmonophosphane ligand XPhos (10 mol-%) and with the reaction carried out in DMF

at 60 °C for 6 hours. It was observed that the yields significantly decreased when the temperature or reaction time was increased. The structures of all products were confirmed by spectroscopic techniques (NMR, IR spectroscopy, mass spectrometry).

Photophysical properties

Absorption

We focussed our work on one representative derivative, *e. g.* (*E*)-*iso*-butyl 3-(pyren-3-yl)acrylate. The electronic absorption spectrum of **3d** shows characteristic patterns which are similar to those in the absorption spectrum of the parent pyrene (Fig. 1) [25, 26]. In earlier studies it was pointed out that the shape of electronic absorption spectra of these classes of compounds depends strongly on the pyrene-type backbone [2, 24]. While the bands in the spectrum of parent pyrene occur at ^{1}B$_a$: 241 nm, ^{1}B$_b$: 273 nm, and ^{1}L$_a$: 335 nm [26], the ^{1}L$_a$ band in the spectra of pyrenylacrylate appear at higher wavelengths. This can be explained by the extension of the conjugated π electron system. The spectrum of **3d**, shown in Fig. 1 contains four bands which have their maxima at 199, 234, 277 and 348 nm. Considering that the electronic structure is similar to that of pyrene, the latter three bands can be assigned using Platt's nomenclature as ^{1}B$_a$ transition (234 nm), ^{1}B$_b$ transition (277 nm) and ^{1}L$_a$ transition (348 nm). All bands except the band of the ^{1}L$_a$ transition occur at similar wavelengths like the bands in the spectra of the 1-(arylalkenyl)pyrenes (^{1}B$_a$: 233 – 238 nm, ^{1}B$_b$: 278 – 289 nm, ^{1}L$_a$: 372 – 374 nm) [13]. Furthermore the band of the ^{1}L$_b$ transition is absent under the selected analysis conditions.
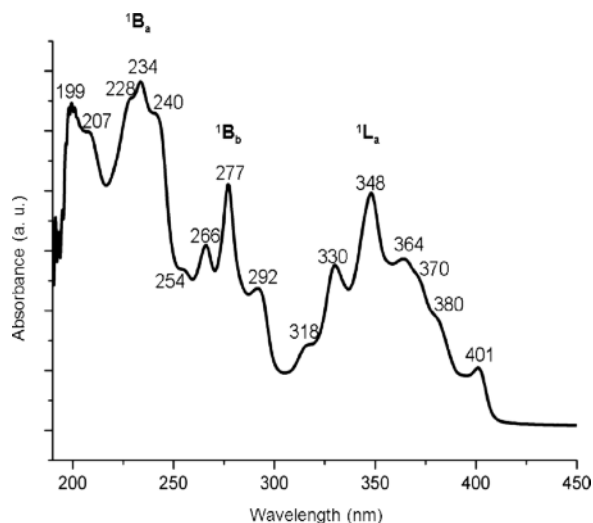
Fig. 1. Electronic absorption spectrum of **3d** measured in *n*-hexane ($c = 1 \times 10^{-6}$ mol L^{-1}).

Fig. 2. Normalized emission spectrum of **3d** measured in selected solvents ($c = 1 \times 10^{-6}$ mol L^{-1}); solvatochromic shift marked on 2nd transition.

All bands in the spectrum of Fig. 1 show a distinct fine structure which can be ascribed to vibronic bands. Planar molecules like trans-stilbene and pyrene show such vibronic bands in their electronic absorption spectra as well, while the spectrum of the less planar cis-stilbene does not show such bands [3, 26]. The vibronic bands in the spectrum of **3d** are more distinct than in the spectra of 1-(arylalkenyl)pyrenes [24]. Hence, it is likely that **3d** has a more planar structure in liquid phase than 1-(arylalkenyl)pyrenes.

Emission

For further photochemical charactization, the emission spectrum of **3d** has been measured in selected solvents (Fig. 2). The spectrum of **3d** measured in *n*-hexane shows one broad band with a maximum at 434 nm and a shoulder at 418 nm. The asymmetric shape of the band indicates that there are more transitions above 450 nm. However, the bands are superposed by each other which prevents making proper assignments. In general the emission spectrum shows fewer details than the spectra of ethynylpyrenes [2] or 1-(arylalkenyl)pyrenes [24]. The absorption spectrum contains a distinct fine structure but the emission spectrum in *n*-hexane has less fine structure as in case of **3d**. In contrast, when the absorption spectrum shows a less pronounced fine structure, like in case of the 1-(arylalkenyl)pyrenes [24], the emission
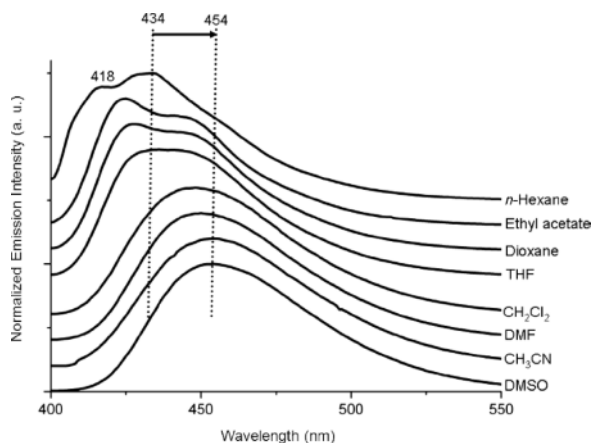
spectra show a more distinct fine structure. This might be an effect of the formation of intermolecular hydrogen bonds between solvent and substrate [27] or of intramolecular charge transfer between the pyrene-type base which depends on the dipole moment of the substrate [2]. Both effects should be favored when the substituent is a polar group like the ester group in case of **3d**. However, the observed bands in the emission spectrum of **3d** in *n*-hexane occur at similar positions as the corresponding bands in the spectra of the 1-(arylalkenyl)pyrenes which appear at 418 ± 1 nm and 442 ± 1 nm, respectively.

Finally solvatochromic studies in selected solvents have been performed for the elucidation of intermolecular dipole-dipole interactions that affect the emission spectra. Fig. 2 shows how the maximum of the band in the spectrum of **3d** is shifted to higher wavelengths due to change of the solvent. The lowest value is observed in *n*-hexane with 434 nm while the highest value with 454 nm occurs in DMSO. The fine structure of the band disappears as the maximum is shifted to higher wavelengths.

Surprisingly the band shape in the spectrum of **3d** measured in *n*-hexane is different from the band shapes of the spectra of **3d** measured in ethyl acetate, dioxane and THF. In *n*-hexane a distinct shoulder appears at 418 nm and the maximum of the band occurs at 434 nm. The shoulder and the maximum are shifted to longer wavelengths when the solvent is changed. Interestingly the shoulder becomes more intense in ethyl acetate, dioxane and THF while the intensity of the max-

imum decreases simultaneously. As a result in these solvents the position of maximum and shoulder are interchanged so that the band maximum appears at shorter wavelengths than the respective shoulder. Due to the loss of fine structure there are no shoulders to be observed in dichloromethane, DMF, acetonitrile or DMSO.

The analysis of the spectra shows that the solvent-substrate interactions are complex. Solvent-substrate interactions are mainly described as dipole-dipole interactions [28], a more exact description based on non-empirical constants is difficult [29]. A proper prediction of solvent effects is neither possible based on terms of simple physical solvent characteristics, nor on theoretical expressions which could be used for calculations. Hence, most solvent effects are described on the basis of empirical parameters of solvent polarity. The importance of the parameters introduced by Kamlet and Taft [28] to explain solvatochromic shifts has been demonstrated successfully in case of ethynyl- and 1-(arylalkenyl)pyrenes [2, 24]. In both studies, the influencing factor was the polarity/polarizability π^*. The shift to longer wavelength increases with increasing value of π^*. Referring to Fig. 2 the solvatochromic shift in the spectra of **3d** can also be assigned to π^*. The value of π^* is -0.08 in n-hexane and $+1.00$ in DMSO. However, the spectra measured in acetonitrile ($\pi^* = 0.75$) shows a greater solvatochromic shift than the spectra measured in dichloromethane ($\pi^* = 0.82$) or DMF ($\pi^* = 0.88$). Although π^* is adequate to explain the loss of fine structure, there is no explanation for the peculiar band shape evolution in solvents like ethyl acetate, dioxane or THF. For these solvents the value of π^* is about 0.55 which is lower than the values for the previously mentioned solvents, but still higher as compared to n-hexane. The analyses of the remaining solvent parameters of Kamlet, of Taft's α and β (see Supporting Information for definition and for selected values of α and β; see note at the end of the paper for availability) or of other constants like the dipole moment or the dielectric constant, all do not allow for a sufficient explanation of the observed peculiar band shape evolution

Electrochemical studies

Cyclovoltammetric and DPV (Differential Pulse Voltammetry) measurements were carried out to determine the electrochemical activity and the potential
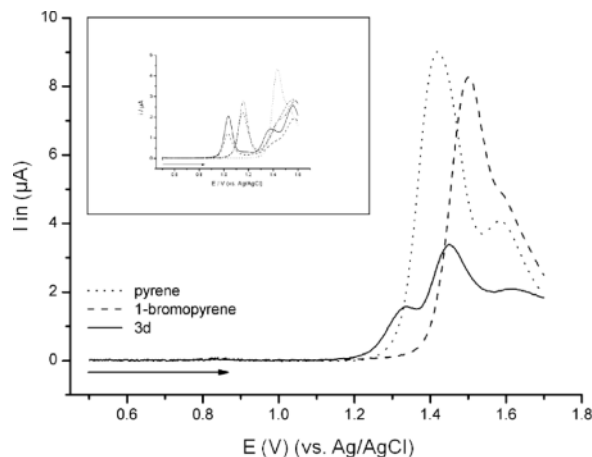

Fig. 3. Oxidative DPVs of **3d** and the precursors, pyrene and 1-bromopyrene in DMF (0.1 mol L^{-1} TBABF$_4$); working electrode: platinum. Inset depicts oxidative DPVs of formerly investigated 1-(arylalkenyl)pyrenes [24] under the same conditions.

values of **3d** in comparison to the precursors pyrene and 1-bromopyrene. The oxidative DPV of **3d** exhibits three oxidation peaks. Two of them can also be found in the DPVs of the precursors (*cf.* Fig. 3).

The oxidative peaks of pyrene are located at 1.42 and 1.58 V. In case of 1-bromopyrene, containing the electron-withdrawing bromine substituent, a shift of these peaks to positive potentials (1.50 and 1.60 V) can be observed. The second oxidation peak of 1-bromopyrene is not well developed and can only be detected as a shoulder of the first oxidation peak. The acrylate substituent of 3-pyrenylacrylate **3d** does not seems to have a strong electron withdrawing effect and, therefore, the oxidative peaks are found at 1.45 and 1.62 V (only weakly developed). The third oxidation peak at 1.33 V results from the influence of the acrylate group. A comparison with the formerly investigated 1-(arylalkenyl)pyrenes [24] (Fig. 3) reveals that the best-developed oxidative peak between 1.0 and 1.2 V can not be found for 3-pyrenylacrylate **3d**. This peak is assigned to the oxidation of the aryl system.

Computational studies

Exploring the geometric and electronic structure of the molecules, we carried out density functional theory (DFT) calculations, using Becke's three parameter set with Lee-Yang-Parr modification (B3LYP) and the 6-31G* basis set for geometry optimization [30 – 32].

Structure

Electrostatic Potential Surface

high el. dens. ▮▮▮ low el. dens.

HOMO

LUMO

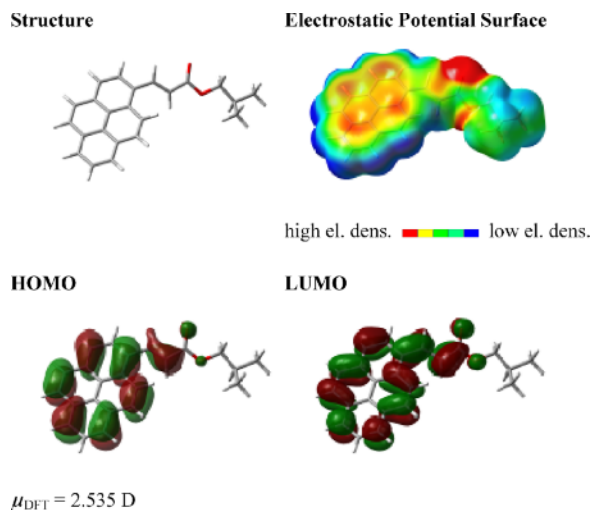$\mu_{\text{DFT}} = 2.535$ D

Fig. 4 (color online). Structure, electrostatic potential surface, HOMO and LUMO molecular orbitals and the dipole moment of compound **3d**.

Furthermore, for the calculation of the excitation energies we used the TD-DFT method with the B3LYP functional. The 6-31G* basis set is basically small, but it yields a better fit of excitation energies to the experimental data than higher basis sets. The latter ones result in a stronger red shift of the bands in the absorbance spectra.

The geometry optimization reveals – as shown in Fig. 4 – that product **3d** is not planar: The pyrene groups is, due to steric effects, twisted against the ethylene group which was also observed for 1-(arylalkenyl)pyrenes in our previous study [24]. As the calculations refer to the gas phase, the structures in solution might be different.

The dipole moment of 2.5 D is relatively high and is the reason for strong intermolecular interactions in solution. We have shown in our previous study [24] that the fine structure in the emission spectra is sensitive to the polarity/polarizability π^* of the solvent. In solvents with low values of π^*, intermolecular dipole-dipole interactions provoke the loss of fine structure in the spectra. However, in the present study, none of the emission spectra, recorded in different solvents, possess a fine structure. Obviously, the strong dipole moment of **3d** causes strong substrate/solvent interactions and, therefore, a loss of the fine structure in the emission spectrum is independent from the polarity/polarizability π^* of the solvent.
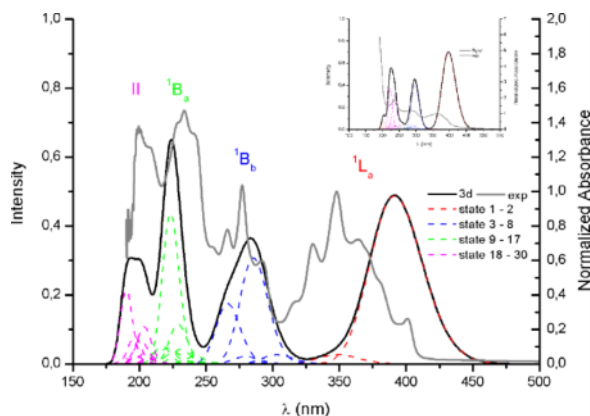

Fig. 5 (color online). Calculated electronic spectrum (black solid line) as sum of single Gaussian functions (short dashed lines, colored according to the bands ^1L_a, ^1B_b, ^1B_a and II) and the experimental absorbance spectra (solid grey lines) for the product **3d**. The right axis corresponds to the experimental absorbance spectrum. Inlay: Calculated spectrum of 1-(arylalkenyl)pyrenes from our previous work [24] for comparison.

Table 2. Excited states, excitation energies and oscillator strengths $f \geq 0.04$, 8 % percentage of the strongest band ^1L_a, which are mainly responsible for the distinct maxima in the absorption spectra of the 3-pyrenylacrylate.

Band	State	λ (nm)	f
^1L_a	1	391.43	0.519
^1B_b	6	285.49	0.328
	8	266.10	0.187
^1B_a	12	230.97	0.045
	13	228.91	0.123
	14	225.70	0.037
	15	223.26	0.465
	16	220.89	0.049
	17	216.85	0.055
II	22	205.00	0.037
	23	203.42	0.116
	24	200.68	0.077
	27	196.29	0.085
	28	190.16	0.228

The excitation energies and the corresponding oscillator strengths were determined by using the TD-B3LYP method (Table 2, Fig. 5). The resulting spectrum and its decomposition were calculated as it is described in our previous work [24]. TD-DFT excitation energies are typically slightly redshifted with respect to the experimental data [33]. The lowest excitation state, which is assigned to band ^1L_a (according to the notation in Fig. 1) appears at about 391 nm. One significant contribution (*cf.* red dashed lines in Fig. 5) of this

band can be assigned to the HOMO-LUMO or π-π^* transition.

In contrast the wavelength of the bands ^1L_a, ^1B_b, ^1B_a and II of the 1-(arylalkenyl)pyrenes are blue-shifted by about 10–20 nm [24]. Hence, the spatial distribution of the delocalized π systems of the 3-pyrenylacrylates, which contain no phenyl group, is smaller than that of the π systems of the 1-(arylalkenyl)pyrenes and affects the excitation energies significantly. Furthermore, the NBO [34–40] 2nd order perturbation calculation shows that the interaction energy between the bonding orbitals of the ethylene group and the antibonding orbitals of the carbonyl group is about 21 kcal mol^{-1} while the strongest interaction energy between this ethylene group and the pyrenyl group is about 9 kcal mol^{-1}. Therefore, the electron withdrawing carboxy group hinders the formation of a delocalized π system over the entire molecule. Thus, the ethylene group interacts predominantly with the carboxy group forming a planar unit.

Conclusion

In conclusion, 3-pyrenylacrylates were prepared by Heck reaction of 1-bromopyrene with acrylates in good to very good yield. DPV measurements were used to study their electrochemical behavior. Similar to our former results with 1-(arylalkenyl)pyrenes [24] the oxidation potentials exhibit a dependence on the nature of the substituent. The photochemical investigations have shown that the selected 3-pyrenylacrylate **3d** has similar properties as the 1-(arylalkenyl)pyrenes of our last study [24]. Comparing the absorption spectrum of **3d** with the spectra of other pyrenyl derivatives like ethynylpyrenes [2] or 1-(arylalkenyl)pyrenes [24] it has turned out that the band of the ^1L_a transition is sensitive to the size of the conjugated π electron system which is introduced by substituting the pyrene moiety. By contrast the bands of the other transitions like ^1B_a and ^1B_b, are less affected by the size of the conjugated π electron system. The TD-DFT calculations and the NBO analysis have confirmed that – compared to the 1-(arylalkenyl)pyrenes – the conjugated π electron system of the title compounds is smaller and more separated. The shape of the fine structure occurring in the absorption and emission spectra seems to be also strongly dependent on the class of the substituent. The DFT calculation gave a high dipole moment of 2.5 D of the molecule, which seems to be the reason for the

missing fine structure in all spectra of **3d** recorded in selected solvents. The observed solvatochromic shifts are similar to those observed for other classes of substituted pyrenes.

Experimental Section

General comments

All reactions were carried out in oven-dried pressure tubes under argon atmosphere. Pyrene, palladium(II) acetate, the 2-dicyclohexylphosphanyl-2′,4′,6′-tri-isopropyl biphenyl ligand (XPhos) and the corresponding acrylates were purchased from a Aldrich. Dry solvents (DMF, DCM) were purged with argon before use. K_2CO_3 was purchased from Aldrich, dried and mortared before use. Thin layer chromatography (TLC) was run on Merck precoated aluminum plates (Si 60 F_{254}). Column chromatography was performed using Merck Silicagel 60 (0.043–0.06 mm). NMR data were recorded on Bruker ARX 300 and ARX 400 spectrometers. ^{13}C and ^1H NMR spectra were referenced to signals of deuterated solvents and residual protonated solvents, respectively. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and an HP-5 capillary column using helium as carrier gas. ESI HR-MS measurements were performed on an Agilent 1969A TOF mass spectrometer. All UV/Vis spectra were recorded on a Lambda 5 (Perkin Elmer) spectrophotometer with a concentration of $c = 10^{-6}$ mol L^{-1}. All fluorescence spectra were recorded on a Hitachi F-4010 fluorescence spectrophotometer using similar solution concentrations in various solvents.

DPV studies

Studies were performed at room temperature in dry DMF under argon atmosphere in the presence of tetrabutylammonium tetrafluoroborate (0.1 mol L^{-1}) as conducting salt using an Autolab (PGSTAT 302N, Eco Chemie). The working electrode was a platinum disk electrode (Eco Chemie, d = 2 mm), the counter electrode a laboratory-made Pt plate electrode. *Via* 3 M KCl salt bridge the reference electrode Ag/AgCl/3 M KCl (Sensortechnik Meinsberg GmbH) was connected. All potentials mentioned in this paper were measured with regard to this reference system and were checked by using the ferrocene/ferrocenium internal reference system. The CV scans were done three times at a scan rate of 25 mV s^{-1}. The differential pulse voltammograms were performed in oxidative and in reductive direction with a scan rate of 5 mV s^{-1} (step potential 2.5 mV, modulation amplitude 25 mV, modulation time 0.05 s, interval time 0.5 s). Concentrations of 1 mmol L^{-1} analyt were used for the measurements.

Theoretical calculations

The optimization of the structures and electrostatic potential surface were calculated with the 6-31G* basis sets and the Becke3LYP density functional method [31, 32] by using the GAUSSIAN 09 package [30]. For the B3LYP method the Becke-3 parameter gradientcorrected exchange functional is combined with the gradient-corrected correlation LYP functional by Lee, Yang and Parr. No imaginary frequencies were found indicating that all geometries represent at least local minimum structures on the potential energy surface. The calculation of the 30 electron transition states requires the solution of the time-dependent Schrödinger equations and was carried out by using the time-dependent density functional theory (TD-DFT) method with the B3LYP functional. Orbitals and energies, atomic charges, vibrational modes and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces and electrostatic potential density maps were then obtained from the output. Additionally we calculated the natural atomic charges by applying the NBO program [41, 42] as implemented in GAUSSIAN 09 [30]. All calculations have been carried out on the HPPC cluster in Rostock.

Synthesis of 1-bromopyrene (1)

The synthesis of 1-bromopyrene was carried out after a known literature procedure [43] To a stirred solution of pyrene (2.02 g, 10.0 mmol) and hydrobromic acid (1.24 mL, 48 %, 11.0 mmol) in methanol-ether (20 mL, 1 : 1) was slowly added hydrogen peroxide (0.34 g; 0.86 mL of a 35 % aqueous solution; 10 mmol) over a period of 15 min at $10 - 15\,^\circ$C. The reaction was left at room temperature for 14 h while its progress was monitored by TLC. After the completion of monobromination, the solvent was removed under reduced pressure and the crude product was taken up in ethyl acetate and washed with water and brine and dried over anhydrous sodium sulfate. The pure product was isolated by column chromatography on silica gel to get pure 1-bromopyrene as a slightly yellow solid (95 %, 2.67 g).

General procedure for the synthesis of 3-pyrenylacrylates 3

Palladium(II) acetate (5 mol-%) and XPhos (10 mol-%) were placed under argon atmosphere in a pressure tube and 5 mL of DMF was added. After stirring for 15 min, 1-bromopyrene (1), the acrylate 2a–j and K_2CO_3 were added. Subsequently, the mixture was heated at $60\,^\circ$C for 6 h. To the mixture were added water and CH_2Cl_2 (20 mL) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was con-

centrated *in vacuo*. The residue was purified by column chromatography (*n*-hexane-ethyl acetate) to afford 3.

(E)-Methyl 3-(pyren-3-yl)acrylate (3a)

Starting with 1 (100 mg, 0.35 mmol), 2a (46.0 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), XPhos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K_2CO_3 (98.0 mg, 0.71 mmol) in DMF (5 mL), 3a was isolated as a yellow solid (91 mg, 90 %); m. p. $135 - 137\,^\circ$C. – ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 3.82$ (s, 3H, OCH$_3$), 6.62 (d, $J = 15.6$ Hz, 1H, CH), 7.92 – 8.19 (m, 8H, CH), 8.39 (d, $J = 9.3$ Hz, 1H, CH), 8.75 (d, $J = 15.9$ Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 51.9$ (OCH$_3$), 119.8 (CH), 122.5 (CH), 124.2 (CH), 124.7 (C), 124.9 (C), 125.1 (CH), 125.9 (CH), 126.0 (CH), 126.3 (CH), 127.4 (CH), 128.2 (C), 128.6 (CH), 128.9 (CH), 129.8 (C), 130.7 (C), 131.3 (C), 132.8 (C), 141.6 (CH), 167.6 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3072$ (w), 3043 (w), 2956 (w), 2927 (w), 2859 (w), 1700 (s), 1611 (m), 1592 (w), 1433 (m), 1368 (m), 1273 (m), 1121 (m), 1071 (m), 982 (m), 838 (s), 760 (m), 707 (m), 677 (w). – GC-MS (EI, 70 eV): m/z (%) = 286 (58) [M]$^+$, 255 (14), 228 (18), 227 (100), 226 (93), 225 (15), 224 (18), 200 (8), 113 (26), 112 (12). – HRMS ((+)-EI): $m/z = 286.098350$ (calcd. 286.09883 for C$_{20}$H$_{14}$O$_2$ [M]$^+$).

(E)-Ethyl 3-(pyren-1-yl)acrylate (3b)

Starting with 1 (100.0 mg, 0.355 mmol), 2b (53.2 mg, 0.532 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), XPhos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K_2CO_3 (98.0 mg, 0.71 mmol) in DMF (5 mL), 3b was isolated as a yellow solid (92 mg, 87 %); m. p. $94 - 96\,^\circ$C. – ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.34$ (t, $J = 6.98$ Hz, 3H, CH$_3$), 4.29 (q, $J = 14.3$ Hz, 2H, CH$_2$), 6.26 (d, $J = 15.74$ Hz, 1H, CH), 7.92 – 8.12 (m, 8H, Py), 8.34 (d, $J = 9.23$ Hz, 1H, Py), 8.75 (d, $J = 15.74$ Hz, 1H, CH) ppm. – ^{13}C NMR (62.89 MHz, CDCl$_3$): $\delta = 30.9$ (CH$_3$), 61.2 (OCH$_2$), 120.3 (CH), 122.5 (CH), 122.9 (C), 124.1 (CH), 124.6 (C), 124.8 (CH), 125.0 (CH), 125.7 (CH), 125.8 (C), 125.9 (CH), 126.2 (CH), 127.3 (CH), 127.4 (C), 128.3 (C), 128.4 (CH), 128.5 (C), 129.7 (C), 130.7 (C), 131.3 (C), 132.6 (C), 141.3 (CH), 167.1 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3041$ (w), 2977 (w), 2925 (w), 2904 (w), 2852 (w), 1731 (w), 1705 (m), 1619 (m), 1538 (w), 1479 (w), 1442 (m), 1391 (w), 1340 (w), 1277 (m), 1210 (m), 1156 (s), 1107 (m), 1053 (m), 971 (m), 897 (m), 837 (s), 788 (m), 748 (m), 700 (m), 616 (m), 593 (m). – MS (EI, 70 eV): m/z (%) = 300(64) [M]$^+$, 255 (16), 227 (100), 226 (86), 224 (13), 113 (27). – HRMS ((+)-EI): $m/z = 300.11448$ (calcd. 300.114633 for C$_{21}$H$_{16}$O$_2$, [M+H]$^+$).

(E)-Butyl 3-(pyren-1-yl)acrylate (3c)

Starting with 1 (100 mg, 0.35 mmol), 2c (68.0 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol),

XPhos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98 mg, 0.71 mmol) in DMF (5 mL), **3c** was isolated as a luminous yellow oil (98 mg, 84 %) – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.01 (t, J = 7.4 Hz, 3H, CH$_3$), 1.50 (m, 2H, CH$_2$), 1.77 (d, J = 6.8 Hz, 2H, CH$_2$), 4.31 (t, J = 6.7 Hz, 2H, OCH$_2$), 7.83 (d, J = 7.84 Hz, 3H, CH), 7.89 – 8.00 (m, 4H, Py), 8.03 – 8.12 (m, 4H, Py), 8.13 – 8.23 (m, 2H, Ar) ppm. – ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 13.2 (CH$_3$), 27.6 (CH$_2$), 35.1 (CH$_2$), 59.6 (OCH$_2$), 121.9 (CH), 123.8 (CH), 123.9 (2CH), 124.8 (CH), 125.8 (CH), 126.0 (CH), 126.4 (CH), 126.5 (CH), 127.5 (C), 127.7 (CH), 129.1 (C), 129.8 (CH), 130.3 (C), 133.5 (C), 135.9 (C), 140.3 (C), 171.9 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v}$ = 3433 (w), 3039 (w), 2955 (w), 2869 (w), 2135 (w), 1920 (w), 1796 (w), 1720 (s), 1619 (m), 1594 (m), 1537 (w), 1487 (w), 1434 (w), 1381 (w), 1312 (m), 1274 (m), 1200 (m), 1162 (s), 1061 (m), 973 (m), 900 (w), 838 (s), 795 (m), 731 (m), 680 (m), 635 (m), 594 (m), 538 (m). – MS (EI, 70 eV): m/z (%) = 328 (61) [M]$^+$, 255 (19), 227 (100), 226 (85), 225 (12), 224 (12), 113 (18). – HRMS ((+)-EI): m/z = 328.145349 (calcd. 328.14578 for C$_{23}$H$_{20}$O$_2$ [M+H]$^+$).

(E)-iso-Butyl 3-(pyren-3-yl)acrylate (3d)

Starting with **1** (100 mg, 0.35 mmol), **2d** (76.0 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), XPhos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98.0 mg, 0.71 mmol) in DMF (5 mL), **3d** was isolated as a luminous yellow oil (100 mg, 86 %). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.97 (d, J = 6.6 Hz, 6H, CH$_3$), 2.05 – 1.99 (m, 1H, CH), 4.00 (d, J = 6.6 Hz, 2H, CH$_2$), 6.61 (d, J = 15.6 Hz, 1H, CH), 7.89 (d, J = 15.5 Hz, 1H, CH), 7.91 – 8.15 (m, 7H, CH), 8.31 (d, J = 8.4 Hz, 1H, CH), 8.70 (d, J = 15.8 Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 19.3 (CH$_3$), 19.3 (CH$_3$), 28.0 (CH), 70.9 (CH$_2$), 120.3 (CH), 122.4 (CH), 124.2 (CH), 124.6 (C), 124.9 (C), 125.0 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 127.3 (CH), 128.3 (C), 128.5 (CH), 128.6 (CH), 129.7, 130.7, 131.3, 132.7 (C), 141.3 (CH), 167.3 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v}$ = 3040 (w), 2958 (w), 2872 (w), 1703 (m), 1619 (m), 1595 (m), 1466 (w), 1374 (w), 1240 (m), 1153 (s), 1013 (m), 971 (m), 839 (s), 755 (m), 704 (m), 679 (w), 488 (w). – GC-MS (EI, 70 eV): m/z (%) = 328 [M]$^+$, 255 (31), 249 (30), 228 (23), 227 (100), 226 (96), 225 (12), 224 (16), 113 (15). – Anal. for C$_{23}$H$_{20}$O$_2$ (328.40): calcd. C 84.12 H 6.14; found C 83.97 H 6.241. – HRMS ((+)-EI): m/z = 328.145716 (calcd. 328.14578 for C$_{23}$H$_{20}$O$_2$ [M]$^+$).

(E)-tert-Butyl 3-(pyren-3-yl)acrylate (3e)

Starting with **1** (100 mg, 0.35 mmol), 2 e (76.0 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98.0 mg, 0.71 mmol) in DMF (5 mL), **3e** was isolated as a luminous yellow oil (108 g, 93 %). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.97 (s, 9H, CH$_3$), 6.55 (d, J = 15.9 Hz, 1H, CH), 7.96 (d, J = 15.6 Hz, 1H, CH), 7.97 – 8.18 (m, 7H, CH), 8.37 (d, J = 9.0 Hz, 1H, CH), 8.69 (d, J = 15.8 Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 28.4 (CH$_3$, *t*Bu), 80.7 (C, *t*Bu), 122.3 (CH), 124.2 (CH), 124.8 (C), 124.9 (C), 125.0 (CH), 125.7 (CH), 125.9 (CH), 126.3 (CH), 127.4 (CH), 128.4 (C), 128.5 (CH), 128.8 (CH), 128.9 (CH), 129.6, 130.8, 131.4, 132.5 (C), 140.3 (CH), 166.5 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v}$ = 3042 (w), 2959 (w), 2928 (w), 2859 (w), 1705 (m), 1621 (m), 1596 (m), 1458 (w), 1390 (w), 1276 (s), 1143 (s), 1070 (m), 1039 (w), 976 (m), 840 (s), 743 (w), 706 (m), 680 (w). – GC-MS (EI, 70 eV): m/z (%) = 328 [M]$^+$, (44), 255 (26), 248 (30), 228 (19), 227 (100), 226 (88), 225 (17), 224 (22). – HRMS ((+)-EI): m/z = 328.145734 (calcd. 328.14578 for C$_{23}$H$_{20}$O$_2$ [M]$^+$).

(E)-Hexyl 3-(pyren-1-yl)acrylate (3f)

Starting with **1** (100 mg, 0.35 mmol), **2f** (82.9 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98 mg, 0.71 mmol) in DMF (5 mL), **3f** was isolated as a yellow oil (101 mg, 80 %). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.86 (t, J = 7.1 Hz 3H, CH$_3$), 1.26 – 1.41 (m, 6H, CH$_2$), 1.70 (d, J = 6.7 Hz 2H, CH$_2$), 4.22 (t, J = 6.76, 2H, OCH2), 6.62 (d, J = 15.73, 1H, CH), 7.90 – 8.19 (m, 8H, Py), 8.38 (d, ^3J = 9.41 Hz, 1H, CH), 8.73 (d, J = 15.73 Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.1 (CH$_3$), 22.6 (CH$_2$), 25.8 (CH$_2$), 28.8 (CH$_2$), 31.6 (CH$_2$), 64.9 (OCH$_2$), 120.4 (CH), 122.5 (CH), 124.2 (CH), 124.6 (C), 124.9 (CH), 125.0 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.2 (C), 127.3 (CH), 128.3 (C), 128.5 (CH), 129.7 (C), 130.7 (C), 131.3 (C), 132.7,(C), 141.3 (CH), 167.3 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v}$ = 3040 (w), 2952 (m), 2926 (m), 2855 (w), 1918 (w), 1707 (s), 1620 (m), 1478 (w), 1416 (w), 1368 (w), 1313 (m), 1241 (m), 1162 (s), 1053 (m), 975 (m), 840 (s), 794 (w), 716 (w), 680 (w), 609 (w), 536 (w). – GC-MS (EI, 70 eV): m/z (%) = 356 (44) [M]$^+$, 167 (36), 149 (100), 228 (19), 227 (100). – HRMS ((+)-EI): m/z = 356.176071 (calcd. 356.17708 for C$_{25}$H$_{24}$O$_2$ [M]$^+$).

(E)-6-Methylheptyl 3-(pyrene-1-yl)acrylate (3g)

Starting with **1** (100 mg, 0.35 mmol), **2g** (98 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98.0 mg, 0.71 mmol) in DMF (5 mL), **3g** was isolated as a yellow oil (107.1 mg, 79 %) – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.76 – 0.90 (m, 8H), 1.19 – 1.37 (m, 7H, CH$_2$), 4.13 – 4.16 (m, 2H, OCH$_3$), 7.91 – 8.22 (m, 9H, Py), 8.39 (d,

$J = 9.15$ Hz, 1H, CH), 9.75 (d, $J = 15.63$ Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 10.1$ (CH$_3$), 14.1 (CH$_3$), 23.0 (CH$_2$), 23.8 (CH$_2$), 28.9 (CH$_2$), 30.4 (CH$_2$), 38.7 (CH), 68.2 (OCH$_2$), 120.4 (CH), 122.5(CH), 124.2 (CH), 125.1 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.3 (CH), 128.3 (C), 128.5 (CH), 128.8 (CH), 129.7 (C), 130.7 (C), 130.9 (CH), 131.3 (C), 132.5, (C), 132.7 (C), 141.3 (C), 167.8 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3435$ (w), 3041 (w), 2955 (w), 2870 (w), 2731 (m), 1722 (s), 1621 (m), 1584 (w), 1510 (w), 1460 (m), 1416 (w), 1312 (m), 1270 (s), 1209 (m), 1163 (m), 1120 (m), 1070 (m), 1039 (m), 975 (m), 866 (m), 841 (s), 741 (m), 705 (m), 651 (w), 609 (w), 538 (w). – HRMS ((+)-EI): $m/z = 384.207745$ (calcd. 384.20838 for C$_{27}$H$_{28}$O$_2$ [M]$^+$).

(E)-2-Ethylhexyl 3-(pyren-3-yl)acrylate (3h)

Starting with **1** (100 mg, 0.35 mmol), **2h** (111 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.03 mmol), K$_2$CO$_3$ (98 mg, 0.71 mmol) in DMF (5 mL), **3h** was isolated as a yellow oil (120 mg, 88%). – ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.81 - 0.90$ (m, 6H, CH$_3$), 1.23 – 1.46 (m, 8H, CH$_2$), 1.65 – 1.71 (m, 1H, CH), 4.15 (d, $J = 6.3$ Hz, 2H, OCH$_2$), 6.66 (d, $J = 15.6$ Hz, 1H, CH), 7.85 – 8.07 (m, 8H, CH), 8.24 (d, $J = 8.7$ Hz, 1H, CH), 8.75 (d, $J = 15.8$ Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 11.2$ (CH$_3$), 14.2 (CH$_3$), 23.0, 23.8, 29.1, 30.6 (CH$_2$), 39.0 (CH chain), 67.2 (OCH$_2$), 120.4 (CH), 122.5 (CH), 124.2 (CH), 124.7 (C), 124.9 (C), 125.1 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.4 (CH), 128.3 (C), 128.6 (CH), 128.6 (CH), 129.7, 130.7, 131.4, 132.7 (C), 141.3 (CH), 167.4 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3041$ (w), 2956 (w), 2925 (w), 2857 (w), 1709 (m), 1620 (m), 1595 (m), 1459 (w), 1379 (w), 1275 (m), 1162 (s), 1030 (w), 975 (w), 840 (s), 756 (w), 705 (m), 680 (w). – GC-MS (EI, 70 eV): m/z (%) = 384 (100) [M]$^+$, 272 (17), 255 (36), 248 (30), 228 (24), 227 (88), 226 (78), 225 (10), 224 (10). – Anal. for C$_{27}$H$_{28}$O$_2$: calcd. C 84.34, H 7.34; found C 83.89, H 7.652. – HRMS ((+)-EI): $m/z = 384.208096$ (calcd. 384.20838 for C$_{27}$H$_{28}$O$_2$ [M]$^+$).

(E)-2,2,2-Trifluoroethyl 3-(pyren-3-yl)acrylate (3i)

Starting with **1** (100 mg, 0.35 mmol), **2i** (67 mg, 0.532 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98.0 mg, 0.71 mmol) in DMF (5 mL), **3i** was isolated as a luminous yellow solid (105 mg, 83%); m. p. 118 – 120 °C. – ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 4.75$ (q, $J = 9.0$ Hz, 2H, OCH$_2$CF$_3$), 6.66 (d, $J = 15.0$ Hz, 1H, CH), 8.08 – 8.37 (m, 8H, CH), 8.24 (d, $J = 9.0$ Hz, 1H, CH), 8.99 (d, $J = 15.0$ Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 68.1$ (OCH$_2$), 117.6 (CH), 122.5 (CH), 124.3 (CH), 124.7 (C), 124.7 (C), 125.0 (CH), 125.2 (CH), 126.1 (CH), 126.3 (CH), 126.4 (CH), 127.4 (CH), 128.6 (C), 128.9 (CH), 129.9, 131.8, 133.5, 133.7 (C), 143.8 (CH), 166.9 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3045$ (w), 2956 (w), 2922 (w), 2852 (w), 1718 (m), 1614 (m), 1538 (m), 1441 (w), 1371 (w), 1267 (m), 1138 (s), 1054 (w), 973 (w), 839 (s), 755 (w), 701 (m), 678 (w). – GC-MS (EI, 70 eV): m/z (%) = 354 (90) [M]$^+$, 255 (23), 228 (19), 227 (100), 226 (92), 225 (15), 224 (17), 113 (34), 112 (13). – HRMS ((+)-EI): $m/z = 354.086153$ (calcd. 354.08622 for C$_{21}$H$_{13}$F$_3$O$_2$ [M]$^+$).

(E)-2-Hydroxyethyl 3-(pyren-3-yl)acrylate (3j)

Starting with **1** (100 mg, 0.35 mmol), **2j** (56.0 mg, 0.53 mmol), Pd(OAc)$_2$ (5 mol-%, 4.3 mg, 0.017 mmol), Xphos ligand (10 mol-%, 16.0 mg, 0.035 mmol), K$_2$CO$_3$ (98.0 mg, 0.71 mmol) in DMF (5 mL), **3j** was isolated as a yellow solid (84 mg, 74%); m. p. 132 – 134 °C. – ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.99$ (s, 1H, OH), 3.86 – 3.89 (m, 2H, CH$_2$), 4.33 – 4.37 (m, 2H, CH$_2$), 6.63 (d, $J = 15.9$ Hz, 1H, CH), 7.89 – 8.01 (m, 8H, CH), 8.38 (d, $J = 8.6$ Hz, 1H, CH), 8.74 (d, $J = 15.9$ Hz, 1H, CH) ppm. – ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 61.6$, 66.4 (CH$_2$), 119.4 (CH), 122.4 (CH), 124.2 (CH), 124.3 (CH), 124.6 (C), 124.7 (C), 125.1 (CH), 125.9 (CH), 126.1 (CH), 126.3 (CH), 127.3 (CH), 128.7 (CH), 130.7, 130.9, 131.3, 132.6, 132.9 (C), 142.3 (CH), 167.5 (CO) ppm. – IR (ATR, cm^{-1}): $\tilde{v} = 3024$ (w), 2961 (w), 2920 (w), 2875 (w), 1698 (m), 1617 (m), 1599 (m), 1435 (w), 1361 (w), 1276 (m), 1088 (s), 1036 (w), 979 (w), 838 (s), 760 (w), 703 (m), 678 (w). – GC-MS (EI, 70 eV): m/z (%) = 316 (63) [M]$^+$, 255 (28), 248 (30), 228 (20), 227 (98), 226 (100), 225 (13), 224 (15), 113 (24). – HRMS ((+)-EI): $m/z = 316.108872$ (calcd. 316.10940 for C$_{21}$H$_{16}$O$_3$ [M]$^+$).

Supporting information

Acknowledgement

[1] S. Nishizawa, Y. Kato, N. Teramae, *J. Am Chem. Soc.* **1999**, *121*, 9463 – 9464.

[2] S.-W. Yang, A. Elangovan, K.-C. Hwang, T.-J. Ho, *J. Phys. Chem. B* **2005**, *109*, 16628 – 16635.

[3] K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **1977**, *99*, 2039 – 2044.

[4] G. Gareis, O. Köthe, J. Daub, *J. Eur. J. Org. Chem.* **1998**, 1549 – 1557.

[5] M. Dominska, K. Jackowska, P. Krysinski, G.-J. Blanchard, *J. Phys. Chem. B* **2005**, *109*, 15812 – 15821.

[6] T.-M. Figueira-Duarte, S.-C. Simon, M. Wagner, S.-I. Druzhinin, K.-A. Zachariasse, K. Mllen, *Angew. Chem. Int. Ed.* **2008**, *120*, 10329 – 10332.

[7] A. L. Nussbaumer, D. Studer, V. L. Malinovskii, R. Häner, *Angew. Chem. Int. Ed.* **2011**, *50*, 5490 – 5494.

[8] S.-N. Uno, C. Dohno, H. Bittermann, V. Malinovskii, R. Häner, K. Nakatani, *Angew. Chem. Int. Ed.* **2009**, *48*, 7362 – 7365.

[9] S. Karuppannan, J.-C. Chambron, *Chem. Asian J.* **2011**, *6*, 964 – 984.

[10] M.-J. Bosdet, W.-P. Piers, T.-S. Sorensen, M. Parvez, *Angew. Chem. Int. Ed.* **2007**, *119*, 5028 – 5031.

[11] D. F. Anghel, V. Alderson, F. M. Winnik, M. Mizusaki, Y. Morishima, *Polymer* **1998**, *39*, 3035 – 3044.

[12] J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.-F. Huang, J.-C. Tahsin, *Org. Lett.* **2007**, *9*, 5215 – 5218.

[13] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891 – 4946.

[14] A. Baheti, C.-P. Lee, K. R. J. Thomas, K.-C. Ho, *Phys. Chem. Chem. Phys.* **2011**, *13*, 17210 – 17221.

[15] P. Rajakumar, K. Visalakshi, S. Ganesan, P. Maruthamuthu, S. A. Suthanthiraraj, *Austral. J. Chem.* **2010**, *7*, 951 – 956.

[16] M. Nowakowska, J. E. Gulliet, *Macromolecules* **1991**, *24*, 474 – 478.

[17] G. G. Sowash, S. E. Webber, *Macromolecules* **1988**, *21*, 1608 – 16011.

[18] F. Ito, T. Kakiuchi, T. Sakano, T. Nagamura, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10923 – 10927.

[19] E. Schopf, R. Broyer, L. Tao, Y. Chen, H. D. Maynard, *Chem. Commun.* **2009**, 4818 – 4820.

[20] S. Pankasem, M. Biscoglio, J. K. Thomas, *Langmuir* **2000**, *16*, 3620 – 3625.

[21] D. Chu, J. K. Thomas, *CRC Handbook of Chemistry and Physics* vol. 3, CRC Press, Boca Raton, FL, **1991**, p. 49.

[22] F. M. Winnik, S. T. A. Regismond, *Colloids Surf. A.* **1996**, *118*, 1 – 39.

[23] A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L.-O. Pålsson, D. J. Tozer, T. B. Marder, *J. Am. Chem. Soc.* **2011**, *133*, 13349 – 13362.

[24] M. Sharif, S. Reimann, K. Wittler, L. R. Knöpke, A.-E. Surkus, C. Roth, A. Villinger, R. Ludwig, P. Langer, *Eur. J. Org. Chem.* **2011**, 5261 – 5271.

[25] H. H. Jaffé, M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley & Sons **1962**, pp. 334.

[26] R.-S. Becker, I.-S. Singh, E. Jackson, *J. Chem. Phys.* **1963**, *38*, 2144 – 2171.

[27] T.-H. Tran-Thi, C. Prayer, Ph. Millié, J. T. Hynes, *J. Phys. Chem. A* **2002**, *106*, 2244 – 2255.

[28] M. J. Kamlet, J.-L. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877 – 2887.

[29] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319 – 2358.

[30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, GAUSSIAN 09, (revision A.1), Gaussian, Inc., Wallingford CT (USA) **200**.

[31] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.

[32] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[33] G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comp. Chem.* **2001**, *22*, 931 – 967.

[34] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211 – 7218.

[35] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066 – 4073.

[36] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735 – 746.

[37] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736 – 1740.

[38] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926.

[39] J. E. Carpenter, *Extension of Lewis structure concepts to open-shell and excited-state molecular species*,

Ph.D. thesis, University of Wisconsin, Madison, WI, **1987**.

[40] J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)* **1988**, *46*, 41 – 62.

[41] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, Nʙo (version 3.1) **2009**.

[42] F. Weinhold, J. E. Carpenter in *The Structure of Small Molecules and Ions*, (Ed.: R. Naaman, Z. Vager), Plenum, New York **1988**, pp. 227 – 236.

[43] P. V. Vyas, A. K. Bhatt, G. Ramachandraiah, A. V. Bedekar, *Tetrahedron Lett.* **2003**, *44*, 4085 – 4088.