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Synthesis of fluorosolvatochromic phenanthrenyl-substituted benzoquinolizinium derivatives

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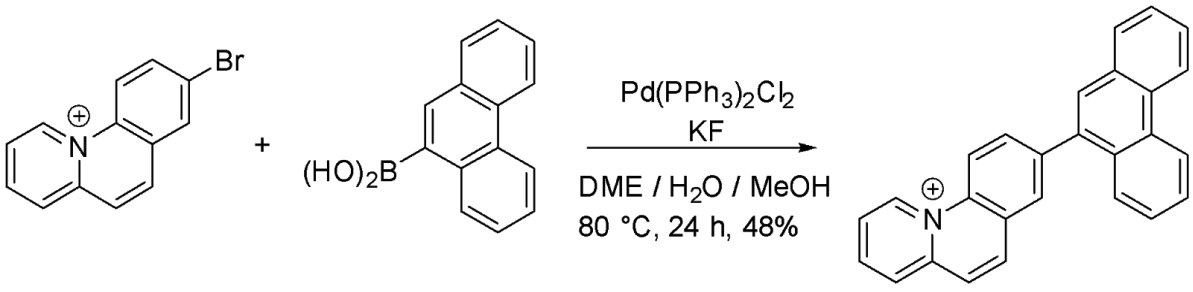
Abstract

The biaryl derivatives 8-(phenanthren-9-yl)benzo[*c*]quinolizinium and 9-(phenanthren-9-yl)benzo[*b*]quinolizinium were synthesized by a Suzuki–Miyaura coupling, and their steady-state absorption and emission properties were investigated. Whereas the absorption properties are essentially independent of the solvent properties, these compounds show a pronounced fluorosolvatochromism. Namely, they exhibit their lowest-energy maximum in aprotic, polar solvents and significantly blue-shifted emission bands in polar protic solvents. Notably, comparison of three different phenanthrenyl-substituted quinolizinium derivatives revealed that these fluorosolvatochromic properties are essentially independent of the annelation pattern of the quinolizinium unit, given that the aryl substituent has the propensity to form a sufficiently stabilized radical cation upon a photoinduced charge shift in the biaryl derivative.



Keywords: Quinolizinium, heterocycles, fluorescence, solvatochromism

Introduction

Cationic heteroaromatic compounds are useful components for the construction and development of functional dyes.[1–6] Because of their intrinsic electron-accepting properties they are easily integrated into donor-acceptor systems with favorable optical properties, such as red-shifted absorption and emission bands, large extinction coefficients, and high emission quantum yields, that are essential prerequisites for application as molecular fluorescent probes.[7,8] In particular, the emission properties of these compounds are often highly sensitive to the surrounding medium so that they can be employed as solvatochromic probes in fluorescence sensing and imaging.[9] In this context, we and others have established benzo-annelated quinolizinium ions as versatile units in water-soluble fluorescent probes,[10] for example for the fluorimetric detection of pH, metal cations, or
DNA.[11-19] In addition, we have demonstrated that biaryl-type quinolizinium derivatives **1a**–**d** and **2a**–**c** (Figure 1), that carry either a donor-substituted phenyl substituent or an electron-rich polycyclic aryl substituent, exhibit a pronounced fluorosolvatochromic behavior, i.e., they cover a large range of emission maxima in different solvents.[20,21] Specifically, the emission energy of these compounds depends on the polarity and hydrogen-bonding properties of the employed solvents because these parameters contribute significantly to the stabilization or destabilization of the intermediates that are formed after a photoinduced charge shift in the excited state. Thus, the biaryl-type quinolizinium fluorophore may be considered as promising structural motif of novel solvatochromic probes with solvent-sensitive emission properties that deserves further investigation to assess its scope and limits. As we have shown that the structural features of the polycyclic aromatic substituents in **2a**–**c** have a significant influence on the solvatochromic properties, we were additionally interested in the effect of the size and shape of the annelated quinolizinium ion. For that purpose, we focussed our attention on biaryl derivatives with a benzo-annelated quinolizinium unit to test whether the interplay of the smaller benzoquinolizinium with the phenanthrenyl substituent in the excited state still leads to fluorosolvatochromic behavior. The phenanthrenyl benzoquinolizinium π-system, the angular derivative **5** and the linearly annelated isomer **8** were designated as target structures. Herein, we present the synthesis of these derivatives, along with an investigation of their absorption and emission properties.

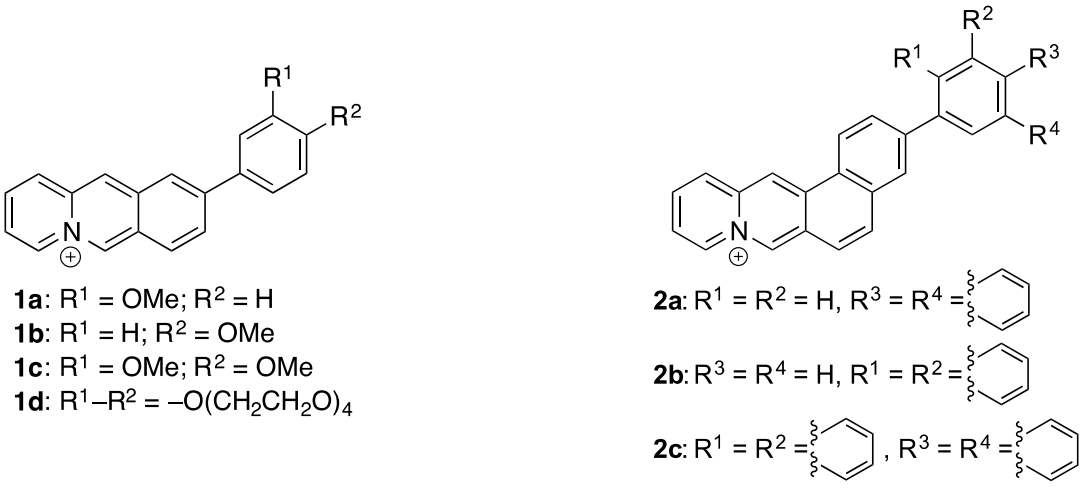
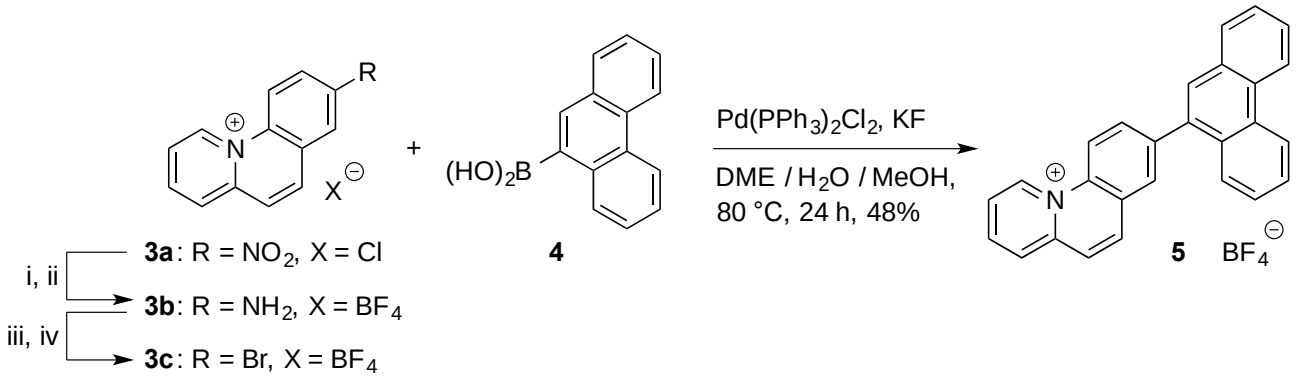


Figure 1. Structures of biaryl-type quinolizinium derivatives **1a**–**d** and **2a**–**c**.

Results and Discussion

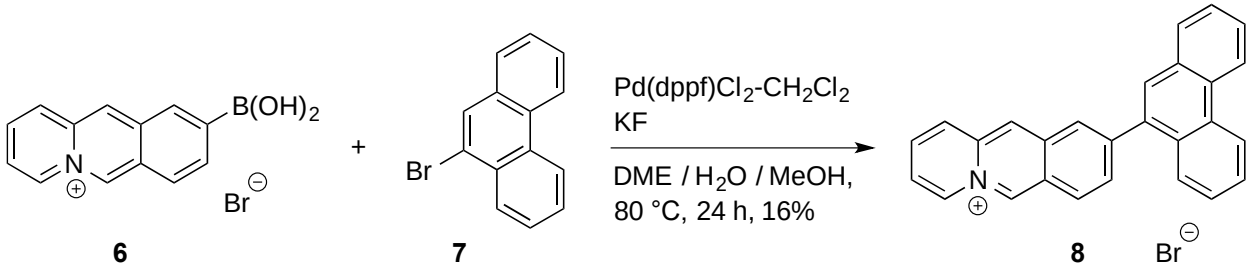
Synthesis

As Pd-mediated coupling reactions are known to be efficient routes to cationic biaryl derivatives,[22–25] the product **5** should be synthesizable by the reaction of the known phenanthrene-9-boronic acid (**4**) and the 8-bromobenzo[*c*]quinolizinium **3c**. However, much to our surprise, the latter compound was not known so far, so that a synthetic route to this substrate had to be explored, first. According to a literature procedure,[26] the nitrobenzo[*c*]quinolizinium **3a**[27,28] was reduced with activated iron to the corresponding amino-substituted compound **3b** that was isolated as its tetrafluoroborate salt by ion metathesis in 62% yield (Scheme 1).



Scheme 1. Synthesis of 8-(phenanthren-9-yl)benzo[*c*]quinolizinium tetrafluoroborate (**5**). Reagents and reaction conditions: i) Fe, aq. HCl (37%), aq. NH_4Cl (25%), EtOH, 65 °C, 2 h; ii) $NaBF_4$, H_2O, 62%; iii) $NaNO_2$, aq. HBr (24%), 0 °C, 10 min; iv) CuBr, aq. HBr (48%), rt, 1 h, 26%.

The use of iron as the reducing agent turned out to be superior to the previously employed method with $SnCl_2$ that gave **3b** only in low yields.[27] The amine **3b** was diazotized with $NaNO_2$ in hydrobromic acid and subsequently converted into 8-bromobenzo[*c*]quinolizinium (**3c**) in a Sandmeyer reaction by the use of CuBr. The intermediate diazonium salt was prone to decomposition under the reaction conditions due to the electron-poor aromatic system resulting only in a moderate yield of 26% for the latter reaction step. According to established protocol,[25] the Suzuki-Miyaura coupling of the benzo[*c*]quinolizinium **3c** with phenanthrene-9-boronic acid (**4**) with $Pd(PPh_3)_2Cl_2$ as catalyst and KF as weak base gave the biaryl product **5** in 48% yield. The linearly annelated derivative **8** was also available by a Suzuki-Miyaura coupling reaction. In this case, the Pd-mediated reaction of the known benzo[*b*]quinolizinium-9-boronic acid (**6**)[25] and 9-bromophenanthrene (**7**) furnished the 9-phenanthrenyl-substituted benzo[*b*]quinolizinium (**8**) in 16% yield (Scheme 2). The structures of the new compounds **3c**, **5**, and **8** were confirmed by NMR spectroscopy (^1H, ^{13}C, COSY, HSQC, HMBC), elemental analysis, and electrospray ionization mass spectrometric analysis (ESI-MS).



6 **7** **8**

Scheme 2. Synthesis of 9-(phenanthren-9-yl)benzo[*b*]quinolizinium bromide (**8**), dppf = 1,1'-bis(diphenylphosphino)ferrocene.

Photophysical properties

The biaryl **5** is soluble in polar protic and polar aprotic solvents and exhibits the characteristic, albeit slightly red-shifted long-wavelength absorption band of the parent benzo[*c*]quinolizinium with two local maxima between 350 and 370 nm.[27] The shift of the absorption maximum of this compound ranges from 368 nm in H_2O (ε = 12 000 M^{-1} cm^{-1}) to 371 nm in DMSO (ε = 17 300 M^{-1} cm^{-1}) and is thus essentially independent of the solvent (Figure 2 A, Table 1). In contrast, the maxima of the broad emission bands vary from 544 nm to 581 nm in those solvents (Figure 2 B, Figure 3, Table 1). At the same time, the highest fluorescence quantum yield was observed in 1-BuOH (Φ_{fl} = 0.14) and the lowest one in H_2O (Φ_{fl} = 0.012). Unfortunately, the absorption and emission properties of **5** in other, non-polar solvents (e.g., CH_2Cl_2 and $CHCl_3$) could not be determined due to very low solubility. Although the investigations of the absorption and emission properties of the linearly annelated quinolizinium derivative **8** were somewhat hampered by its low solubility in organic solvents and water, the data obtained in representative solvents revealed a similar trend as with the angular isomer **5** (Table 1, Figure 4). Specifically, the absorption properties do not change significantly in different solvents and range from 397 nm in H_2O and MeCN to 402 nm in $CHCl_3$ (Figure 4A). In contrast, this compound has a pronounced fluorosolvatochromic behavior as indicated by a shift of the emission maximum from 500 nm in $CHCl_3$ to
557 nm and 558 nm in DMSO and MeCN, respectively (Figure 4B). It should be noted that compound **8** does not dissolve well in water and may tend to aggregation at higher concentrations in this solvent, as indicated by the absorption spectrum; however, the solubility is suffient at the low concentrations employed for fluorescence measurements.

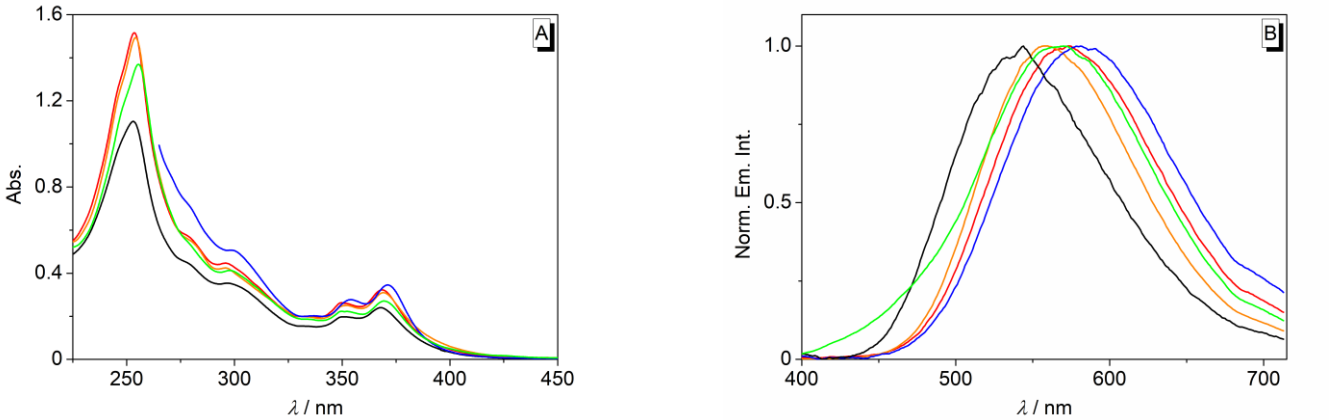


Figure 2. Absorption (c = 20 µM) (A) and normalized emission spectra (Abs. = 0.10 at λ_{ex} = 365 nm) (B) of derivative **5** in H_2O (black), MeOH (red), 2-PrOH (orange), THF (green), and DMSO (blue).

Table 1. Absorption and emission properties of derivatives **5** and **8**

	5				**8**			
Solvent[a]	λ_{abs}[b]	lg ε[c]	λ_{fl}[d]	Φ_{fl}[e] / 10^{-2}	λ_{abs}[b]	lg ε[c]	λ_{fl}[g]	Φ_{fl}[e] / 10^{-2}
H_2O	368	4.08	544	1.2	397	3.62	532	5.6
MeOH	369	4.21	573	3.9	398	4.06	553	15
EtOH	369	4.18	563	9.0	–[h]	–[h]	–[h]	–[h]
AcOH	369	4.18	562	8.1	–[h]	–[h]	–[h]	–[h]
1-BuOH	370	4.19	564	14	–[h]	–[h]	–[h]	–[h]
2-PrOH	369	4.19	558	13	–[f]	–[f]	–[f]	–[f]
MeCN	368	4.19	581	6.4	397	4.06	558	14
DMSO	371	4.24	581	4.8	399	4.00	557	15
$CHCl_3$	–[f]	–[f]	–[f]	–[f]	402	4.02	500	5.9
THF	369	4.13	570	8.4	–[f]	–[f]	–[f]	–[f]

[a] Solvents arranged in order of decreasing E_T^{30} values. [b] Long-wavelength absorption maximum in nm; c = 20 µM. [c] Molar extinction coefficient in cm^{-1} M^{-1}. [d] Fluorescence emission maximum (Abs = 0.10 at excitation wavelength λ_{ex} = 365 nm). [e] Fluorescence quantum yield relative to Coumarin 153 (Φ_{fl} = 0.38 in EtOH) [Ref. 30–32]; estimated error for fluorescence quantum yields: ±10%. [f] Not sufficiently soluble. [g] Fluorescence emission maximum (Abs. = 0.10 at excitation wavelength λ_{ex} = 399 nm). [h] Not determined.

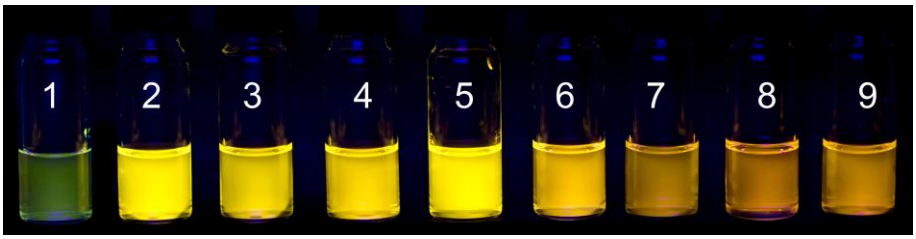


Figure 3. Emission colors of derivative **5** in various solvents; λ_{ex} = 366 nm. 1: H_2O, 2: 2-PrOH, 3: AcOH, 4: EtOH, 5: 1-BuOH, 6: THF, 7: MeOH, 8: MeCN, 9: DMSO.

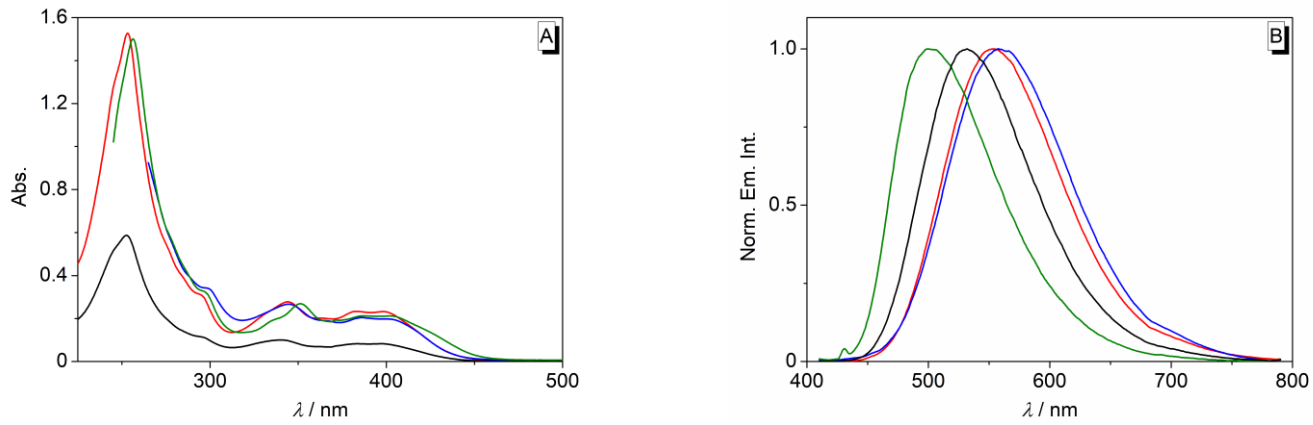
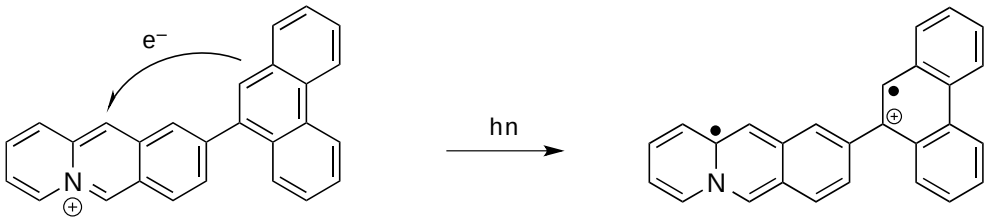


Figure 4. Absorption (*c* = 20 µM) (A) and normalized emission spectra (Abs. = 0.10 at λ_{ex} = 399 nm) (B) of derivative **8** in H_2O (black), MeOH (red), $CHCl_3$ (olive), and DMSO (blue).

Altogether, all three phenanthrenyl-substituted, annelated quinolizinium derivatives **2c**, **5**, and **8** possess similar solvatochromic properties. Namely, they exhibit their lowest-energy maximum in the polar aprotic solvents MeCN and DMSO and a blue-shifted emission band in polar protic solvents, mostly pronounced in water. Moreover, in the case of derivatives **2c** and **8** the strongest blue shift was observed in $CHCl_3$ solution, whereas **5** is not sufficiently soluble in this solvent. The origin of this solvatochromism has been discussed previously, and it was proposed that it is mainly caused and influenced by the polarity and the hydrogen-bonding properties of the solvents.[20] According to this model, a photoinduced charge shift (CS) leads to the formation of a quinolizinyl intermediate, e.g. $\mathbf{8}^{CS}$, that is connected with the phenanthrene radical cation (Scheme 3). In turn, the specific energetic stabilization of the excited CS state by the various solvents leads to varying emission energies. Nevertheless, as already observed with derivative **2c**, the emission maxima do correlate reasonably well with the established solvent parameters, that quantify, for example, the polarity, polarizability, or the hydrogen bond donating and accepting properties, which clearly indicates that the different solvent parameters affect the emission properties to different extents and with different trends. Unfortunately, the low solubility of the substrates in most organic solvents hampers a multiparameter analysis of the solvent effect. In summary, we deduce from the comparison of the fluorosolvatochromic properties of derivatives **2c**, **5**, and **8** that in all cases the CS state is formed on photoexcitation and that the interaction with the surrounding medium of the corresponding intermediate after solvent relaxation is specific for each solvent. And although this a rather small sample size, so far, the results seem to indicate that the fluorosolvatochromic properties of biaryl-type quinolizinium ions are essentially independent of the size and shape of the annelated quinolizinium fluorophore.



8 $\mathbf{8}^{CS}$

Scheme 3. Intramolecular charge shift of benzoquinolizinium ion **8** upon photoexcitation.

Conclusions

In summary, Suzuki–Miyaura coupling was employed as key step for the synthesis of two novel phenanthrenyl-substituted benzoquinolizinium derivatives **5** and **8**, whose emission properties depend strongly on the solvent. Notably, comparison of three different phenanthrenyl-substituted quinolizinium derivatives revealed that the pronounced fluorosolvatochromic properties are essentially independent of the annelation pattern of the quinolizinium unit. Therefore, it may be concluded that an annelated quinolizinium fluorophore with a biaryl structure is generally fluorosolvatochromic as long as the aryl substituent has the propensity to form a stabilized radical cation upon a photoinduced charge shift. This observation emphasizes the utility of the quinolizinium ion as a key element in fluorescent probes[10] and should be relevant for the development of functional solvatochromic probes, because the size and shape of the annelated quinolizinium unit may be simply adapted to a particular application without loss of fluorosolvatochromic properties.

Experimental Section

General. 8-Nitrobenzo[*c*]quinolizinium chloride (**3a**) was prepared from 2-chloro-5-nitrobenzaldehyde and 2-methylpyridine as previously described.[27,28] Phenanthrene-9-boronic acid (**4**) was synthesized from 9-bromophenanthrene (**7**) according to a literature procedure.[29] Benzo[*b*]quinolizinium-9-boronic acid (**6**) was synthesized as previously described.[25] 9-Bromophenanthrene (**7**) was purchased from Merck KGaA (Darmstadt, D). The commercially available chemicals were reagent-grade and used without further purification. Absorption and emission spectra were recorded from solutions prepared with spectroscopic grade solvents.

For experiments in different solvents, aliquots of the stock solution of **5** (*c* = 1.0 mM in MeCN) or **8** (*c* = 1.0 mM in MeOH) were evaporated under a stream of nitrogen and redissolved in the respective solvent. In general, absorption spectra were determined in a range between 225 nm and 500 nm (265–500 nm for DMSO and AcOH, 245–500 nm for $CHCl_3$) and subsequently smoothed in the Origin software with the function "adjacent-averaging" (factor of 10). For the detection of emission spectra, the excitation and emission slits were adjusted to 5 nm, the detection speed was 120 nm min^{-1}, and the detector voltage was adjusted to 600 V. The emission spectra were smoothed with the implemented moving-average function by a factor of 5, but they are otherwise uncorrected despite a potentially reduced detector sensitivity above 600 nm. The fluorescence quantum yields of derivative **5** and **8** were determined relative to Coumarin 153 (Φ_{fl} = 0.38 in EtOH)[30] according to the established procedures.[31,32]

8-Aminobenzo[*c*]quinolizinium tetrafluoroborate (**3b**). A suspension of iron powder (1.40 g, 25.0 mmol) in EtOH (8 mL) and aq. HCl solution (*w* = 37%, 208 µL) was stirred at 65 °C for 2 h, after which an aq. NH_4Cl solution (*w* = 25%, 4 mL) was added. Then, the nitroquinolizinium **3a** (1.30 g, 5.00 mmol) was added in portions over a period of 30 min. The reaction mixture was stirred at 60 °C for 2 h, cooled to 40 °C, and filtered through a pad of SiO_2 (10 g). The latter was washed with EtOH (350 mL), and the solvent was removed under reduced pressure. The residue was dissolved in H_2O (20 mL) and a sat. solution of $NaBF_4$ (3.29 g, 30.0 mmol) in H_2O was added. After cooling to 0 °C, the precipitate was filtered off and washed with cold H_2O (5 mL) and MeOH (5 mL). The product **3b** was crystallized from MeOH/H_2O (1:1, 8 mL), dried in a vacuum desiccator over $CaCl_2$ and obtained in the form of fine, brown needles (878 mg, 3.11 mmol, 62%); mp 238–240 °C (dec.) (lit.[27] mp 228–229 °C). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 6.42 (s, 2 H, 8-NH_2), 7.13 (d, ^4J 2 Hz, 1 H, 7-H), 7.38 (dd, ^3J

9 Hz, ^4J 2 Hz, 1 H, 9-H), 8.07–8.14 (m, 2 H, 2-H, 5-H), 8.35–8.42 (m, 2 H, 3-H, 6-H), 8.49 (d, ^3J 8 Hz, 1 H, 4-H), 8.78 (d, ^3J 9 Hz, 1 H, 10-H), 10.04 (d, ^3J 7 Hz, 1 H, 1-H). Anal. for $C_{13}H_{11}BF_4N_2$ (282.05), calcd (%): C 55.36, H 3.93, N 9.93, found: C 55.36, H 3.94, N 9.80.

8-Bromobenzo[*c*]quinolizinium tetrafluoroborate (**3c**). To prepare the CuBr catalyst solution, first NaBr (309 mg, 3.00 mmol) was added to a solution of $CuSO_4 \cdot 7\ H_2O$ (499 mg, 2.00 mmol) in H_2O (1.60 mL) at 60 °C. Then, a solution of Na_2SO_3 (126 mg, 1.00 mmol) in H_2O (400 µL) was added dropwise. After cooling to rt, the precipitated white CuBr was washed with H_2O (3 x 5 mL) and dissolved in aq. HBr solution (*w* = 48%, 800 µL).
To a solution of the amine **3b** (423 mg, 1.50 mmol) in aq. HBr solution (*w* = 24%, 1.50 mL) was added a solution of $NaNO_2$ (109 mg, 1.58 mmol) in H_2O (630 µL) while stirring vigorously at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then added to the CuBr catalyst solution. The resulting suspension was stirred at rt for 1 h, after which H_2O (40 mL) was added and the mixture was filtered from insoluble components. The filtrate was mixed with a sat. solution of $NaBF_4$ (1.65 g, 15.0 mmol) in H_2O and extracted with $MeNO_2$ (2 x 25 mL). The combined organic layers were washed with H_2O (2 x 20 mL), dried with Na_2SO_4 and filtered from the drying agent. The solvent was removed under reduced pressure. The product **3c** was crystallized from MeCN/H_2O, dried in a vacuum desiccator over $CaCl_2$, and obtained as a brown, microcrystalline solid (134 mg, 387 µmol, 26%); mp 235–237 °C (dec.). – ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.29 (ddd, ^3J 7 Hz, ^3J 7 Hz, ^4J 2 Hz, 1 H, 2-H), 8.37 (dd, ^3J 9 Hz, ^4J 2 Hz, 1 H, 9-H), 8.42 (d, ^3J 9 Hz, 1 H, 5-H), 8.64 (d, ^3J 9 Hz, 1 H, 6-H), 8.67–8.72 (m, 3 H, 3-H, 4-H, 7-H), 9.09 (d, ^3J 9 Hz, 1 H, 10-H), 10.38 (d, ^3J 7 Hz, 1 H, 1-H). – ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 120.4 (C10), 123.5 (C8), 124.1 (C5), 124.5 (C2), 128.3 (C6a), 128.5 (C4), 132.2 (C7), 133.4 (C10a), 134.8 (C1), 135.1 (C9), 135.2 (C6), 141.0 (C3), 143.1 (C4a). – MS (ESI$^+$): *m*/*z* = 258 (100) $[M - BF_4]^+$. – MS (ESI$^-$): *m*/*z* = 779 (100) $[2M + BF_4]^-$. Anal. for $C_{13}H_9BBrF_4N$ (345.93), calcd (%): C 45.14, H 2.62, N 4.05, found: C 45.54, H 2.61, N 4.76.

8-(Phenanthren-9-yl)benzo[*c*]quinolizinium tetrafluoroborate (**5**). Under an argon atmosphere, a suspension of the bromo-substituted quinolizinium **3c** (120 mg, 350 µmol), phenanthrene-9-boronic acid (**4**, 81.6 mg, 368 µmol), KF (81.3 mg, 1.40 mmol) and $Pd(PPh_3)_2Cl_2$ (7.37 mg, 10.5 µmol) in DME/MeOH/H_2O (2/1/1, 4.2 mL) was stirred for 24 h at 80 °C. After cooling to rt, MeCN (40 mL) was added, and the reaction mixture was filtered from insoluble components. The solvents were removed under reduced pressure, and the residue was dissolved in $MeNO_2$ (50 mL). The organic layer was washed with H_2O (3 x 20 mL), dried with Na_2SO_4 and filtered from the drying agent. The solvent was removed under reduced pressure. The residue was dissolved in DMSO (4 mL) and added dropwise to EtOAc (100 mL) under vigorous stirring. The precipitate was filtered off, washed with EtOAc and Et_2O (20 mL each) and dried *in vacuo*. The product **5** was obtained as beige, amorphous solid (74.0 mg, 167 µmol, 48%); mp 286–290 °C (dec.). – ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 7.64–7.67 (m, 1 H, 7'-H), 7.69–7.72 (m, 1 H, 2'-H), 7.74–7.78 (m, 2 H, 3'-H, 6'-H), 7.81 (d, ^3J 8 Hz, 1 H, 8'-H), 7.95 (s, 1 H, 10'-H), 8.07 (d, ^3J 7 Hz, 1 H, 1'-H), 8.31 (ddd, ^3J 7 Hz, ^3J 7 Hz, ^4J 2 Hz, 1 H, 2-H), 8.37 (dd, ^3J 9 Hz, ^4J 2 Hz, 1 H, 9-H), 8.39 (d, ^3J 9 Hz, 1 H, 5-H), 8.60 (d, ^4J 2 Hz, 1 H, 7-H), 8.67–8.73 (m, 2 H, 3-H, 4-H), 8.75 (d, ^3J 9 Hz, 1 H, 6-H), 8.87 (d, ^3J 8 Hz, 1 H, 4'-H), 8.95 (d, ^3J 8 Hz, 1 H, 5'-H), 9.26 (d, ^3J 9 Hz, 1 H, 10-H), 10.43 (d, ^3J 7 Hz, 1 H, 1-H). – ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 118.4 (C10), 122.9 (C4'), 123.3 (C5), 123.6 (C5'), 124.5 (C2), 125.7 (C8'), 127.1 (C6a), 127.2 (C6'), 127.3 (C7'), 127.4 (C2'), 127.6 (C3'), 128.5 (C4), 128.5 (C10'), 128.9 (C1'), 129.6 (C8a'), 129.7 (C4a'), 130.2 (C4b'), 130.8 (C10a'), 130.9 (C7), 133.6 (C10a), 134.3 (C9), 134.6 (C1), 135.4 (C9'), 136.5 (C6), 140.6 (C3), 141.9 (C8), 143.2 (C4a). – MS (ESI$^+$): *m*/*z* = 356 (100) $[M - BF_4]^+$. – MS (ESI$^-$): *m*/*z* = 973 (100) $[2M + BF_4]^-$. Anal. for $C_{27}H_{18}BF_4N \cdot ½\ H_2O$ (452.26), calcd (%): C 71.71, H 4.23, N 3.10, found: C 71.60, H 3.88, N 3.16.

9-(Phenanthren-9-yl)benzo[*b*]quinolizinium bromide (**8**). Under a nitrogen-gas atmosphere, a solution of benzo[*b*]quinolizinium-9-boronic acid (**6**, 650 mg, 2.14 mmol), 9-bromophenanthrene (**7**, 500 mg, 1.94 mmol), KF (450 mg, 7.76 mmol), and Pd(dppf)Cl_2-CH_2Cl_2 (47.1 mg, 63.0 µmol) in DME/MeOH/H_2O (2/1/1, 24 mL) was stirred for 24 h at 80 °C. After cooling to rt, the reaction mixture was filtered from insoluble components. The solvents were removed under reduced pressure, and the residue was recrystallized from MeOH to give the product **8** as a yellow microcrystalline solid (112 mg, 312 µmol, 16%); mp 278–280 °C (dec.). – ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 7.67 (dd, ^3J 7 Hz, ^3J 7 Hz, 1 H, 7'-H), 7.73 (dd, ^3J 7 Hz, ^3J 7 Hz, 1 H, 2'-H), 7.78–7.83 (m, 3 H, 3'-H, 6'-H, 8'-H), 7.99 (dd, ^3J 7 Hz, ^3J 7 Hz, 1 H, 3-H), 8.03 (s, 1 H, 10'-H), 8.08–8.11 (m, 2 H, 2-H, 1'-H), 8.18 (d, ^3J 9 Hz, 1 H, 8-H), 8.57 (d, ^3J 9 Hz, 1 H, 1-H), 8.58–8.62 (m, 2 H, 10-H, 7-H), 8.91 (d, ^3J 8 Hz, 1 H, 4'-H), 8.99 (d, ^3J 8 Hz, 1 H, 5'-H), 9.27 (s, 1 H, 11-H), 9.34 (d, ^3J 7 Hz, 1 H, 4-H), 10.54 (s, 1 H, 6-H). ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 122.4 (C3), 123.0 (C4'), 123.8 (C5'), 124.7 (C11), 125.2 (C6a), 125.8 (C8'), 126.9 (C1), 127.2 (C10), 127.4 (C6'), 127.5 (C7'), 127.5 (C2'), 127.9 (C3'), 128.2 (C7), 128.8 (C10'), 129.1 (C1'), 129.4 (C8a'), 129.9 (C4a'), 130.3 (C4b'), 130.8 (C10a'), 131.3 (C2), 133.4 (C8), 134.4 (C4), 135.6 (C10a), 136.1 (C9'), 137.8 (C11a), 140.1 (C6), 146.1 (C9). MS (ESI$^+$): *m/z* = 356 (100) [M – Br]$^+$. Anal. for $C_{27}H_{18}BrN{\cdot}2\,H_2O$ (472.38), calcd (%): C 68.65, H 4.69, N 2.97, found: C 68.85, H 4.37, N 3.10.

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Supplementary Material

Supplementary material (SI) available: Emission colors of compound **8**; ^{1}H and ^{13}C NMR spectra of compounds **3b**, **3c**, **5**, and **8** can be found in the online version of the text.

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