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Cyanine Dyes as Optical Contrast Agents for Ophthalmological Surgery

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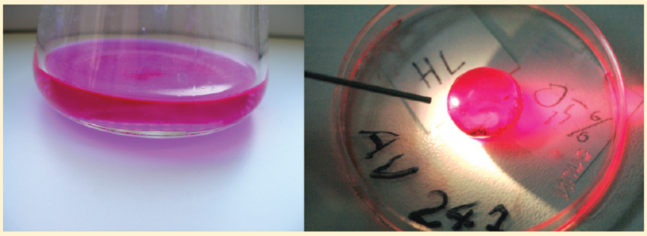
S *Supporting Information*

ABSTRACT: Cyanine dyes were prepared as optical contrast media for supporting the surgery of the lamina limitans interna (LLI) of the retina and other structures of the human eye. Their absorption spectra were adapted both to the spectral sensitivity of the human eye and to standard illumination. The contrast could be further amplified by the application of the strong fluorescence of the dyes used. The binding of the dyes to various surfaces was studied. No toxic effects could be detected for the applied dyes.



INTRODUCTION

The progress in the development of intraocular surgical techniques requires the visualization of delicate and barely visible structures reaching the limit of a surgeon's visual performance. For example, a relevant target structure in ophthalmic surgery is the lamina limitans interna (LLI) of the retina, a delicate and barely visible basement membrane of only a few micrometers thickness. Therefore, the use of visualizing agents has become a field of great interest for ophthalmic surgeons. The recognition of small structures can be improved by the application of optical contrast media[1] and promises to induce further progress in vitreoretinal surgery. The optical contrast for surgical interventions at the level of the LLI could be successfully improved by the application[2] of indocyanine green[3,4] (ICG, RN 3599-32-4).[5] The latter was previously used in cardiology. However, ICG proved not to be an optimal dye for ophthalmologic surgery. The toxic response[6,7] in the macula caused problems in application and may be caused by metabolic products;[8−10] ICG must be applied in comparably high concentrations because most of its light absorption lies in the near-infrared (NIR) and is therefore useless for visible detection; see Figure 1.

The tendency of ICG for aggregation at high concentration shifts its light absorption slightly hypsochromic; however, the improvement is not fundamental; see Figure 1. A more hypsochromic shift of the absorption would bring about an appreciable benefit.

RESULTS AND DISCUSSION

An optical contrast medium should match both the spectral sensitivity of the visible detection and the spectral light intensity of the applied lamps for illumination. An additional criterion for detection such as fluorescence would bring about a further improvement. Targeted substances should exhibit a moderate stability because residual material should be degraded quickly. Specific binding properties to human tissues may be modulated by peripheral structures not being involved into the chromophoric system.

We targeted cyanine dyes because of their strong light absorption, their limited stability, and a matched light absorption expected for pentamethin cyanine dyes. The termini of the cyanine structure were stabilized by naphthalene units. Thus, we started synthesis with the trimethyl benzindole[11] **1** where peripheral structures for the selectivity of binding to tissues were introduced by nucleophilic substitution reactions[12] to form **2**; see Figure 2. Compound **2** was condensed under basic conditions according to a similarly reported[15] procedure with orthoformic ester to form **3**; **3a** has been previously described;[16] however, the reported UV/vis spectra could not be reproduced. The less toxic 2-picoline could replace pyridine as the base; however, the latter gave better yields for some derivatives; see the Experimental Section. Carboxylic groups and their derivatives were applied as well as the sulfonic acid groups in **3t...3v** as the polar building blocks for the binding to tissues; **3t** has been previously mentioned,[13,14] however, without an explicit preparation procedure or spectroscopic data. The water solubility of the cyanine dyes being important for applications in surgery was appreciably increased by the sulfonic acid groups in **3t...3v**. As a consequence, we introdcuced sulfonic acid groups into the aromatic nuclei of **3** and started with the sulfonation of **1** in nitrobenzene with oelum. The problem of removing residual nitrobenzene can be solved with the application of steam distillation. The sulfonation allows the preparation of **4** in a one-step synthesis, whereas a multistep synthesis was reported in the literature.[17] Compound **4** was alkylated similarly to the reaction of **1** to form **5**. Alternatively, **2** could be sulfonated to **5**. The sulfonation of the nucleus allows the introduction of multiple sulfonic acid groups either by an alkylation of **4** with a sulfonic acid derivative or by

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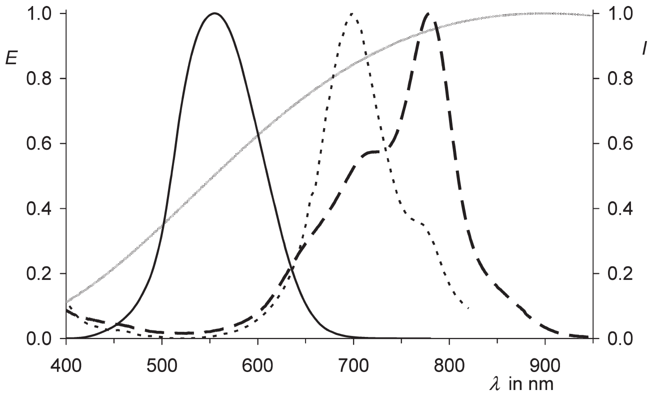
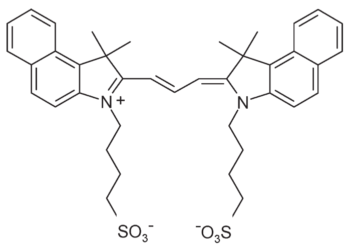


Figure 1. UV/vis spectra. Dashed line, ICG in water; dotted line, aggregated ICG; straight line, spectral sensitivity of the human eye; and gray line, spectral radiation characteristic of a tungsten lamp (3200 K).

the nucleophilic substitution of X = Br in **5** with sulfite. Compound **5** was condensed with orthoformic ethylester to form **6**. Both steps, the alkylation of **4** and the condensation to **6**, could be done in one pot. The arrangement of polar and lipophilic groups in **3** and **6**, respectively, was organized by the length *n* of an alkyl spacer.

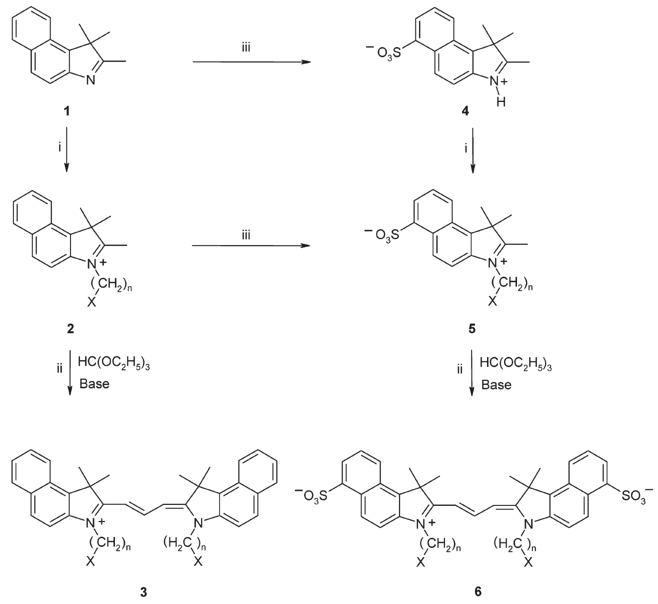


3t

Special care was taken for the purification of **3** and especially the sulfonic acids of **3** and **6**, respectively. Standard chromatographic procedures proved to be problematic. Better results were obtained with the application of reversed-phase silica column separation (RP18); compare refs 17 and 18.

The UV/vis absorption spectra of **3** and **6**, respectively, are essentially independent from the selectivity controlling side chains and only slightly dependent on the medium and are reported in Figure 3 for the example **3i**. The molar absorptivity of **3b** at the absorption maximum at 591 in ethanol was thoroughly measured and found to be 100000 and may be applied for the determination of the concentration of other derivatives in solution; a maximum at 590 nm was found in the lipophilic chloroform. The absorption of **3** corresponds quite well with the spectral sensitivity of the human eye. The point of gravity of the spectrum is slightly more bathochromic than the spectral sensitivity; this may be advantageous for the surgeon because standard tungsten lamps are applied for illumination with more intense radiation in the bathochromic region; see Figure 3. Dyes **3** exhibit an appreciable red fluorescence of some 40% quantum yield being hypsochromic enough for visual contrast. Thus, there are two indicators for the surgeon concerning the target tissue: The blue staining can be seen even at low intensity of illumination, and the red fluorescence becomes visually dominating at higher intensities.

The selectivity of the affinity to various surfaces of natural polymers controlled by the side chains in **3** and **6**, respectively, was investigated with the adsorption to wool and hair as typical polypeptides and to cotton with cellulose as a typical polysaccharide; see Table 1 (no staining effect was observed for ICG). The affinity to cellulose was generally higher than to polypeptides, although an influence of the net charge of the dye is expected because positive charges dominate at the surface of wool and negative at the surface of cellulose; the dyes **3h**...**3q** are positively charged, and **3t** is negatively charged because of the dissociated sulfonic acid groups, whereas **3a**...**3g** are positively charged in strong acid and negatively charged in the applied neutral to weakly basic media. The affinity to the



2, 3	*n*	X
a	2	CO_2H
b	4	CO_2H
c	5	CO_2H
d	7	CO_2H
e	9	CO_2H
f	10	CO_2H
g	11	CO_2H
h	2	CO_2CH_3
i	4	CO_2CH_3
j	9	CO_2CH_3
k	10	CO_2CH_3
l	2	$CO_2C_2H_5$
m	3	$CO_2C_2H_5$
n	4	$CO_2C_2H_5$
o	5	$CO_2C_2H_5$
p	6	$CO_2C_2H_5$
q	4	$CO_2CH_2C{\equiv}CH$
r	10	$CO_2CH_2C{\equiv}CH$
s	2	CN
t	4	SO_3^-
u	5	SO_3^-
v	10	SO_3^-
w	5	Br
x	10	Br
y	5	H

5, 6	*n*	X
a	4	SO_3^-
b	2	CO_2H
c	10	CO_2H
d	10	CO_2CH_3
e	2	$CO_2C_2H_5$
f	4	$CO_2C_2H_5$
g	5	$CO_2C_2H_5$
h	5	Br
i	10	Br

Figure 2. Synthesis of the cyanine dyes **3** and **6**. (i) Butanesultone for $n = 4$ and $X = SO_3^-$ or $Br(CH_2)_nX$. (ii) Pyridine or 2-picoline. (iii) Oleum in nitrobenzene.

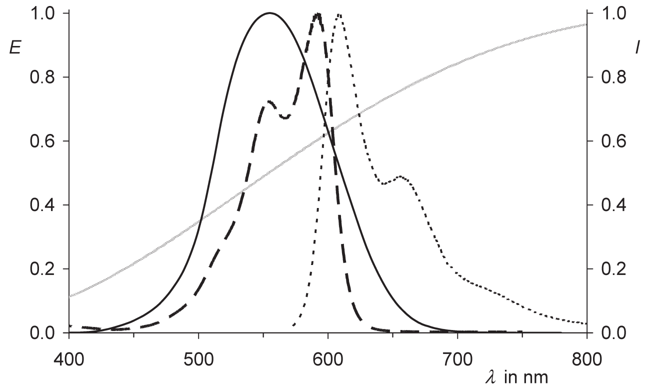


Figure 3. UV/vis spectra. Dashed line, absorption of **3i**; dotted line, fluorescence of **3i** (ethanol); straight line, spectral sensitivity of the human eye; and gray line, spectral radiation characteristic of a tungsten lamp (3200 K).

polypeptides can be controlled by the size of the side groups indicated by *n* where a tendency for lower selectivity is observed for longer chains. A low affinity was observed for the alkynyl derivative **3q**, whereas carbonyl derivatives and sulfonic acids give better results.

A good affinity was observed for the methyl esters (**3h**...**3k**) for short and long chain lengths, whereas generally good affinities were found for the ethyl esters (**3l**...**3o**) for chain lengths larger than 3.

Pig's lens capsule is a good model for staining because it is a basement membrane similar to the human LLI of the retina, and both represent important target structures for surgery; the intensity of the staining of such lens capsules varied and was concentration dependent as presented. Good staining was obtained at comparably high concentrations of dyes; see Table 2. A decrease of the concentration lowers the affinity; however, a visual detection is still possible. The red fluorescence of the dyes forms a second criterion and is helpful for the visible detection; this is even more important for low concentrations. The staining with **3t** is of special interest because of its very good water solubility. Good staining was observed with **3c** in the carboxylic series and **3l** for the ethyl esters. The methyl esters (**3h**...**3k**) were generally not efficient. Short chain and long chain carboxylic acids and ethyl esters (**3a**, **3c**, **3e**, **3l**, **3m**, and **3o**), respectively, gave generally better results than the derivatives with medium chain lengths (**3d** and **3n**). The tetrasulfonic acid **6a** and the carboxylic acid **6b** gave very good staining effects; the long chain carboxylic ester **6g** was acceptable, whereas the decomposition of the other derivatives of **6** is problematic. The results in Table 2 were compared with the staining effect of the biopolymers of Table 1 where an acceptable similarity was obtained with the staining of cotton exposing a surface of carbohydrates; obviously, such a surface seems to present the binding efficiencies of the dyes to the capsule better than the surface of peptides in wool and hair. This may be a consequence of either charges or carbohydrate-containing structures at the surface of the lens capsule.

A toxicity test was performed for the chromophore of the cyanine dyes **3**. The very good water-soluble dye **3t** was investigated as a model compound. Possible toxic effects were studied using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay where cells were incubated with dye concentrations higher than those being relevant for surgery to detect even minor toxic effects. The vitality of cells concerning proliferation was measured with the reduction of tetrazolium compounds (modified MTT assay); control experiments were performed without the addition of dyes and with the addition of hydrogen peroxide, respectively.

Table 1. Adsorption of the Cyanine Dyes 3 to the Natural Polymers Hair, Wool, and Cotton from Ethanol Solution Followed by Washing with Water[a]

	subjective staining effect			coloration of the BSS solution for surgery			
3	hair	wool	cotton	0.5%	0.25%	0.025%	0.0025%
a	−	+	++	++	++	++	+
b	−	+	++	[b]	[b]	[b]	[b]
c	−	+	++	++	++	++	+
d	+	+	++	++	++	+	−
e	+	+	+	++	++	++	−
f	+	+	++	[b]	[b]	[b]	[b]
g	+	+	++	++	+	−	−
h	+	++	++	++	++	++	+
i	−	−	+	++	++	++	+
j	−	−	+-	++	++	−	−
k	++	++	++	++	++	−	−
l	+	+	++	++	++	++	+
m	++	++	++	++	++	+	+
n	++	++	++	++	++	+	−
o	++	++	++	++	++	+	−
p	--	++	++				
q	--	++	++		+	−	−
r	−	−	−				
s	--	−	−				
t	-	+	+	++	++	++	+
u	--	+	+				
v	--	+	+				
w	--	+	+				
x	--	++	++				
6a	--	+	+				
6b	--	++	++				
6c	--	−	−				
6d	--	−	−				
6e	--	−	−				
6f	--	+	−				
6g	--	+	−				
6h	--	−	−				
6i	--	−	−				

[a] Staining of the BSS plus solution (BSS and content of dye in %). ++ stands for visually estimated efficient adsorption, + stands for medium adsorption, − stands for low adsorption, and -- stands for no visible adsorption. For BSS plus solution, see the Experimental Section. No staining effect was observed for ICG. [b] Solubility too small for measurements.

CONCLUSION

Cyanine dyes with the structures **3** and **6**, respectively, are useful as optical contrast media for the staining of tissues that are relevant for intraocular microsurgery. Compounds **3t** and **6a** proved intersting dyes for staining basement membranes, and **6b** gave surprising results because it decomposes comparably readily in solution; however, it is effective in staining and even induces a strong fluorescence. The UV/vis spectral characteristics of the dyes are suitable for the optical detection both in absorption and in fluorescence. Toxic effects of the dyes were not detected. The variable, structure-dependent coloration in the region of the basement membrane of the eye indicates a relation between molecular structure and binding to the target structure of the

Table 2. Staining of Porcine Lens Capsules (−, Absent; +, Fair; ++, Good; and +++, Excellent) with Various Dye Concentrations in BSS in %[a]

dye	1.0%	0.5%	0.25%	0.025%	0.0025%
3a		++	++	+	−
3c		+++	+++	−	−
3d		+++	+	−	−
3e		++	++	−	−
3g		++	++	−	−
3h		+++	++	+	−
3i		++	+	+	−
3j		++	+	−	−
3k		++	+	−	−
3l		+++	+++	+	−
3m		+++	++	−	−
3n		++	+	−	−
3o		++	++	−	−
3t		+++	++	+	−
3u	+	−			
3v	−	−			
6a	+++	+++			
6b	+++	+++			
6c	++	++			
6d	dec.	dec.			
6e	dec.	dec.			
6f	dec.	dec.			
6g	++	++			
6h	dec.	dec.			
6i	dec.	dec.			

[a] "dec." stands for the decomposition of the dyes during staining. The solubility of **3b** and **3f**, respectively, was not high enough, and **3q** and **3p**, respectively, were precipitated with BSS.

tissue. The wide variation of the properties of dyes by means of peripheral substituents makes these dyes attractive for the adaption to various requirements of the surgery of eyes.

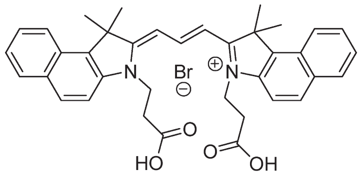
EXPERIMENTAL SECTION

General. IR spectra, Perkin-Elmer Spektrum BX II with ATR; UV/vis spectra, Varian Cary; fluorescence spectra, Varian Eclispe; NMR spectroscopy, Varian Vnmrs 600 (600 MHz), Vnmrs 400 (400 MHz), Mercury 200 (200 MHz); and mass spectroscopy, Thermo Finnigan LQT FT. The prepared dyes were estimated to be typically more than 95% pure; the purity was controlled by ^{1}H NMR spectroscopy and HPLC; see the Supporting Information. Dye **3b** was further characterized by an elemental analysis, and the molar absorptivity of this sample was determined; the latter can be applied for the determination of the dye content of solutions for the other derivatives.

BSS Plus. Abacterial solution for intraocular spilling was obtained by a 1:1 mixture of two liquid components. Component 1: 1 mL contained 7.44 mg of NaCl, 0.395 mg of KCl, and 0.433 mg of Na_2HPO_4, in water where HCl and NaOH, respectively, were added for the adjustment of a physiological pH value. Component 2: 1 mL contained 3.85 mg of $CaCl_2 \cdot 2H_2O$, 5 mg of $MgCl_2 \cdot 6H_2O$, 23 mg of glucose, and 4.6 mg of glutathiondisulfide in water.

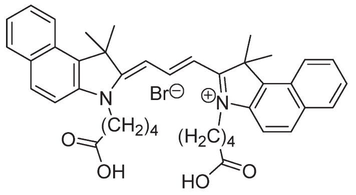
Five milligrams of the dye was dissolved in ethanol (500 μL) for the test staining and diluted to 2 mL by means of BSS to form the stock solution and then diluted according to the requirements for staining. Alternatively, stock solutions of dye **4** was prepared by dissolving dye 4 (for example, 5 mg) in distilled water (1 mL), adding it to BSS solution (7 mL), and treating it with a sodium chloride solution (1 mL) of an osmolarity of 620 (ca. 2%) to re-establish the genuine osmolarity of the BSS solution (308). This stock solution may be diluted according to the requirements.

Synthesis of Carbocyanine Dyes with Carboxylic Groups



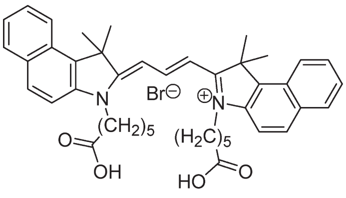
3a

*3,3′-Di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3a**).* 3-(2-Carboxyethyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2a**, 540 mg, 1.50 mmol) was dissolved in pyridine (2.00 mL) under argon atmosphere, heated to 116 °C, treated dropwise slowly with orthoformic triethylester (0.250 mL, 3.00 mmol, color change to bluish violet), heated to reflux for 2 h, allowed to cool, treated with diethyl ether (10.0 mL, precipitation of the golden shiny dye), decanted, dissolved repeatedly in a small amount of ethanol, precipitated with diethylether, collected by vacuum filtration, dried in vacuo, and purified by flash chromatography (RP 18, methanol/H_2O/acetic acid 1:1:0.4 for adsorption to the stationary phase, methanol/H_2O/acetic acid 2:1:0.4 for the elution of byproduct, methanol/H_2O/acetic acid 10:1:0.4 for the elution of the dye). Yield, 600 mg (70%) of a golden shiny solid forming violet, red fluorescent solutions; mp 199 °C. R_f (RP 18, methanol/H_2O/acetic acid 10:1:0.4) = 0.62. IR (ATR): ν = 3344 (w, br), 2921 (m, br), 1723 (s), 1633 (w), 1586 (w), 1552 (s), 1519 (m), 1471 (m), 1422 (s), 1350 (m), 1279 (w), 1226 (m), 1153 (m), 1127 (m), 1011 (m), 924 (s), 876 (w), 803 (w), 787 (w), 747 (w), 729 (w), 681 (w), 651 cm^{-1} (w). ^{1}H NMR (200 MHz, CD_3OD): δ = 8.27 (d, 2 H, H_{aromatic}, ^3J = 8.7 Hz), 8.01 (t, 4 H, H_{aromatic}, ^3J = 7.6 Hz), 7.67 (t, 5 H, H_{aromatic}, ^3J = 6.6 Hz), 7.50 (t, 2 H, H_{aromatic}, H_{allyl}, ^3J = 7.5 Hz), 6.57 (d, 2 H, H_{allyl}, ^3J_E = 12.9 Hz), 4.68−4.45 (m, 4 H, 2 × NCH_2), 2.95−2.75 (m, 4 H, 2 × CH_2), 2.06 ppm (s, 12 H, 4 × CH_3). ^{13}C NMR (100 MHz, CD_3OD): δ = 176.1, 149.4, 139.2, 133.5, 132.2, 130.4, 129.7, 127.9, 127.4, 124.9, 121.9, 110.9, 110.9, 110.8, 65.5, 51.0, 26.6, 14.0 ppm. UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 591 (1.0), 554 nm (0.68). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 599 (1.0), 555 nm (0.98). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 559 (1.0), 595 nm (0.98). UV/vis (solid state/hair): $\lambda_{\max}$ (E_{rel}) 595 (1.0), 555 nm (0.98). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 622 (1.0), 664 nm (0.70). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 667 (1.0), 643 nm (0.85). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 635 (1.0), 667 nm (0.95). Fluorescence (solid state/hair): $\lambda_{\max}$ (I_{rel}) 624 (1.0), 665 nm (0.69). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 562 nm, $E_{562/1\text{cm}}$ = 0.0146; reference: S-13 with Φ = 1.00): 0.35. High-resolution mass spectrum (HRMS) (ESI) ($C_{37}H_{37}N_2O_4^{+}$): calcd, 573.2748; found, 573.2747; Δ = −0.1 mmu.



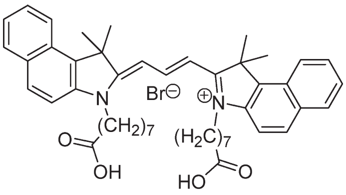
3b

*3,3′-Di-(4-carboxybutyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3b**).* 3-(4-Carboxybutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2b**, 140 mg, 0.36 mmol), 3-picoline (1.00 mL), and orthoformic triethylester (0.12 mL, 0.72 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 100 mg (39%) of golden shiny solid forming violet, red fluorescent solutions. R_f (RP 18, methanol/H_2O/acetic acid 10:1:0.4) = 0.43. IR (ATR): ν = 2922 (s), 2348 (m), 2213 (w), 1707 (m), 1555 (s), 1519 (s), 1479 (m), 1427 8s), 1360 (m), 1226 (m), 1154 (m), 1014 (m), 936 (m), 805 (8w), 746 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.28 (d, 2 H, H_{aromatic}, J = 8.5 Hz), 8.03 (dd, 5 H, H_{aromatic}, H_{allyl}, ^3J = 8.5 Hz, ^3J_E = 12.3 Hz), 7.70−7.64 (m, 4 H, H_{aromatic}), 7.55−7.48 (m, 2 H, H_{aromatic}), 6.55 (d, 2 H, H_{allyl}, ^3J_E = 13.0 Hz), 4.39−4.28 (m, 4 H, 2 × NCH_2), 2.49−2.35 (m, 4 H, 2 × CH_2), 2.09 (s, 12 H, 4 × CH_3), 2.00−1.91 (m, 4 H, 2 × CH_2) 1.90−1.80 ppm (m, 4 H, 2 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 149.3, 139.4, 133.5, 132.2, 130.5, 129.7, 127.9, 127.4, 124.8, 121.9, 110.8, 101.9, 101.9, 50.9, 43.8, 26.6 ppm. UV/vis ($CHCl_3$): $\lambda_{\max}$ (ε) 598.9 (100000), 559.0 nm (60830). UV/vis (ethanol): $\lambda_{\max}$ (ε) 591.4 (110800), 554.5 nm (76920). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 598 (1.0), 559 nm (0.98). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 558 (1.0), 591 nm (0.95). UV/vis (solid state/hair): $\lambda_{\max}$ (E_{rel}) 598 (1.0), 560 nm (0.81). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 608 (1.0), 652 nm (0.30). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 667 (1.0), 628 nm (0.66). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 635 (1.0), 668 nm (0.97). Fluorescence (solid state/hair): $\lambda_{\max}$ (I_{rel}) 624 (1.0), 665 nm (0.68). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{559/1\text{cm}}$ = 0.0120, reference: S-13 with Φ = 1.00): 0.49. HRMS (ESI) ($C_{41}H_{45}N_2O_4$): calcd, 629.3374; found, 629.3380; Δ = 0.6 mmu. $C_{41}H_{45}N_2O_4Br$ (709.7) calcd: C, 69.39; H, 6.39; N, 3.95. Found: C, 70.21; H, 6.79; N, 3.91.



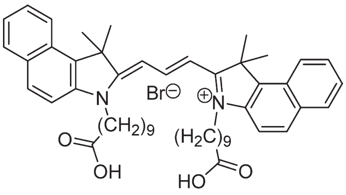
3c

*3,3′-Di-(5-carboxypentyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3c**).* 3-(5-Carboxypentyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2c**, 150 mg, 0.37 mmol), 3-picoline (2.00 mL), and orthoformic triethylester (0.10 mL, 0.74 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 150 mg (55%) of golden shiny solid forming violet, red fluorescent solutions. R_f (RP 18, methanol/H_2O/acetic acid 10:1:0.4) = 0.66. IR (ATR): ν = 3416 (w, br), 3054 (w), 2978 (w), 2935 (w), 2859 (w), 1727 (s), 1626 (w), 1588 (w), 1547 (s), 1519 (m), 1487 (m), 1469 (w), 1424 (s), 1370 (w), 1348 (w), 1275 (w), 1227 (s), 1170 (m), 1140 (m), 1125 (m), 1031 (w), 1011 (m), 977 (m), 926 (s), 891 (w), 878 (w), 865 (w), 829 (w), 805 (m), 787 (w), 769 (w), 748 (w), 725 (w), 684 (w), 652 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.78 (t, 1 H, H_{allyl}, ^3J = 13.5 Hz), 8.30 (d, 2 H, H_{aromatic}, ^3J = 8.5 Hz), 8.06 (d, 2 H, H_{aromatic}, ^3J = 8.8 Hz), 8.02 (d, 2 H, H_{aromatic}, ^3J = 8.2 Hz), 7.68 (ddd, 2 H, H_{aromatic}, ^4J = 1.3 Hz, ^3J = 6.9 Hz, ^3J = 8.4 Hz), 7.64 (d, 2 H, H_{aromatic}, ^3J = 8.9 Hz), 7.52 (ddd, 2 H, H_{aromatic}, ^4J = 1.0 Hz, ^3J = 6.9 Hz, ^3J = 8.1 Hz), 6.53 (d, 2 H, H_{allyl}, ^3J_E = 13.5 Hz), 4.30 (t, 4 H, 2 × NCH_2, ^3J = 7.5 Hz), 2.35 (t, 4 H, 2 × CH_2CO_2H, ^3J = 7.2 Hz), 2.11 (s, 12H, 4 × CH_3), 2.04−1.86 (m, 4H, 2 × CH_2), 1.79−1.70 (m, 4H, 2 × CH_2), 1.63−1.55 ppm (m, 4 H, 2 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 149.3, 139.4, 133.5, 132.2, 130.5, 129.7, 127.9, 127.4, 124.9, 121.9, 110.8, 101.7, 51.0, 43.9, 27.1, 26.6, 26.1, 22.8, 16.9 ppm. UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 591 (1.0), 554 nm (0.68). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 598 (1.0), 554 nm (0.99). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 558 (1.0), 594 nm (0.97). UV/vis (solid state/hair): $\lambda_{\max}$ (E_{rel}) 598 (1.0), 556 nm (0.90). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 611 (1.0), 655 nm (0.50). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 661 (1.0), 644 nm (0.93). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 632 (1.0), 667 nm (0.88). Fluorescence (solid state/hair): $\lambda_{\max}$ (I_{rel}) 623 (1.0), 660 nm (0.71). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{562/1\text{cm}}$ = 0.0126; reference: S-13 with Φ = 1.00): 0.50. HRMS (ESI) ($C_{43}H_{49}N_2O_4^+$): calcd, 657.3687; found, 657.3691; Δ = 0.4 mmu.



3d

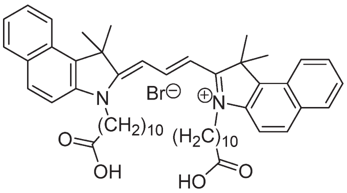
*3,3′-Di-(7-carboxyheptyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3d**).* 3-(7-Carboxyheptyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2d**, 150 mg, 0.35 mmol), 3-picoline (1.00 mL), and orthoformic triethylester (0.12 mL, 0.70 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 80.0 mg (54%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 2927 (s), 2348 (w), 2233 (w), 1720 (s, br), 1552 (s), 1519 (m), 1479 (w), 1422 (s), 1351 (m), 1225 (m), 1141 (m), 1011 (m), 931 (m), 806 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.78 (t, 1 H, H_{allyl}, ^3J_E = 13.5 Hz), 8.30 (d, 2 H, H_{aromatic}, ^3J = 8.3 Hz), 8.05 (t, 4 H, H_{aromatic}, ^3J = 7.8 Hz), 7.73−7.61 (m, 4 H, H_{aromatic}), 7.57−7.49 (m, 2 H, H_{aromatic}), 6.53 (d, 2 H, H_{allyl}, ^3J_E = 13.3 Hz), 4.29 (t, 4 H, 2 × NCH_2, ^3J = 7.7 Hz), 2.29 (t, 4 H, 2 × CH_2CO_2H, ^3J = 7.3 Hz) 2.11 (s, 12 H, 4 × CH_3), 1.99−1.84 (m, 4 H, 2 × CH_2), 1.63−1.40 ppm (m, 16 H, 8 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 133.5, 132.2, 130.5, 129.7, 127.9, 127.4, 125.2, 124.9, 121.9, 112.4, 110.7, 101.7, 57.0, 51.0, 26.6, 16.9 ppm. UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 591 (1.0), 554 nm (0.70). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 599 (1.0), 554 nm (0.99). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 558 (1.0), 595 nm (0.97). UV/vis (solid state/hair): $\lambda_{\max}$ (E_{rel}) 599 (1.0), 555 nm (0.92). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 602 (1.0), 661 nm (0.25). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 669 (1.0), 646 nm (0.94). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 632 (1.0), 668 nm (0.89). Fluorescence (solid state/hair): $\lambda_{\max}$ (I_{rel}) 635 (1.0), 666 nm (0.86). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 558 nm, $E_{562/1\text{cm}}$ = 0.0161, reference: S-13 with Φ = 1.00): 0.43. HRMS (ESI) ($C_{47}H_{57}N_2O_4^+$): calcd, 713.4313; found, 713.4324; Δ = 1.1 mmu.



3e

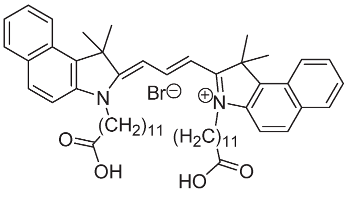
*3,3′-Di-(9-carboxynonyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3e**).* 3-(9-Carboxynonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2e**, 100 mg, 0.21 mmol), 3-picoline (1.00 mL), and orthoformic triethylester (0.07 mL, 0.43 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 41.0 mg (23%) of golden shiny solid forming violet, red fluorescent solutions. R_f (RP 18, methanol/H_2O/acetic acid 10:1:0.4) = 0.4. IR (ATR): ν = 3381 (w), 3056 (w), 2923 (s), 2852 (s), 2350 (w), 2287 (w), 1711 (m), 1626 (w), 1588 (w), 1554 (s), 1520 (m), 1479 (m), 1423 (s), 1357 (m), 1277 (w), 1224 (m), 1168 (m), 1142 (m), 1127 (m), 1012 (m), 971 (w), 930 (s), 898 (w), 867 (w), 806 (m), 786 (w), 746 (w), 726 (w), 685 (w), 676 (w), 652 (m) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.78 (t, 1 H, H_{allyl}, ^3J_E = 13.2 Hz), 8.29 (d, 2 H, H_{aromatic}, ^3J = 8.6 Hz), 8.06 (d, 2 H, H_{aromatic}, ^3J = 8.8 Hz), 8.03 (d, 2 H, H_{aromatic}, ^3J = 8.1 Hz), 7.72−7.62 (m, 4 H, H_{aromatic}), 7.55−7.50 (m, 2 H,

$H_{aromatic}$), 6.51 (d, 2 H, H_{allyl}, ^3J_E = 13.5 Hz), 4.29 (t, 4 H, 2 × NCH_2, ^3J = 7.5 Hz), 2.20 (t, 4 H, 2 × CH_2CO_2H, ^3J = 7.2 Hz), 2.11 (s, 12 H, 4 × CH_3), 1.96−1.88 (m, 8 H, 4 × CH_2), 1.60−1.50 (m, 8 H, 4 × CH_2), 1.49−1.40 (m, 4 H, 2 × CH_2), 1.33−1.30 ppm (m, 8 H, 4 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 149.3, 139.4, 133.5, 132.2, 130.5, 129.8, 127.9, 127.5, 124.9, 121.9, 110.8, 101.6, 51.0, 44.0, 28.9, 28.9, 28.8, 27.4, 26.6, 26.3, 25.2, 16.9 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 594 (1.0), 555 nm (0.65). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 569 (1.0), 557 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 565 (1.0), 597 nm (0.90). UV/vis (solid state/hair): λ_{max} (E_{rel}) 603 (1.0), 557 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 604 (1.0), 651 nm (0.25). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 669 (1.0), 645 nm (0.94). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 632 (1.0), 668 nm (0.89). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 635 (1.0), 666 nm (0.87). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 557 nm, $E_{562/1cm}$ = 0.0180; reference: S-13 with Φ = 1.00): 0.59. HRMS (ESI) ($C_{51}H_{65}N_2O_4^+$): calcd, 769.4939; found, 769.4941; Δ = 0.2 mmu.



3f

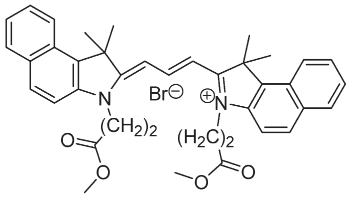
*3,3′-Di-(10-carboxydecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3f**).* 3-(10-Carboxy-decyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2f**, 117 mg, 0.25 mmol), pyridine (2.5 mL), and orthoformic triethylester (0.08 mL, 0.5 mmol) were allowed to react (120 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 118 mg (54%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3381 (w), 3056 (w), 2923 (s), 2852 (s), 2350 (w), 2287 (w), 1711 (m), 1626 (w), 1588 (w), 1554 (s), 1520 (m), 1479 (m), 1423 (s), 1357 (m), 1277 (w), 1224 (m), 1012 (m), 971 (w), 930 (s), 898 (w), 867 (w), 806 (m), 786 (w), 746 (w), 726 (w), 685 (w), 676 (w), 652 (m) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.77 (t, 1 H, CH_{allyl}, ^3J_E = 13.4 Hz), 8.29 (d, 2 H, $CH_{aromatic}$, ^3J = 8.6 Hz), 8.05 (d, 2 H, $CH_{aromatic}$, ^3J = 8.7 Hz), 8.02 (d, 2 H, $CH_{aromatic}$, ^3J = 8.4 Hz), 7.70−7.62 (m, 4 H, $CH_{aromatic}$), 7.52 (t, 2 H, $CH_{aromatic}$, ^3J = 7.5 Hz), 6.50 (d, 2 H, CH_{allyl}, ^3J_E = 13.6 Hz), 4.28 (t, 4 H, 2 × NCH_2, ^3J = 7.1 Hz), 2.30−2.13 (m, 4 H, 2 × CH_2CO_2H), 2.10 (s, 12 H, 4 × CH_3), 1.98−1.88 (m, 4 H, 2 × CH_2), 1.58−1.50 (m, 8 H, 4 × CH_2), 1.35−1.22 ppm (m, 20 H, 10 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 149.2, 139.4, 133.5, 132.2, 131.3, 130.5, 129.7, 127.9, 127.5, 124.9, 121.9, 114.7, 110.8, 101.6, 51.0, 44.0, 29.0, 29.0, 28.9, 27.4 26.6, 26.3, 22.8 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 590 (1.0), 553 nm (0.70). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 597 (1.0), 555 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 557 (1.0), 596 nm (0.96). UV/vis (solid state/hair): λ_{max} (E_{rel}) 601 (1.0), 556 nm (0.97). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 656 nm (0.54). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 670 (1.0), 641 nm (0.83). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 667 (1.0), 641 nm (0.98). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 640 (1.0), 667 nm (0.93). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 557 nm, $E_{562/1cm}$ = 0.0131; reference: S-13 with Φ = 1.00): 0.33. HRMS (ESI) ($C_{53}H_{69}N_2O_4^+$): calcd, 797.5252; found, 797.5267; Δ = 1.5 mmu.



3g

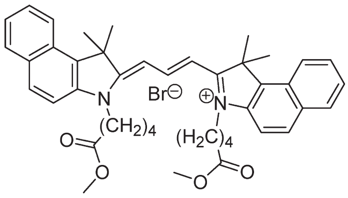
*3,3′-Di-(11-carboxyundecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3g**).* 3-(11-Carboxyundecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2g**, 340 mg, 7.00 μmol), 3-picoline (1.00 mL), and orthoformic triethylester (0.020 mg, 0.020 mL, 0.014 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) (chromatography with aqueous 2 N HCl instead of acetic acid). Yield, 12.0 mg (19%) of golden shiny solid forming violet, red fluorescent solutions. R_f (RP 18, methanol/H_2O/HCl 10:1:0.4) = 0.8. IR (ATR): ν = 3350 (w), 2922 (s), 2851 (m), 1710 (m), 1625 (w), 1587 (w), 1553 (s), 1519 (m), 1479 (m), 1422 (s), 1356 (m), 1278 (w), 1259 (w), 1224 (m), 1169 (m), 1141 (w), 1127 (m), 1012 (m), 973 (w), 931 (s), 896 (w), 806 (m), 786 (w), 746 (w), 726 (w), 685 (w), 675 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.78 (t, 2 H, H_{allyl}, ^3J_E = 13.5 Hz), 8.29 (d, 2 H, $H_{aromatic}$, ^3J = 8.5 Hz), 8.06 (d, 2 H, $H_{aromatic}$, ^3J = 8.8 Hz), 8.03 (d, 2 H, $H_{aromatic}$, ^3J = 8.2 Hz), 7.68 (ddd, 3 H, $H_{aromatic}$, ^4J = 1.2 Hz, ^3J = 6.9 Hz, ^3J = 8.4 Hz), 7.64 (d, 2 H, $H_{aromatic}$, ^3J = 8.9 Hz), 7.53 (ddd, 2 H, $H_{aromatic}$, ^4J = 0.9 Hz, ^3J = 6.9 Hz, ^3J = 8.0 Hz), 6.50 (d, 2 H, H_{allyl}, ^3J_E = 13.5 Hz), 4.29 (t, 4 H, 2 × NCH_2, ^3J = 7.4 Hz), 2.18 (t, 4 H, 2 × CH_2CO_2H, ^3J = 7.4 Hz), 2.11 (s, 12 H, 4 × CH_3), 1.96−1.88 (m, 4 H, 2 × CH_2), 1.57−1.49 (m, 8 H, 4 × CH_2), 1.47−1.40 (m, 4 H, 2 × CH_2), 1.36−1.28 ppm (m, 20 H, 10 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 178.6, 175.9, 149.2, 139.4, 133.5, 132.2, 130.5, 129.7, 127.9, 127.5, 124.9, 121.9, 110.8, 101.7, 56.9, 51.0, 44.0, 29.1, 29.0, 29.0, 29.0, 28.9, 27.3, 26.6, 26.3, 25.4, 16.9 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 590 (1.0), 553 nm (0.70). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 555 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 603 (1.0), 556 nm (0.95). UV/vis (solid state/hair): λ_{max} (E_{rel}) 607 (1.0), 556 nm (0.93). Fluorescence (ethanol): λ_{max} (I_{rel}) 604 (1.0), 656 nm (0.20). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 667 (1.0), 643 nm (0.94). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 638 (1.0), 667 nm (0.93). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 634 (1.0), 668 nm (0.88). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 560 nm, $E_{562/1cm}$ = 0.0127; reference: S-13 with Φ = 1.00): 0.35. HRMS (ESI) ($C_{55}H_{73}N_2O_4^+$): calcd, 825.5565; found, 825.5567; Δ = 0.2 mmu.

Synthesis of Carbocyanine Dyes with Methylester Groups



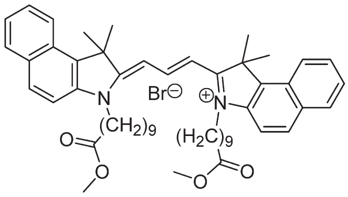
3h

*3,3′-Di-(2-methoxycarbonylethyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3h**).* 3-(2-Methoxycarbonylethyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2h**, 300 mg, 0.797 mmol), 3-picoline (2.0 mL), and orthoformic triethylester (0.26 mL, 1.60 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) and isolated wihout chromatography. Yield, 290 mg (53%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 2925 (s), 2856 (w), 2541 (w), 1960 (w), 1722 (s), 1625 (m), 1567 (m), 1555 (s), 1519 (m), 1476 (m), 1422 (s), 1352 (m), 1278 (m), 1232 (w), 1155 (m), 1126 (w), 1011 (m), 924 (m, br), 875 (w), 804 (m), 786 (w), 804 (m), 786 (w), 744 (m) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.42 (t, 2 H, H_{allyl}, ^3J_E = 13.4 Hz), 8.11 (d, 4 H, $H_{aromatic}$, H_{allyl}, ^3J = 8.0 Hz), 7.96 (d, 2 H, $H_{aromatic}$, ^3J = 8.5 Hz), 7.40−7.30 (m, 4 H, $H_{aromatic}$), 7.16 (t, 2 H, $H_{aromatic}$, ^3J = 7.5 Hz), 6.38 (d, 2 H, H_{allyl}, ^3J_E = 13.4 Hz), 4.35−4.30 (m, 4 H, 2 × NCH_2), 3.31 (s, 6 H, 2 × OCH_3), 2.68 (t, 4 H, 2 × $CH_2CO_2CH_3$, ^3J = 6.6 Hz), 1.71 ppm (s, 12 H, 4 × CH_3). ^{13}C NMR (100 MHz, CD_3OD): δ = 177.7, 172.5, 151.1, 140.5, 134.9, 133.7, 131.9, 131.3, 131.2, 129.3, 129.0, 126.5, 123.5, 112.3, 52.5, 41.5, 33.0, 28.2, 24.2 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 592 (1.0), 553 nm (0.67). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 554 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 597 (1.0), 560 nm (0.97). UV/vis (solid state/hair): λ_{max} (E_{rel}) 597 (1.0), 558 nm (0.98). Fluorescence (ethanol): λ_{max} (I_{rel}) 609 (1.0), 656 nm (0.53). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 562 nm, $E_{562/1cm}$ = 0.0178; reference: S-13 with Φ = 1.00): 0.24. HRMS (ESI) ($C_{39}H_{41}N_2O_4^+$): calcd, 601.3061; found, 601.3044; $\Delta = -1.7$ mmu.



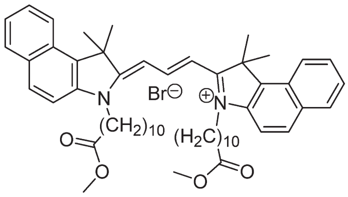
3i

*3,3′-Di-(4-methoxycarbonylbutyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3i**).* 3-(4-Methoxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2i**, 253 mg, 0.626 mmol), 3-picoline (2.2 mL), and orthoformic triethylester (0.2 mL, 1.3 mmol) were allowed to react (120 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) (chromatography with aqueous 2 N HCl instead of acetic acid). Yield, 50 mg (11%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3354 (w, br), 3140 (w), 3030 (w), 2960 (w), 2924 (s), 2855 (w), 2167 (w), 1705 (m, br), 1623 (w), 1587 (w), 1554 (s), 1520 (m), 1479 (m), 1425 (s), 1353 (m), 1278 (w), 1260 (w), 1226 (m), 1153 (s), 1128 (m), 1066 (w), 1013 (m), 982 (w), 937 (m), 917 (w), 895 (w), 865 (w), 807 (m), 786 (w), 746 (w), 727 (w) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 8.79−8.76 (m, 1 H, $H_{aromatic}$), 8.30 (d, 2 H, $H_{aromatic}$, ^3J = 8.4 Hz), 8.04 (dd, 4 H, $H_{aromatic}$, H_{allyl}, ^3J = 8.5 Hz, ^3J_E = 14.9 Hz), 7.71−7.64 (m, 4 H, $H_{aromatic}$), 7.55−7.51 (m, 2 H, $H_{aromatic}$), 6.54 (d, 2 H, H_{allyl}, ^3J_E = 13.5 Hz), 4.31 (t, 4 H, 2 × NCH_2 ^3J = 7.3 Hz), 2.48 (t, 4 H, 2 × $CH_2CO_2CH_3$, ^3J = 7.0 Hz), 2.10 (s, 12 H, 4 × CH_3), 1.99−1.92 (m, 4 H, 2 × CH_2), 1.87−1.80 ppm (m, 4 H, 2 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 174.0, 149.3, 149.2, 139.4, 133.5, 132.2, 130.5, 129.7, 127.5, 125.0, 121.9, 110.8, 101.8, 51.0, 43.6, 32.7, 26.6, 21.7 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 592 (1.0), 555 nm (0.72). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 602(1.0), 555 nm (0.98). UV/vis (solid state/wool): λ_{max} (E_{rel}) 557 (1.0), 556 nm (0.98). UV/vis (solid state/hair): λ_{max} (E_{rel}) 602 (1.0), 558 (0.92), 631 nm (0.89). Fluorescence (ethanol): λ_{max} (I_{rel}) 608 (1.0), 658 nm (0.49). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 668 (1.0), 630 nm (0.55). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 667 (1.0), 635 nm (0.98). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 667 (1.0), 623 nm (0.66). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 558 nm, $E_{558/1cm}$ = 0.0114; reference: S-13 with Φ = 1.00): 0.40. HRMS (ESI) ($C_{43}H_{49}N_2O_4^+$): calcd, 657.3687; found, 657.3675; $\Delta = -1.2$ mmu.



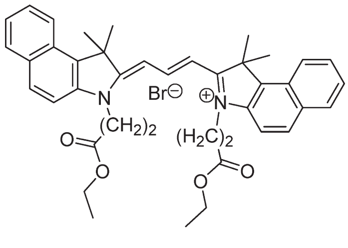
3j

*3,3′-Di-(9-methoxycarbonylnonyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3j**).* 3-(9-Methoxycarbonylnonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2j**, 300 mg, 0.633 mmol), 3-picoline (2.0 mL), and orthoformic triethylester (0.20 mL, 1.26 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) and isolated without chromatography. Yield, 113 mg (20%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3413 (s, br), 3032 (m), 2971 (w), 2932 (m), 2855 (w), 2361 (s), 2339 (m), 2066 (w), 1729 (m), 1634 (s), 1591 (w), 1555 (m), 1505 (s), 1483 (w), 1429 (s), 1385 (w), 1357 (w), 1324 (w), 1246 (w), 1230 (w), 1204 (w), 1160 (s), 1096 (w), 1051 (w), 1014 (w), 981 (w), 934 (m), 893 (w), 810 (s), 751 (w), 728 (w), 685 (s) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 551 nm (0.73). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 559 nm (0.94). UV/vis (solid state/wool): λ_{max} (E_{rel}) 599 (1.0), 559 nm (0.92). UV/vis (solid state/hair): λ_{max} (E_{rel}) 699 (1.0), 558 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 658 nm (0.51). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{559/1cm}$ = 0.0145; reference: S-13 with Φ = 1.00): 0.47. HRMS (ESI) ($C_{53}H_{69}N_2O_4^+$): calcd, 797.5252; found, 797.5252; Δ = 0.03 mmu.



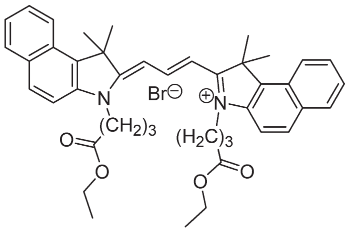
3k

*3,3′-Di-(10-methoxycarbonyldecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3k**).* 3-(10-Methoxycarbonyldecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2k**, 300 mg, 0.633 mmol), pyridine (1.0 mL), and orthoformic triethylester (0.16 mL, 0.94 mmol) were allowed to react (115 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) and isolated without chromatography. Yield, 149 mg (35%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3403 (s, br), 3131 (w), 3055 (w), 2972 (w), 2927 (s), 2853 (m), 2361 (w), 2337 (w), 2170 (w), 1731 (s), 1633 (m), 1586 (w), 1553 (s), 1519 (m), 1484 (m), 1425 (s), 1392 (w), 1356 (w), 1277 (w), 1227 (m), 1171 (s), 1143 (w), 1128 (w), 1050 (w), 1012 (m), 975 (w), 930 (m), 897 (w), 808 (w), 780 (w), 748 (w), 726 (w), 682 (w) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 550 nm (0.69). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 603(1.0), 559 nm (0.95). UV/vis (solid state/wool): λ_{max} (E_{rel}) 596 (1.0), 557 nm (0.97). UV/vis (solid state/hair): λ_{max} (E_{rel}) 600 (1.0), 557 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 657 nm (0.53). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 560 nm, $E_{562/1cm}$ = 0.0174; reference: S-13 with Φ = 1.00): 0.36. HRMS (ESI) ($C_{55}H_{73}N_2O_4^+$): calcd, 825.5565; found, 8525.5569; Δ = 0.4 mmu.



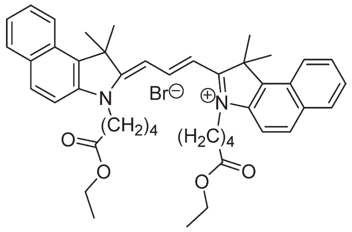
3l

*3,3′-Di-(2-ethoxycarbonylethyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3l**).* 3-(2-Ethoxycarbonylethyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2l**, 200 mg, 0.51 mmol), 3-picoline (1.1 mL), and orthoformic triethylester (0.17 mL, 1.02 mmol) were allowed to react (120 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) (chromatography with aqueous 2 N HCl instead of acetic acid). Yield, 121 mg (33%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3054 (w), 2973 (w), 2927 (w), 2574 (w), 2366 (w), 1723 (s), 1626 (w), 1587 (w), 1554 (s), 1520 (m), 1477 (m), 1425 (s), 1393 (w), 1353 (m), 1279 (w), 1227 (m), 1154 (m), 1128 (w), 1047 (w), 1012 (m), 987 (w), 925 (s), 877 (w), 806 (m), 786 (w), 746 (w), 728 (w), 684 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.80−8.75 (m, 1 H, H_{aromatic}), 8.28 (d, 2 H, H_{aromatic}, ^{3}J = 8.6 Hz), 8.03 (dd, 4 H, H_{aromatic}, H_{allyl}, ^{3}J = 8.6 Hz, $^{3}J_{\mathrm{E}}$ = 13.5 Hz), 7.70−7.65 (m, 4 H, H_{aromatic}), 7.54−7.49 (m, 2 H, H_{aromatic}), 6.54 (d, 2 H, H_{allyl}, $^{3}J_{\mathrm{E}}$ = 13.4 Hz), 4.13(t, 4 H, 2 × NCH_2, ^{3}J = 6.8 Hz), 3.60 (q, 4 H, 2 × CH_2CH_3, ^{3}J = 7.0 Hz), 2.73 (t, 4 H, 2 × $CH_2CO_2CH_2$, ^{3}J = 6.9 Hz), 1.58 (s, 12 H, 4 × CH_3), 1.17 ppm (t, 6 H, 2 × CH_2CH_3, ^{3}J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 178.1, 172.9, 151.4, 140.8, 135.2, 134.0, 132.2, 131.5, 129.6, 129.3, 126.8, 123.1, 112.6, 111.6, 52.8, 41.7, 37.6, 33.2, 28.4, 24.5 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 598 (1.0), 561 nm (0.69). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 560 (1.0), 555 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 597 (1.0), 555 nm (0.98). UV/vis (solid state/hair): λ_{max} (E_{rel}) 560 (1.0), 554 nm (0.94). Fluorescence (ethanol): λ_{max} (I_{rel}) 608 (1.0), 659 nm (0.54). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 666 (1.0), 642 nm (0.93). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 664 (1.0), 639 nm (0.98). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 636 (1.0), 664 nm (0.92). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 561 nm, $E_{561/1\mathrm{cm}}$ = 0.0135; reference: S-13 with Φ = 1.00): 0.33. HRMS (ESI): ($C_{41}H_{45}N_2O_4^{+}$): calcd, 629.3374; found, 629.3385; Δ = 1.1 mmu.



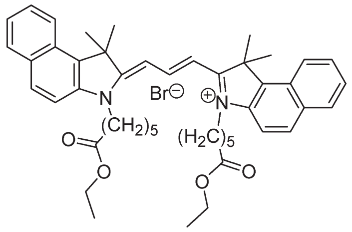
3m

*3,3′-Di-(3-ethoxycarbonylpropyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3m**).* 3-(3-Ethoxycarbonylpropyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2m**, 250 mg, 0.620 mmol), 3-picoline (1.0 mL), and orthoformic triethylester (0.200 mL, 1.24 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) (chromatography with aqueous 2 N HCl instead of acetic acid). Yield, 215 mg (47%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3391 (w), 2969 (w), 2921 (m), 1726 (s), 1622 (m), 1589 (w), 1557 (s), 1520 (m), 1477 (m), 1427 (s), 1352 (m), 1227 (m), 1154 (s), 1123 (w), 1067 (w), 1014 (m), 941 (s), 899 (w), 805 (m), 791 (w), 757 (m), 728 (w), 675 (w), 652 (m), 638 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.81−8.73 (m, 1 H, H_{aromatic}), 8.28 (d, 2 H, H_{aromatic}, ^{3}J = 8.4 Hz), 8.01 (dd, 4 H, H_{aromatic}, H_{allyl}, ^{3}J = 8.3 Hz, $^{3}J_{\mathrm{E}}$ = 14.5 Hz), 7.71−7.62 (m, 4 H, H_{aromatic}), 7.52−7.47 (m, 2 H, H_{aromatic}), 6.54 (d, 2 H, H_{allyl}, $^{3}J_{\mathrm{E}}$ = 13.8 Hz), 4.34−4.28 (m, 4 H, 2 × NCH_2), 4.11 (q, 4 H, 2 × CH_2CH_3, ^{3}J = 7.1 Hz), 2.62−2.57 (m, 4 H, 2 × $CH_2CO_2CH_2$), 2.20−2.13 (m, 4 H, 2 × CH_2), 2.07 (s, 12 H, 4 × CH_3), 1.20 ppm (t, 6 H, 2 × CH_2CH_3, ^{3}J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 176.1, 173.0, 149.5, 139.3, 133.5, 132.2, 130.6, 129.8, 127.9, 125.0, 121.9, 110.7, 101.8, 60.4, 51.0, 46.9, 43.2, 30.2, 26.6, 22.8, 13.1 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 598 (1.0), 559 nm (0.63). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 555 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 559 (1.0), 594 nm (0.98). UV/vis (solid state/hair): λ_{max} (E_{rel}) 597 (1.0), 554 nm (0.96). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 657 nm (0.56). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 667 (1.0), 642 nm (0.88). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 635 (1.0), 665 nm (0.97). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 665 (1.0), 639 nm (0.97). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 560 nm, $E_{562/1\mathrm{cm}}$ = 0.0132; reference: S-13 with Φ = 1.00): 0.61. HRMS (ESI) ($C_{43}H_{49}N_2O_4^{+}$): calcd, 657.3687; found, 657.3695; Δ = 0.8 mmu.



3n

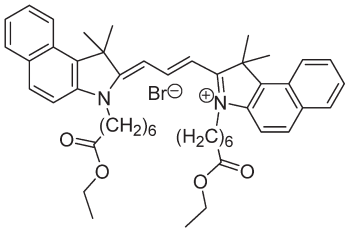
*3,3′-Di-(4-Ethoxycarbonylbutyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3n**).* 3-(4-Ethoxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2n**, 250 mg, 0.6 mmol), 3-picoline (1.1 mL), and orthoformic triethylester (0.2 mL, 1.2 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**) (chromatography with aqueous 2 N HCl instead of acetic acid). Yield, 105 mg (23%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3420 (w), 2921 (s), 2851 (m), 1726 (s), 1622 (m), 1589 (w), 1555 (s), 1520 (s), 1477 (m), 1428 (s), 1352 (m), 1227 (m), 1154 (s), 1123 (w), 1067 (w), 1014 (m), 941 (m), 899 (w), 805 (m), 785 (w), 744 (m), 728 (w), 685 (w), 652 (m) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.76 (t, 1 H, H_{aromatic}, ^{3}J = 13.1 Hz), 8.28 (d, 2 H, H_{aromatic}, ^{3}J = 8.3 Hz), 8.03 (dd, 4 H, H_{aromatic}, H_{allyl}, ^{3}J = 8.6 Hz, $^{3}J_{\mathrm{E}}$ = 12.3 Hz), 7.75−7.60 (m, 4 H, H_{aromatic}), 7.55−7.49 (m, 2 H, H_{aromatic}), 6.51 (d, 2 H, H_{allyl}, $^{3}J_{\mathrm{E}}$ = 13.0 Hz), 4.35−4.28 (m, 4 H, 2 × NCH_2), 4.10 (q, 4 H, 2 × CH_2CH_3, ^{3}J = 7.1 Hz), 2.45 (t, 4 H, 2 × $CH_2CO_2CH_2$, ^{3}J = 6.5 Hz), 2.09 (s, 12 H, 4 × CH_3), 2.00−1.92 (m, 4 H, 2 × CH_2), 1.20 ppm (t, 6 H, 2 × CH_2CH_3, ^{3}J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 177.5, 174.9, 169.4, 150.8, 140.8, 133.7, 132.0, 131.2, 129.3, 129.0, 126.4, 123.4, 112.2, 103.2, 79.5, 69.2, 61.6, 52.5, 34.5, 28.1, 23.2, 14.5 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 598 (1.0), 558 nm (0.64). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 560 (1.0), 556 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 598 (1.0), 557 nm (0.98). UV/vis (solid state/hair): λ_{max} (E_{rel}) 598 (1.0), 555 nm (0.94). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 660 nm (0.52). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 670 (1.0), 643 nm (0.95). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 631 (1.0), 664 nm (0.95). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 625 (1.0), 664 nm (0.96). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{562/1\mathrm{cm}}$ = 0.0128; reference: S-13 with Φ = 1.00): 0.43. HRMS (ESI) ($C_{45}H_{53}N_2O_4^{+}$): calcd, 685.4000; found, 685.4010; Δ = 1.0 mmu.



3o

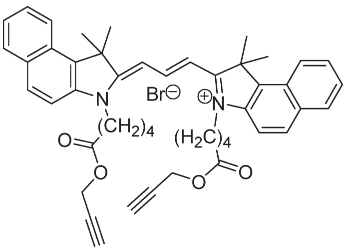
*3,3′-Di-(5-ethoxycarbonylpentyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3o**).* 3-(5-Ethoxycarbonylpentyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2o**, 400 mg, 0.93 mmol), pyridine (1.5 mL), and orthoformic triethylester (0.30 mL, 1.85 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**); a chromatographic purification was left out because the material decomposes with the contact of the stationary phase to form the carboxylic acid. Yield, 363 mg

(50%) of golden shiny solid forming violet, red fluorescent solutions. IR (ATR): ν = 3312 (w), 2930 (m), 2859 (m), 2361 (w), 2338 (w), 1724 (s), 1626 (w), 1587 (w), 1553 (s), 1520 (m), 1480 (m), 1423 (s), 1356 (m), 1278 (w), 1225 (m), 1169 (w), 1143 (w), 1126 (w), 1071 (w), 1012 (m), 972 (w), 927 (m), 898 (w), 877 (w), 806 (m), 747 (w), 726 (w), 685 (w) cm^{-1}. ^1H NMR (200 MHz, CD_3OD): δ = 8.78 (t, 1 H, $H_{aromatic}$, ^3J = 13.6 Hz), 8.31 (d, 2 H, $H_{aromatic}$, ^3J = 7.8 Hz), 8.10−8.00 (m, 4 H, $H_{aromatic}$, H_{allyl}), 7.75−7.63 (m, 4 H, $H_{aromatic}$), 7.57−7.49 (m, 2 H, $H_{aromatic}$), 6.55 (d, 2 H, H_{allyl}, ^3J_E = 13.4 Hz), 4.30 (t, 4 H, 2 × NCH_2, ^3J = 7.5 Hz), 4.07 (q, 4 H, 2 × CH_2CH_3, ^3J = 7.1 Hz), 2.37 (t, 4 H, 2 × $CH_2CO_2CH_2$, ^3J = 7.0 Hz), 2.11 (s, 12 H, 4 × CH_3), 2.00−1.81 (m, 4 H, 2 × CH_2), 1.79−1.55 (m, 8 H, 4 × CH_2), 1.18 ppm (t, 6 H, 2 × CH_2CH_3, ^3J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 177.4, 175.3, 150.8, 145.7, 140.9, 135.0, 133.7, 132.0, 131.2, 129.6, 126.4, 123.4, 112.3, 103.3, 61.5, 52.5, 45.9, 34.9, 28.6, 28.1, 27.3, 25.8, 16.8, 14.8 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 554 nm (0.73). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 598 (1.0), 554 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 599 (1.0), 554 nm (0.99). UV/vis (solid state/hair): λ_{max} (E_{rel}) 600 (1.0), 554 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 615 (1.0), 655 nm (0.57). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 666 (1.0), 642 nm (0.93). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 664 (1.0), 638 nm (0.98). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 636 (1.0), 665 nm (0.92). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 558 nm, $E_{558/1cm}$ = 0.0138; reference: S-13 with Φ = 1.00): 0.36. HRMS (ESI) ($C_{47}H_{57}N_2O_4^+$): calcd, 713.4313; found, 713.4331; Δ = 1.8 mmu.



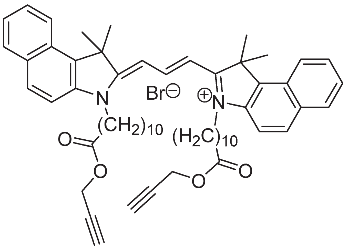
3p

*3,3′-Di-(6-ethoxycarbonylhexyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3p**).* 3-(6-Ethoxycarbonylhexyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2p**, 95.0 mg, 0.213 mmol), 3-picoline (1.00 mL), and orthoformic triethylester (0.070 mL, 0.426 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**); a chromatographic purification was left out because the material decomposes with the contact of the stationary phase to form the carboxylic acid. Yield, 49 mg (28%). IR (ATR): ν = 3064 (w), 2936 (s), 2864 (w), 2540 (w), 2361 (s), 2338 (s), 2162 (w), 1718 (s, br), 1654 (w), 1636 (w), 1558 (m), 1522 (m), 1507 (w), 1431 (s), 1362 (w), 1226 (w), 1174 (m), 1155 (w), 1017 (w), 938 (m), 814 (w), 750 (w), 668 (m) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 588 (1.0), 553 nm (0.76). Fluorescence (ethanol): λ_{max} (I_{rel}) 608 (1.0), 655 nm (0.51). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 561 nm, $E_{562/1cm}$ = 0.0154; reference: S-13 with Φ = 1.00): 0.35. HRMS (ESI) ($C_{49}H_{61}N_2O_4^+$): calcd, 741.4626; found, 741.4613; Δ = 1.3 mmu.



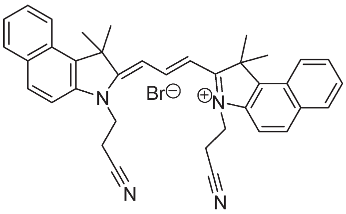
3q

*3,3′-Di-(4-propargylcarbonylbutyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3q**).* 3-(4-Propargyloxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2q**, 200 mg, 0.467 mmol), pyridine (1.0 mL), orthoformic triethylester (0.160 mL, 0.934 mmol), and diethylether (30 mL) were allowed to react (105 °C, 2 h) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**), decanted, and dried in vacuo. Yield, 165 mg (90%) of golden shiny solid forming violet, red fluorescent solutions; mp > 120 °C (dec.). IR (ATR): ν = 3393 (s), 3058 (w), 2972 (w), 2933 (m), 2865 (w), 2119 (w), 1734 (s), 1645 (s), 1587 (w), 1554 (s), 1520 (m), 1482 (m), 1425 (s), 1354 (m), 1278 (w), 1227 (m), 1169 (w), 1152 (w), 1128 (w), 1013 (m), 974 (w), 937 (m), 917 (w), 896 (w), 808 (m), 786 (w), 749 (w), 727 (w), 682 (m), 652 (m) cm^{-1}. ^1H NMR (200 MHz, CD_3OD): δ = 8.79 (t, 1H, H_{dien}, ^3J_E = 13.4 Hz), 8.30 (d, 2H, H_{aromat}, ^3J = 8.4 Hz), 8.13−8.05 (m, 4H, H_{aromat}), 7.68 (t, 4H, H_{aromat}, ^3J = 8.6 Hz), 7.53 (t, 2H, H_{aromat}, ^3J = 7.2 Hz), 6.57 (d, 2H, H_{dien}, ^3J_E = 13.5 Hz), 4.69 (d, 4H, OCH_2CCH, ^4J = 2.5 Hz), 4.33 (t, 4H, 2 × NCH_2, ^3J = 6.8 Hz), 2.86 (t, 2H, OCH_2CCH, ^4J = 2.5 Hz), 2.53 (t, 4H, 2 × CH_2CO_2H, ^3J = 7.7 Hz), 2.11 (s, 12H, 4 × CH_3), 1.98−1.83 ppm (m, 8H, 4 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 172.4, 145.4, 144.2, 133.5, 132.2, 130.6, 129.7, 128.1, 127.9, 121.9, 110.8, 106.8, 101.9, 77.4, 74.8, 51.4, 43.6, 38.8, 33.3, 32.7, 26.6, 25.3, 24.6, 21.7 ppm. UV/vis (EtOH): λ_{max} (E_{rel}) 591 (1.0), 554 nm (0.71). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 598 (1.0), 555 nm (0.99). UV/vis (solid state/wool): λ_{max} (E_{rel}) 546 (1.0), 600 nm (0.98). Fluorescence (ethanol): λ_{max} (I_{rel}) 608 (1.0), 652 nm (0.12). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 659 (1.0), 647 nm (0.98). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 635 (1.0), 668 nm (0.98). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 555 nm, $E_{555\ nm/1cm}$ = 0.0189; reference S-13 with Φ = 1.00): 0.20. HRMS (ESI) ($C_{47}H_{49}N_2O_4^+$): calcd, 705.3687; found, 705.3680; Δ = −0.7 mmu.



3r

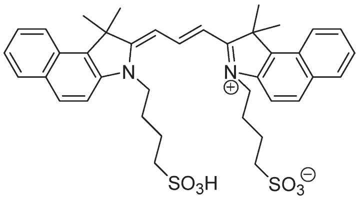
*3,3′-Di-(10-propargyloxycarbonyldecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3r**).* 3-(10-Propargyloxycarbonyldecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2r**) (900 mg, 1.76 mmol), pyridine (2.0 mL), and orthoformic triethylester (0.6 mL, 3.51 mmol) were allowed to react (100 °C) as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**, a chromatographic purification was leaved out because the material decomposes with the contact of the stationary phase to form the carboxylic acid). Yield, 621 mg (37%) of golden shiny solid forming violet, red fluorescent solutions. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 550 nm (0.77). Fluorescence (ethanol): λ_{max} (I_{rel}) 609 (1.0), 655 nm (0.50). HRMS (ESI) ($C_{59}H_{73}N_2O_4^+$): calcd, 873.5565; found, 873.5571; Δ = 0.6 mmu.



3s

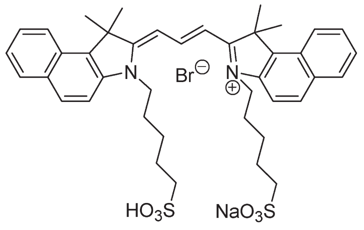
*3,3′-Di-(2-cyanoethyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanin Bromide (**3s**).* 3-(2-Cyanoethyl)-1,1,2-trimethyl-1*H*-

benz[e]indolenium bromide (**2s**, 100 mg, 0.291 mmol) under nitrogen was dissolved in pyridine (1.0 mL), heated at 90 °C, treated slowly dropwise with orthoformic ethylester (0.10 mL, 0.58 mmol, color change to bluish violet), heated at 105 °C for 1 h at 105 °C, allowed to cool, precipitated with diethylether (15 mL), and collected by vacuum filtration. Yield, 80 mg (89%) of golden shiny solid forming violet, red fluorescent solutions; mp >100 °C (dec.). IR (ATR): ν = 3391 (s, br), 3133 (w), 3060 (m), 2978 (w), 2941 (w), 2054 (w), 1633 (s), 1584 (w), 1558 (w), 1521 (w), 1487 (s), 1454 (w), 1433 (w), 1390 (w), 1355 (w), 1318 (w), 1234 (w), 1216 (w), 1173 (s), 1133 (w), 1094 (w), 1059 (w), 1017 (w), 974 (w), 937 (m), 868 (w), 808 (w), 778 (m), 764 (w), 680 (m) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 557 nm (0.80). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 603 (1.0), 557 nm (0.98). UV/vis (solid state/wool): λ_{max} (E_{rel}) 560 (1.0), 594 nm (0.95). Fluorescence (ethanol): λ_{max}(I_{rel}) 618 (1.0), 663 nm (0.46). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 634 (1.0), 671 nm (0.98). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 633 (1.0), 666 nm (0.87). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 474 nm, $E_{474\ nm/1cm}$ = 0.0141; reference S-13 with Φ = 1.00): 0.10. HRMS (ESI) ($C_{37}H_{35}N_4^{+}$): calcd, 535.2856; found, 535.2856; Δ = 0 mmu.



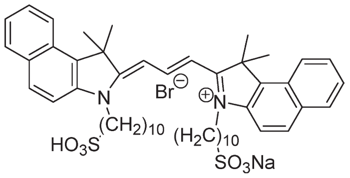
3t

*3,3′-Di-(4-sulfobutyl)-1,1,1′,1′-tetramethyl-di-1H-benz[e]indocarbocyanine (**3t**).* 3-(4-Sufobutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indole (**2t**, 500 mg, 1.40 mmol), pyridine (2.00 mL), and orthoformic triethylester (0.500 mL, 2.90 mmol) were allowed to react as was described for 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3a**). Yield, 522 mg (53%) of golden shiny solid forming violet, red fluorescent solutions; mp >250 °C. R_f (RP 18, methanol/$CHCl_3$/acetic acid 10:1:0.4) = 0.62. IR (ATR): ν = 3454 (w), 3054 (m), 2973 (w), 2933 (w), 2860 (w), 1626 (w), 1588 (w), 1555 (s), 1519 (m), 1490 (s), 1426 (s), 1369 (m), 1348 (w), 1124 (w), 1030 (m), 1012 (m), 977 (w), 948 (m), 925 (m), 891 (w), 805 (w), 767 (w), 740 (w), 728 (w), 688 (w), 650 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.28 (d, 2 H, $H_{aromatic}$, ^{3}J = 8.2 Hz), 8.02 (t, 4 H, $H_{aromatic}$, ^{3}J = 7.5 Hz), 7.67 (t, 5 H, $H_{aromatic}$, ^{3}J = 8.5 Hz), 7.50 (t, 2 H, $H_{aromatic}$, H_{allyl}, ^{3}J = 7.5 Hz), 6.59 (d, 2 H, H_{allyl}, $^{3}J_E$ = 13.7 Hz), 4.42–4.26 (m, 4 H, 2 × NCH_2), 3.05–2.87 (m, 4 H, 2 × CH_2CO_2H), 2.02–2.19 ppm (m, 20 H, 4 × CH_3, 4 × CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 176.8, 149.3, 139.5, 133.4, 132.2, 130.5, 129.7, 127.9, 127.4, 124.8, 121.9, 110.9, 56.9, 51.0, 43.8, 26.6, 26.2, 22.8, 22.2, 16.9 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 591 (1.0), 553 nm (0.68). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 593 (1.0), 559 nm (0.99). UV/vis (solid state/hair): λ_{max} (E_{rel}) 553 (1.0), 593 nm (0.90). Fluorescence (ethanol): λ_{max} (I_{rel}) 620 (1.0), 660 nm (0.50). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 662 (1.0), 630 nm (0.96). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 667 (1.0), 640 nm (0.98). Fluorescence (solid state/hair): λ_{max} (I_{rel}) 621 (1.0), 661 nm (0.67). Fluorescence quantum yield $CHCl_3$, λ_{exc} = 559 nm, $E_{559/1cm}$ = 0.0124, reference: S-13 with Φ = 1.00): 0.32. HRMS (ESI) ($C_{39}H_{45}N_2O_6S_2$): calcd, 701.2719; found, 701.2726; Δ = 0.7 mmu.



3u

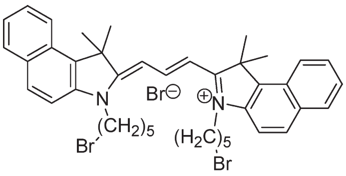
*3,3′-Di-(5-sulfopentyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3u**).* 3-(5-Sulfopentyl)-1,1,2-trimethyl-1*H*-benz[*e*]indoleniumbromide sodium salt (**2u**, 122 mg, 0.264 mmol), pyridine (1.3 mL), methanol (1 mL), and orthoformic triethylester (0.080 mL, 0.52 mmol) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h at 100 °C), dissolved in a small amount of ethanol, precipitated with diethylether, decanted, evaporated in vacuo, and purified by flashchromatograpy (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for absorption, methanol/H_2O/1 M HCl 2:1:0.4 for removing byproduct, and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 56.0 mg (51%) of golden shiny solid forming violet, strongly red fluorescent solutions. IR (ATR): ν = 3376 (w), 3058 (w), 2969 (w), 2931 (m), 2860 (w), 1702 (w), 1626 (w), 1586 (w), 1553 (s), 1520 (s), 1479 (m), 1422 (s), 1357 (m), 1224 (m), 1184 (m), 1171 (m), 1142 (m), 1126 (m), 1074 (w), 1036 (w), 1013 (m), 968 (w), 926 (s), 899 (w), 884 (w), 870 (w), 810 (m), 786 (w), 745 (w), 698 (w), 686 (w), 676 (w), 652 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.78 (t, 1H, H_{dien}, $^{3}J_E$ = 13.8 Hz), 8.30 (d, 2H, H_{aromat}, ^{3}J = 8.7 Hz), 8.04 (t, 4H, H_{aromat}, ^{3}J = 7.8 Hz), 7.68 (t, 4H, H_{aromat}, ^{3}J = 8.0 Hz), 7.57–7.48 (m, 2H, H_{aromat}), 6.60 (d, 2H, H_{dien}, $^{3}J_E$ = 13.9 Hz), 4.32 (t, 4H, 2 × NCH_2, ^{3}J = 7.8 Hz), 2.85–2.81 (m, 4H, 2 × CH_2SO_3H), 2.11 (s, 12H, 4 × CH_3), 1.99–1.69 ppm (m, 12H, 6 × CH_2). UV/vis (ethanol): λ_{max} (E_{rel}) 590 (1.0), 553 nm (0.68). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 599 (1.0), 553 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 600 (1.0), 553 nm (0.96). Fluorescence (ethanol): λ_{max} (I_{rel}) 611 (1.0), 655 nm (0.54). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 664 (1.0), 636 nm (0.93). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 667 (1.0), 644 nm (0.84). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 553 nm, $E_{553\ nm/1cm}$ = 0.0158; reference: S-13 with Φ = 1.00): 0.13. HRMS (ESI) ($C_{41}H_{47}N_2Na_2O_6S_2^{+}$): calcd, 773.2671; found, 773.2669; Δ = −0.2 mmu.



3v

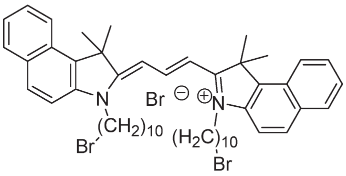
*3,3′-Di-(10-sulfodecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanin-Bromide (**3v**).* 3-(10-Sulfodecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indoleniumbromide sodium salt (**2v**, 152 mg, 0.285 mmol), 3-picoline (1.5 mL), and orthoformic triethylester (0.09 mL, 0.57 mmol) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h, 100 °C). Flash chromatography (RP 18, methanol/H_2O/1 M HCl) caused decomposition. As a consequence, the dye was applied without further purification. Yield, 185 mg. IR (ATR): ν = 3409 (w), 3055 (w), 2974 (w), 2926 (s), 2853 (m), 1705 (m), 1624 (w), 1588 (w), 1554 (s), 1519 (m), 1479 (m), 1425 (s), 1352 (m), 1278 (w), 1227 (m), 1169 (w), 1144 (w), 1124 (w), 1044 (w), 1012 (m), 974 (w), 931 (s), 898 (w), 806 (m), 787 (w), 747 (w), 727 (w), 684 (w), 652 (w), 637 (w), 612 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.76–8.64 (m, 1H, H_{dien}), 8.34–8.32 (m, 2H, H_{aromat}), 8.03–7.96 (m, 4H, H_{aromat}), 7.71–7.67 (m, 4H, H_{aromat}), 7.37–7.31 (m, 2H, H_{aromat}), 6.55 (d, 2H, H_{dien}, $^{3}J_E$ = 13.9 Hz), 4.38–4.20 (m, 4H, 2 × NCH_2), 2.51–2.40 (m, 4H, 2 × CH_2SO_3H), 2.10–1.99 (m, 16H, 4 × CH_3, 2 × CH_2), 1.95–1.80 (m, 8H, 4 × CH_2), 1.52–1.25 ppm (m, 20H, 10 × CH_2). UV/vis (ethanol): λ_{max} (E_{rel}) 592 (1.0), 553 nm (0.72). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 601 (1.0), 559 nm (0.95). UV/vis (solid state/wool): λ_{max} (E_{rel}) 599 (1.0), 556 nm (0.97). Fluorescence (ethanol): λ_{max} (I_{rel}) 609 (1.0), 658 nm (0.52).

Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 637 (1.0), 665 nm (0.97). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 630 (1.0), 662 nm (0.92). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 554 nm, $E_{554\ nm/1cm}$ = 0.0170; reference: S-13 with Φ = 1.00): 0.14.



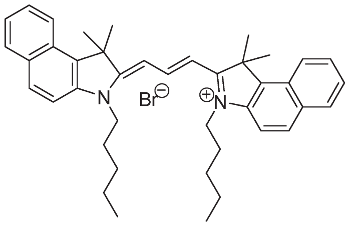
3w

*3,3′-Di-(5-bromopentyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3w**).* 3-(5-Bromopentyl)-1,1,2-trimethyl-1*H*-benz[*e*]indoleniumbromide (**2w**, 400 mg, 0.911 mmol), pyridine (2.0 mL), and orthoformic triethylester (0.300 mL, 1.82 mmol) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2.5 h at 120 °C). Flash chromatograpy (RP 18, methanol/H$_2$O/1 M HCl 10:1:0.4) caused decomposition. As a consequence, the dye was applied without further purification; mp > 100 °C. IR (ATR): ν = 3408 (m), 2970 (s), 2927 (m), 2865 (m), 2362 (w), 1728 (w), 1627 (w), 1588 (w), 1558 (m), 1520 (w), 1430 (m), 1372 (m), 1296 (w), 1278 (w), 1249 (w), 1226 (w), 1191 (w), 1100 (s), 1013 (m), 936 (m), 863 (w), 809 (w), 787 (w), 748 (w), 728(w), 701 (w), 653 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD$_3$OD): δ = 8.82 (t, 1H, H_{dien}, ^3J_E = 13.7 Hz), 8.27−8.26 (m, 2H, H_{aromat}), 8.16−8.09 (m, 4H, H_{aromat}), 7.71−7.64 (m, 4H, H_{aromat}), 7.56−7.51 (m, 2H, H_{aromat}), 7.08 (d, 2H, H_{dien}, ^3J_E = 13.8 Hz), 4.34−4.33 (m, 8H, 2 × NCH_2, 2 × CH_2Br), 2.11 (s, 12H, 4 × CH_3), 2.05−1.94 ppm (m, 12H, 6 × CH_2). UV/vis (ethanol): λ_{max} (E_{rel}) 592 (1.0), 553 nm (0.86). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 558 (1.0), 597 nm (0.98). UV/vis (solid state/wool): λ_{max} (E_{rel}) 556 (1.0), 598 nm (0.97). Fluorescence (ethanol): λ_{max} (I_{rel}) 612 (1.0), 662 nm (0.61). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 678 (1.0), 632 nm (0.51). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 678 (1.0), 628 nm (0.46). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 549 nm, $E_{549\ nm/1cm}$ = 0.0254; reference S-13 with Φ = 1.00): 0.15. HRMS (ESI): (M$^+$ − C$_{36}$H$_{37}$N$_2$$^+$) calcd, 497.2951; found, 497.2951; Δ = 0 mmu.



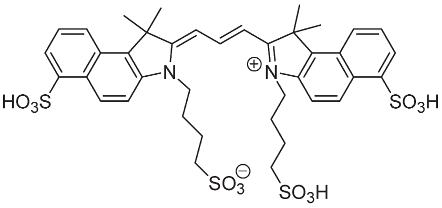
3x

*3,3′-Di-(5-bromodecyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3x**).* 3-(10-Bromodecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indoleniumbromide (**2x**, 250 mg, 0.491 mmol), pyridine (2.0 mL), and orthoformic triethylester (0.16 mL, 0.98 mmol) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h at 120 °C) and purified by flash chromatography (RP 18, methanol/H$_2$O/1 M HCl 1:1:0.4 for absorption, methanol/H$_2$O/1 M HCl 2:1:0.4 for removing byproduct, and methanol/H$_2$O/1 M HCl 10:1:0.4 for collection). Yield, 170 mg (73%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp 113 °C. IR (ATR): ν = 3387 (m), 3058 (w), 2919 (s), 2851 (s), 1722 (m), 1627 (w), 1588 (w), 1555 (m), 1520 (m), 1479 (w), 1468 (w), 1427 (s), 1358 (m), 1226 (m), 1171 (w), 1144 (w), 1111(m), 1013 (w), 933 (m), 898 (w), 808 (m), 787 (w), 748 (w), 727 (w), 700 (w), 686 (w), 653 (w) cm^{-1}. ^{1}H NMR: strong aggregation in concentrated solution caused broad signals. UV/vis (ethanol): λ_{max} (E_{rel}) 593 (1.0), 553 nm (0.73). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 601 (1.0), 557 nm (0.96). UV/vis (solid state/wool): λ_{max} (E_{rel}) 602 (1.0), 570 nm (0.97). Fluorescence (ethanol): λ_{max} (I_{rel}) 608 (1.0), 658 nm (0.53). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 672 (1.0), 650 nm (0.89). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 671 (1.0), 651 nm (0.87). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 558 nm, $E_{558\ nm/1cm}$ = 0.0125; reference S-13 with Φ = 1.00): 0.10. HRMS (ESI): (M$^+$ − C$_{41}$H$_{47}$N$_2$$^+$): calcd, 567.3734; found, 567.3736; Δ = 0.2 mmu.



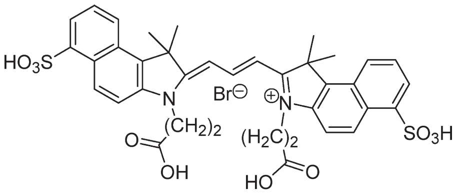
3y

*3,3′-Di(pentyl)-1,1,1′,1′-tetramethyl-1H-dibenz[e]indocarbocyanine Bromide (**3y**).* 1,1,2-Trimethyl-3-pentyl-1*H*-benz[*e*]indoleniumbromide (**2y**, 100 mg, 0.277 mmol) was dissolved under N$_2$ atmosphere in pyridine (1.0 mL), heated at 100 °C, treated slowly dropwise with othoformic ethylester (0.1 mL, 0.5 mmol), heated at 100 °C for 2 h, allowed to cool, treated with diethylether (20 mL), and collected by vacuum filtration. Yield, 71 mg (79%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3393 (s), 3133 (w), 3060 (m), 2979 (w), 2941 (w), 2871 (w), 2054 (w), 1634 (s), 1584 (w), 1555 (m), 1519 (w), 1487 (s), 1466 (w), 1446 (w), 1428 (w), 1388 (w), 1356 (w), 1318 (w), 1227 (w), 1173 (s), 1127 (w), 1060 (w), 1029 (w), 973 (w), 937 (w), 880 (w), 807 (w), 778 (m), 680 (s) cm^{-1}. ^{1}H NMR (200 MHz, CD$_3$OD): δ = 8.79 (t, 1H, H_{dien}, ^3J_E = 13.5 Hz), 8.30 (d, 2H, H_{aromat}, ^3J = 8.5 Hz), 8.07−8.02 (m, 4H, H_{aromat}), 7.71−7.67 (m, 2H, H_{aromat}), 7.64 (d, 2H, H_{aromat} ^3J = 8.8 Hz), 7.55−7.51 (m, 2H, H_{aromat}), 6.54 (d, 2H, H_{dien}, ^3J_E = 13.5 Hz), 4.29 (t, 4H, 2 × NCH_2, ^3J = 7.5 Hz), 2.11 (s, 12H, 4 × CH_3), 1.96−1.89 (m, 4H, 2 × CH_2), 1.55−1.44 (m, 8H, 4 × CH_2), 0.97 ppm (t, 6H, 2 × CH_3, ^3J = 7.2 Hz). ^{13}C NMR (100 MHz, CD$_3$OD): δ = 177.8, 147.2, 146.1, 141.3, 134.1, 132.4, 131.6, 130.0, 126.8, 112.6, 103.5, 59.0, 52.8, 45.9, 30.5, 29.0, 28.5, 24.0, 17.1, 14.7 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 590 (1.0), 552 nm (0.70). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 553 nm (0.98). UV/vis (solid state/wool): λ_{max} (E_{rel}) 539 (1.0), 600 nm (0.93). Fluorescence (ethanol): λ_{max} (I_{rel}) 607 (1.0), 657 nm (0.50). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 671 (1.0). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 623 (1.0), 662 nm (0.79). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 553 nm, $E_{553\ nm/1cm}$ = 0.0133; reference: S-13 with Φ = 1.00): 0.20. HRMS (ESI) (C$_{41}$H$_{49}$N$_2$$^+$): calcd, 569.3890; found, 569.3884; Δ = −0.6 mmu.



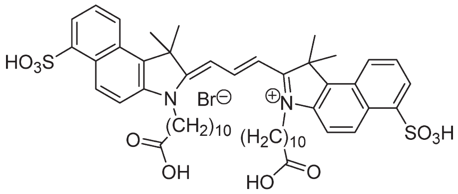
6a

*3,3′-Di-(4-sulfobutyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine (**6a**).* 3-(4-Sulfobutyl)-1,1,2-trimethyl-1*H*-sulfobenz[*e*]indole (**5a**, 140 mg, 0.276 mmol), pyridine (1.5 mL), orthoformic triethylester (0.090 mL, 0.55 mmol), and diethylether (15 mL) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h at 120 °C), repeatedly dissolved in a small amount of ethanol, precipitated with diethylether, and purified by flash chromatograpy (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsoption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 100 mg (77%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C. IR(ATR): ν = 3774 (w), 3450 (s, br), 2976 (w), 2938 (w), 2873 (w), 2361 (w), 2331 (w), 2008 (w), 1691 (w), 1640 (w), 1556 (s), 1515 (m), 1484 (m), 1431 (s), 1364 (m), 1277 (w), 1173 (s, br), 1103 (w), 1034 (m), 940 (m), 900 (w), 812 (w), 783 (w), 756 (w), 692 (w), 636 (w), 610 (w) cm^{-1}. ^1H NMR (200 MHz, CD_3OD): δ = 8.71−8.54 (m, 7H, H_{dien}, H_{aromat}), 8.40−8.33 (m, 2H, H_{aromat}), 7.80−7.64 (m, 2H, H_{aromat}), 6.63 (d, 2H, H_{dien}, ^3J_E = 13.2 Hz), 4.37−4.34 (m, 4H, 2 × NCH_2), 2.98−2.97 (m, 4H, 2 × CH_2SO_3H), 2.11−2.00 (m, 16H, 4 × CH_3, 2 × CH_2), 1.65 ppm (t, 4H, 2 × CH_2, ^3J = 7.7 Hz). UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 593 (1.0), 556 nm (0.66). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 546 (1.0), 586 nm (0.94). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 554 (1.0), 588 nm (0.92). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 608 (1.0), 655 nm (0.47). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 654 (1.0), 629 nm (0.94). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 631 (1.0), 661 nm (0.99). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 556 nm, $E_{556\text{ nm/1cm}}$ = 0.0099; reference: S-13 with Φ = 1.00): 0.33. HRMS (ESI) ($C_{39}H_{45}N_2O_{12}S_4^+$): calcd, 861.1850; found, 861.1851; Δ = 0.1 mmu.



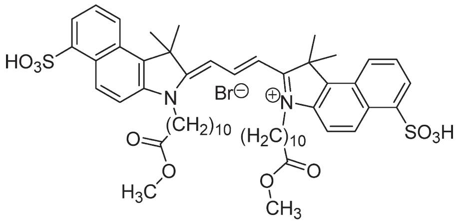
6b

*3,3′-Di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanin Bromide (**6b**).* 1,1,2-Trimethyl-1*H*-sulfobenz[*e*]indole (**4**, 245 mg, 0.847 mmol) was dissolved under N_2 in 3-picoline (1.0 mL) and methanol (0.3 mL), heated at 120 °C, treated with 3-bromopropionic acid (388 mg, 2.54 mmol), stirred at 120 °C for 10 min, treated with orthoformic triethylester (0.300 mL, 1.69 mmol, color change to bluish violet), stirred at 120 °C for 2 h, allowed to cool, precipitated with diethylether (20 mL), collected by vacuum filtration, and purified by flash chromatography (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for absorption, methanol/H_2O/1 M HCl 2:1:0.4 for removing byproduct, and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 200 mg (58%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >180 °C (dec.). IR (ATR): ν = 3387 (w), 2972 (w), 2927 (w), 2858 (w), 2367 (w), 1719 (w), 1626 (w), 1562 (s), 1490 (s), 1453 (s), 1414 (m), 1384 (m), 1168 (m, br), 1124 (w), 1097 (w), 1060 (w), 1046 (w), 1025 (s), 979 (m), 927 (m), 808 (m), 761 (w), 735 (w), 689 (m), 643 (m) cm^{-1}. ^1H NMR (200 MHz, CD_3OD): δ = 8.80 (t, 1H, H_{allyl}, ^3J_E = 13.4 Hz), 8.35−8.25 (m, 4H, H_{aromat}), 8.08−7.97 (m, 4H, H_{aromat}), 7.58−7.47 (m, 2H, H_{aromat}), 6.56 (d, 2H, H_{allyl}, ^3J_E =13.6 Hz), 4.59−4.53 (m, 4H, 2 × NCH_2), 2.94 (t, 4H, 2 × CH_2CO_2H, ^3J = 7.3 Hz), 2.10 ppm (s, 12H, 4 × CH_3). UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 588 (1.0), 554 nm (0.74). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 591 (1.0), 550 nm (0.99). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 565 (1.0), 589 nm (0.99). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 612 (1.0), 657 nm (0.41). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 648 (1.0), 662 nm (0.94). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 629 (1.0), 664 nm (0.72). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 482 nm, $E_{482\text{ nm/1cm}}$ = 0.0197; reference: S-13 with Φ = 1.00): 0.21. MS (FAB^+): *m/z* 733.6 [M^+ ($C_{37}H_{37}N_2O_{10}S^+$)].



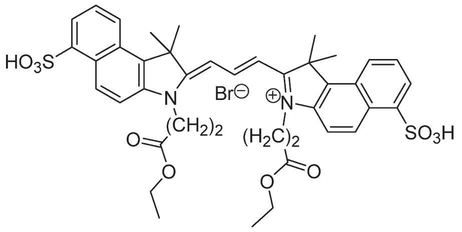
6c

*3,3′-Di-(10-carboxydecyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz-[e]indocarbocyanine Bromide (**6c**).* 3-(10-Carboxyldecyl)-1,1,2-trimethyl-1*H*-sulfobenz[*e*]indole (**5c**, 100 mg, 0.180 mmol) under N_2 atmosphere was dissolved in pyridine (1.0 mL) and methanol (0.3 mL), heated at 120 °C, treated very slowly dropwise with orthoformic triethylester (0.06 mL, 0.36 mmol), treated with a second portion of pyridine (0.5 mL) and orthoformic triethylester (0.03 mL, 0.18 mmol, 2 h auf 120 °C), allowed to cool, precipitated with diethylether (20 mL), collected by vacuum filtration, and purified by flashchromatograpy (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption, methanol/H_2O/1 M HCl 2:1:0.4 for removing byproduct, and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 66.0 mg (71%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3392 (w), 2922 (s), 2852 (s), 2362 (w), 1718 (s, br), 1585 (w), 1554 (s), 1515 (m), 1480 (m), 1420 (s), 1361 (m), 1274 (w), 1224 (w), 1166 (m), 1131 (m), 1100 (m), 1029 (w), 1015 (w), 932 (s), 898 (w), 827 (w), 806 (w), 746 (w), 689 (m), 657 (w), 630 (w) cm^{-1}. ^1H NMR (200 MHz, CD_3OD): δ = 8.79 (t, 1H, H_{dien}, ^3J_E = 13.4 Hz), 8.47−8.35 (m, 4H, H_{aromat}), 8.22−8.05 (m, 4H, H_{aromat}), 7.72 (t, 2H, H_{aromat}, ^3J = 7.7 Hz), 6.54 (d, 2H, H_{dien}, ^3J_E = 13.7 Hz), 4.29 (t, 4H, 2 × NCH_2, ^3J = 8.7 Hz), 2.31−2.21 (m, 4H, 2 × CH_2CO_2H), 2.11 (s, 12H, 4 × CH_3), 1.97−1.85 (m, 4H, 2 × CH_2) 1.59−1.13 ppm (m, 28H, 14 × CH_2). UV/vis (ethanol): $\lambda_{\max}$ (E_{rel}) 593 (1.0), 554 nm (0.68). UV/vis (solid state/cotton): $\lambda_{\max}$ (E_{rel}) 594 (1.0), 553 nm (0.94). UV/vis (solid state/wool): $\lambda_{\max}$ (E_{rel}) 598 (1.0), 556 nm (0.94). Fluorescence (ethanol): $\lambda_{\max}$ (I_{rel}) 608 (1.0), 656 nm (0.48). Fluorescence (solid state/cotton): $\lambda_{\max}$ (I_{rel}) 663 (1.0), 646 nm (0.89). Fluorescence (solid state/wool): $\lambda_{\max}$ (I_{rel}) 664 (1.0), 641 nm (0.91). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 554 nm, $E_{554\text{ nm/1cm}}$ = 0.0157; reference: S-13 with Φ = 1.00): 0.31. HRMS (ESI) ($C_{53}H_{69}N_2O_{10}S_2^+$): calcd, 957.4388; found, 957.4392; Δ = −0.4 mmu.



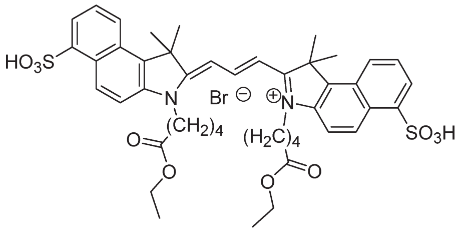
6d

*3,3′-Di-(10-methoxycarbonyldecyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine Bromide (**6d**).* 1,1,2-Trimethyl-1*H*-sulfobenz[*e*]indole (**4**, 267 mg, 0.923 mmol) under N_2, pyridine (0.5 mL), methanol (0.25 mL), 11-bromoundecaneacidmethylester (0.700 mL, 2.78 mmol, 10 min, 120 °C), orthoformic triethylester (0.300 mL, 1.86 mmol), and diethylether (20 mL) were allowed to react analogously 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-disulfobenz[*e*]indocarbocyanine bromide (**6b**, 1.5 h at 120 °C). Flash chromatography (RP 18, methanol/H_2O/1 M HCl) causes decomposition. Alternatively, the product was dissolved several times in the minimal amount of ethanol and precipitated with diethylether. Yield, 200 mg (41%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3430 (m), 3180 (w), 3140 (w), 3072 (m), 2927 (m), 2855 (w), 2158 (w), 1712 (m), 1637 (s), 1583 (w), 1544 (m), 1489 (s), 1466 (w), 1393 (w), 1316 (w), 1176 (s), 1100 (m), 1044 (w), 1021 (s), 931 (w), 857 (w), 754 (s), 681 (s), 658 (m), 643 (w), 608 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.50−8.42 (m, 1H, H_{dien}), 8.40−8.24 (m, 6H, H_{aromat}), 7.90−7.64 (m, 4H, H_{aromat}), 6.56 (d, 2H, H_{dien}, ^3J_E = 13.9 Hz), 4.35−4.30 (m, 4H, 2 × NCH_2), 3.31 (s, 6H, 2 × OCH_3), 2.29−2.20 (m, 4H, 2 × $CH_2CO_2CH_3$), 2.10 (s, 12H, 4 × CH_3), 1.98−1.88 (m, 4H, CH_2), 1.65−1.45 (m, 12H, 6 × CH_2), 1.38−1.30 ppm (m, 16H, 8 × CH_2). UV/vis (ethanol): λ_{max} (E_{rel}) 587 (1.0), 556 nm (0.78). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 588 (1.0), 555 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 551 (1.0), 586 nm (0.87). Fluorescence (ethanol): λ_{max} (I_{rel}) 607 (1.0), 657 nm (0.48). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 624 (1.0), 660 nm (0.74). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 617 (1.0), 660 nm (0.60). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 556 nm, $E_{556\ nm/1cm}$ = 0.0159; reference S-13 with Φ = 1.00): 0.25. MS (FAB$^-$): m/z 1063.3 [M$^-$ ($C_{55}H_{72}BrN_2O_{10}S^-$].



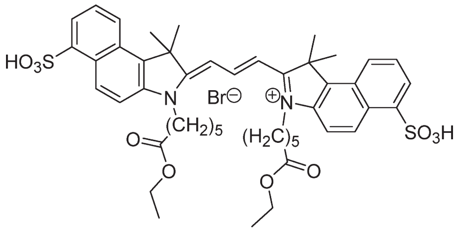
6e

*3,3′-Di-(2-ethoxycarbonylethyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine Bromide (**6e**).* 3-(2-Ethoxycarbonylethyl)-1,1,2-trimethyl-1*H*-sulfobenz[*e*]indole (**5e**, 210 mg, 0.446 mmol), 3-picoline (1.0 mL), and orthoformic triethylester (0.15 mL, 0.89 mmol) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h, 120 °C) and purified by flash chromatography (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 100 mg (52%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3411 (w), 3068 (w), 2951 (w), 2924 (s), 2854 (m), 1725 (m), 1623 (w), 1584 (w), 1559 (w), 1514 (w), 1478 (w), 1458 (w), 1426 (m), 1390 (w), 1362 (w), 1168 (s), 1100 (m), 1060 (w), 1030 (s), 940 (m), 827 (w), 809 (w), 762 (w), 692 (m), 649 (w), 624 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): Strong line-broadening was caused by aggregation. UV/vis (ethanol): λ_{max} (E_{rel}) 596 (1.0), 569 nm (0.79). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 599 (1.0), 564 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 563 (1.0), 597 nm (0.94). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 660 nm (0.51). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 654 (1.0), 633 nm (0.98). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 627 (1.0), 662 nm (0.88). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{559\ nm/1cm}$ = 0.0145; reference: S-13 with Φ = 1.00): 0.18.



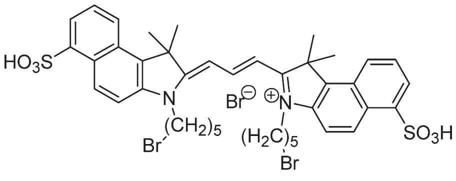
6f

*3,3′-Di-(4-ethoxycarbonylbutyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine Bromide (**6f**).* 1,1,2-Trimethyl-1H-sulfobenz[*e*]indole (**4**, 250 mg, 0.864 mmol), 3-picoline (1.0 mL), methanol (0.2 mL), 5-bromopentaneacidethylester (0.40 mL, 2.6 mmol, 10 min, 120 °C), orthoformic triethylester (0.300 mL, 1.73 mmol), and diethylether (20 mL) were allowed to react analogously to 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-disulfobenz[*e*]indocarbocyanine bromide (**6b**, 2 h, 120 °C, the dye decomposes within 1 day with yellowing) and purified by flash chromatography (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 33.0 mg (8%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3362 (w), 2971 (w), 2931 (w), 1724 (w), 1623 (w), 1564 (m), 1519 (w), 1492 (s), 1455 (m), 1416 (m), 1386 (m), 1185 (s, br), 1099 (m), 1060 (w), 1046 (w), 1027 (s), 980 (m), 929 (m), 809 (m), 763 (w), 736 (w), 691 (m), 643 (m) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 588 (1.0), 556 nm (0.76). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 591 (1.0), 550 nm (0.98). UV/vis (solid state/wool): λ_{max} (E_{rel}) 559 (1.0), 591 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 613 (1.0), 662 nm (0.40). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 636 (1.0), 671 nm (0.76). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 637 (1.0), 664 nm (0.93). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 478 nm, $E_{478\ nm/1cm}$ = 0.0170; reference: S-13 with Φ = 1.00): 0.11. HRMS (ESI) ($C_{45}H_{51}N_2O_{10}S_2^-$): calcd, 843.2991; found, 843.3797; Δ = 80.6 mmu.



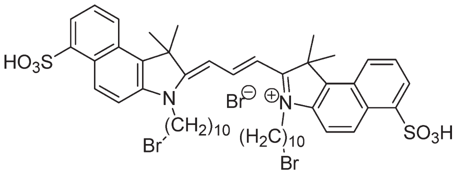
6g

*3,3′-Di-(5-ethoxycarbonylpentyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine Bromide (**6g**).* 3-(5-Ethoxycarbonylpentyl)-1,1,2-trimethyl-1*H*-sulfobenz[*e*]indole (**5g**, 100 mg, 0.195 mmol), 3-picoline (1.0 mL), methanol (0.3 mL), orthoformic triethylester (0.06 mL, 0.39 mmol), and diethylether (20 mL) were allowed to react analogously to 3,3′-di(pentyl)-1,1,1′,1′-tetramethyl-1*H*-dibenz[*e*]indocarbocyanine bromide (**3w**, 2 h, 120 °C) and purified by flash chromatograpy (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 20 mg (2%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >150 °C (dec.). IR (ATR): ν = 3410 (w), 3069 (w), 2926 (m), 2856 (w), 1710 (s), 1623 (w), 1556 (m), 1515 (m), 1480 (m), 1426 (s), 1362 (m), 1157 (s), 1135 (w), 1100 (m), 1029 (s), 1018 (s), 932 (s), 901 (w), 808 (w), 764 (w), 693 (m), 627 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.79 (t, 1H, H_{dien}, ^3J_E = 13.9 Hz), 8.45−8.34 (m, 4H, H_{aromat}), 8.21−8.04 (m, 4H, H_{aromat}), 7.72 (t, 2H, H_{aromat}, ^3J = 7.7 Hz), 6.55 (d, 2H, H_{dien}, ^3J_E = 13.8 Hz), 4.35−4.24 (m, 4H, 2 × NCH_2), 3.88−3.77 (m, 4H, 2 × CH_2CH_3), 2.38−2.31 (m, 4H, 2 × CH_2CO_2), 2.10 (s, 12H, 4 × CH_3), 1.99−1.87 (m, 8H, 4 × CH_2), 1.78−1.61 (m, 4H, 2 × CH_2), 1.00−0.90 ppm (m, 6H, 2 × CH_2CH_3). Additional signals of the carboxylic acid as the product of saponification. ^{13}C NMR (100 MHz, CD_3OD): δ = 175.9, 142.2, 133.1, 132.7, 131.6, 129.9, 128.6, 127.7, 126.6, 125.6, 123.9, 113.3, 112.4, 52.6, 45.5, 34.7, 28.3, 27.4, 25.8, 24.5, 13.8 ppm. UV/vis (ethanol): λ_{max} (E_{rel}) 593 (1.0), 557 nm (0.69). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 597 (1.0), 556 nm (0.97). UV/vis (solid state/wool): λ_{max} (E_{rel}) 561 (1.0), 596 nm (0.98). Fluorescence (ethanol): λ_{max} (I_{rel}) 610 (1.0), 660 nm (0.51). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 622 (1.0), 654 nm (0.97). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 660 (1.0), 641 nm (0.96). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 559 nm, $E_{559\ nm/1cm}$ = 0.0115; reference: S-13 with Φ = 1.00): 0.22.



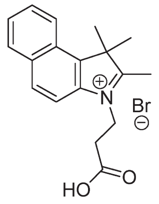
6h

*3,3′-Di-(5-brompentyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]indocarbocyanine Bromide (**6h**).* 1,1,2-Trimethyl-1*H*-sulfobenz[*e*]indole (**4**, 215 mg, 0.743 mmol), 3-picoline (1.5 mL), methanol (1.0 mL), 1,5-dibromopentane (0.30 mL, 2.2 mmol, 10 min, 120 °C), orthoformic triethylester (0.250 mL, 1.45 mmol), and diethylether (20 mL) were allowed to react analogously to 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-disulfobenz[*e*]indocarbocyanine bromide (**6b**, 2 h, 120 °C) and purified by flash chromatography (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 98 mg (27%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >75 °C (dec.). IR (ATR): ν = 3398 (s, br), 3056 (m), 3036 (w), 2866 (w), 2074 (w), 1634 (m), 1592 (w), 1559 (w), 1505 (s), 1483 (w), 1463 (w), 1387 (w), 1325 (w), 1250 (w), 1202 (m), 1155 (m), 1098 (w), 1048 (m), 1031 (m), 928 (w), 808 (m), 749 (w), 683 (m), 657 (w) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 590 (1.0), 559 nm (0.78). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 600 (1.0), 565 nm (0.95). UV/vis (solid state/wool): λ_{max} (E_{rel}) 558 (1.0), 587 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 611 (1.0), 659 nm (0.50). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 626 (1.0), 660 nm (0.83). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 615 (1.0), 658 nm (0.60). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 553 nm, $E_{553\ nm/1cm}$ = 0.0124; reference: S-13 with Φ = 1.00): 0.19.



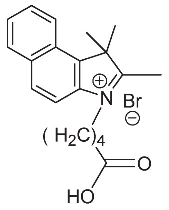
6i

*3,3′-Di-(10-bromdecyl)-1,1,1′,1′-tetramethyl-1H-disulfobenz[e]-indocarbocyanin Bromide (**6i**).* 1,1,2-Trimethyl-1*H*-sulfobenz-[*e*]indole (**4**, 205 mg, 0.708 mmol), 3-picoline (1.0 mL), methanol (0.3 mL), 1,10-dibromodecane (0.50 mL, 2.1 mmol, 10 min, 120 °C), orthoformic triethylester (0.24 mL, 1.4 mmol), and diethylether (20 mL) were allowed to react analogously to 3,3′-di-(2-carboxyethyl)-1,1,1′,1′-tetramethyl-1*H*-disulfobenz[*e*]indocarbocyanine bromide (**6b**, 2 h, 120 °C) and purified by flash chromatography (RP 18, methanol/H_2O/1 M HCl 1:1:0.4 for adsorption and methanol/H_2O/1 M HCl 10:1:0.4 for collection). Yield, 58 mg (14%) of golden shiny solid forming violet, strongly red fluorescent solutions; mp >100 °C (dec.). IR (ATR): ν = 3387 (s), 3059 (w), 2927 (s), 2855 (s), 1706 (m), 1635 (m), 1591 (w), 1562 (m), 1504 (m), 1489 (m), 1456 (m), 1414 (w), 1388 (w), 1364 (w), 1186 (s), 1098 (m), 1047 (w), 1029 (s), 981 (m), 932 (m), 811 (m), 765 (w), 734 (w), 688 (m), 645 (m) cm^{-1}. UV/vis (ethanol): λ_{max} (E_{rel}) 587 (1.0), 555 nm (0.77). UV/vis (solid state/cotton): λ_{max} (E_{rel}) 500 (1.0), 591 nm (0.75). UV/vis (solid state/wool): λ_{max} (E_{rel}) 551 (1.0), 591 nm (0.95). Fluorescence (ethanol): λ_{max} (I_{rel}) 614 (1.0), 661 nm (0.42). Fluorescence (solid state/cotton): λ_{max} (I_{rel}) 620 (1.0), 655 nm (0.70). Fluorescence (solid state/wool): λ_{max} (I_{rel}) 628 (1.0), 665 nm (0.77). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 481 nm, $E_{481\ nm/1cm}$ = 0.0181; reference: S-13 with Φ = 1.00): 0.13.



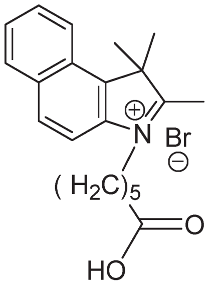
2a

*3-(2-Carboxyethyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2a**)*[11]. 1,1,2-Trimethylbenz[*e*]indole (**1**, 2.0 g, 9.5 mmol) and 3-bromopropioic acid (1.5 g, 9.5 mmol) were dissolved in 1,2-dichlorobenzene (30 mL), heated at 100 °C for 20 h, allowed to cool, collected by vacuum filtration (brown solid), and washed with dichloromethane until colorless. Yield, 2.38 g (69%) of colorless solid; mp 192 °C. IR (ATR): ν = 3353 (m), 3188 (w), 2904 (s, br), 1746 (m), 1724 (s), 1633 (m), 1612 (w), 1577 (m), 1523 (m), 1463 (m), 1455 (m), 1387 (s), 1284 (w), 1205 (s), 1183 (s), 1123 (m), 1063 (w), 1034 (m), 994 (w), 916 (w), 873 (w), 813 (m), 802 (s), 791 (m), 757 (s), 690 (w), 658 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.37 (d, 1H, H_{aromat}, ^3J = 8.4 Hz), 8.28 (d, 1H, H_{aromat}, ^3J = 8.9 Hz), 8.26−8.14 (m, 2H, H_{aromat}), 7.78 (ddd, 1H, H_{aromat}, ^4J = 1.3 Hz, ^3J = 7.0 Hz, ^3J = 8.4 Hz), 7.74−7.70 (m, 1H, H_{aromat}), 4.79 (t, 2H, NCH_2, ^3J = 7.0 Hz), 3.06 (t, 2H, CH_2CO_2H, ^3J = 7.0 Hz), 2.98 (s, 3H, CH_3), 1.76 ppm (s, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 189.2, 171.9, 138.8, 137.2, 133.4, 131.1, 130.1, 128.8, 127.7, 127.6, 123.8, 113.9, 31.8, 21.9, 14.7 ppm. HRMS (ESI) ($C_{18}H_{19}BrNO_2^-$): calcd, 360.0605; found, 360.0612; Δ = 0.7 mmu.



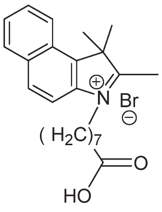
2b

*3-(4-Carboxybutyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2b**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 360 mg, 1.65 mmol) and 5-bromovalerianic acid (300 mg, 1.65 mmol) were heated to reflux for 1 h (bath 145 °C), allowed to cool, stirred with diethylether (50 mL) for 3 h, collected by vacuum filtration, and washed with dichloromethane. Yield, 243 mg (38%) of colorless solid, mp 187 °C. IR (ATR): ν = 2984 (w), 2913 (w), 1713 (s), 1581 (m), 1524 (m), 1474 (m), 1455 (m), 1397 (m), 1368 (w), 1258 (w), 1236 (w), 1208 (m), 1171 (s), 1157 (s), 1084 (w), 896 (w), 869 (w), 811 (s), 791 (m), 762 (m), 747 (w), 692 (w), 641 (w) cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ = 8.49−8.31 (m, 1 H, $H_{aromatic}$), 8.30−8.13 (m, 2 H, $H_{aromatic}$), 8.09−7.96 (m, 1 H, $H_{aromatic}$), 7.85−7.70 (m, 1 H, $H_{aromatic}$), 7.68−7.50 (m, 1 H, $H_{aromatic}$), 4.60 (t, 2 H, NCH_2, ^3J = 7.0 Hz), 2.94 (s, 3 H, CH_3), 2.32 (t, 2 H, CH_2, ^3J = 7.2 Hz), 1.99−1.84 (m, 2 H, CH_2), 1.76 (s, 6 H, 2 × CH_3), 1.73−1.63 ppm (m, 2 H, CH_2). HRMS (ESI) ($C_{20}H_{24}NO_2^+$): calcd, 310.1802; found, 310.1801; Δ = −0.1 mmu.



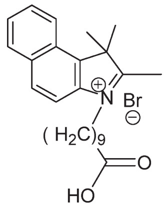
2c

*3-(5-Carboxypentyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2c**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 500 mg, 2.30 mmol) and 6-bromohexanoic acid (1.15 g, 6.00 mmol) were dissolved in DMPU (10.0 mL), heated under argon at 120 °C for 2 days, collected by vacuum filtration, and washed with diethylether and dichloromethane. Yield, 350 mg (37%) of slightly bluish solid. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.33 (d, 1 H, H_{aromatic}, ^3J = 8.5 Hz), 8.25 (d, 1 H, H_{aromatic}, ^3J = 9.1 Hz), 8.17 (d, 1 H, H_{aromatic}, ^3J = 8.3 Hz), 8.01 (d, 1 H, H_{aromatic}, ^3J = 9.0 Hz), 7.81 (ddd, 1 H, H_{aromatic}, ^4J = 1.3 Hz, ^3J = 6.9 Hz, ^3J = 8.4 Hz), 7.73 (ddd, 1 H, H_{aromatic}, ^4J = 1.1 Hz, ^3J = 7.0 Hz, ^3J = 8.1 Hz), 4.70−4.60 (m, 2 H, NCH_2), 2.89 (s, 3 H, CH_3), 2.36 (t, 2 H, CH_2, ^3J = 7.0 Hz), 2.18−1.97 (m, 2 H, CH_2), 1.85 (s, 6 H, 2 × CH_3), 1.79−1.68 (m, 2 H, CH_2), 1.68−1.53 ppm (m, 2 H, CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 196.1, 175.7, 174.2, 138.3, 137.3, 131.0, 129.6, 128.3, 127.7, 127.3, 123.0, 112.3, 55.9, 32.8, 27.3, 25.6, 24.0, 20.9 ppm. HRMS (ESI) ($C_{21}H_{26}NO_2^+$): calcd, 324.1958; found, 324.1956; Δ = −0.2 mmu.



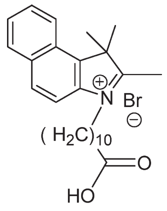
2d

*3-(7-Carboxyheptyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2d**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 938 mg, 4.48 mmol) and 8-bromooctanoic acid (1.00 g, 4.48 mmol) were heated at 120 °C for 2 h, allowed to cool, stirred with diethylether (50 mL) for 16 h, collected by vacuum filtration, dissolved in a small amount of dichlormethane, and precipitated with diethylether. Yield, 1.69 mg (87%) of black solid; mp 150 °C. IR (ATR): ν = 3055 (w), 2928 (s), 2854 (w), 1720 (s), 1633 (w), 1580 (m), 1522 (m), 1463 (m), 1382 (w), 1178 (w), 1085 (w), 827 (w), 744 (w) cm^{-1}. ^{1}H NMR (600 MHz, CD_3Cl_3): δ = 8.12 (d, 1 H, H_{aromatic}, ^3J = 8.8 Hz), 8.10−8.04 (m, 2 H, H_{aromatic}, ^3J = 8.3 Hz,), 7.80 (d, 1 H, H_{aromatic}, ^3J = 8.9 Hz), 7.73 (ddd, 1 H, H_{aromatic}, ^4J = 1.1 Hz, ^3J = 7.0 Hz, ^3J = 8.3 Hz), 7.68−7.65 (m, 1 H, H_{aromatic}), 4.86−4.82 (m, 2 H, NCH_2), 3.22 (s, 3 H, CH_3), 2.36 (t, 1 H, CH_2, ^3J = 7.1 Hz), 2.01−1.97 (m, 2 H, CH_2), 1.86 (s, 6 H, 2 × CH_3), 1.65−1.60 (m, 2 H, CH_2), 1.57−1.51 (m, 2 H, CH_2), 1.46−1.40 (m, 2 H, CH_2), 1.39−1.33 ppm (m, 2 H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.6, 176.5, 138.2, 137.1, 133.7, 131.5, 130.1, 128.6, 127.9, 127.6, 122.8, 112.5, 55.9, 49.6, 34.0, 28.3, 28.1, 28.0, 26.2, 24.2, 22.7, 16.0 ppm. HRMS (ESI) ($C_{23}H_{30}NO_2^+$): calcd, 352.2271; found, 352.2271; Δ = 0 mmu.



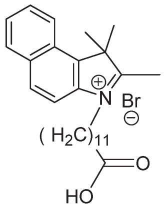
2e

*3-(9-Carboxynonyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2e**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 345 mg, 1.65 mmol) and 10-bromodecanoic acid (414 mg, 1.65 mmol) were heated at 120 °C for 1 h, allowed to cool, stirred with diethylether (50 mL) for 16 h, collected by vacuum filtration, dissolved in dichlormethane, and precipitated with ethylacetate (2 d). Yield, 112 mg (15%) of blue oil. IR (ATR): ν = 2925 (s), 2851 (s), 1720 (s), 1633 (w), 1615 (w), 1580 (m), 1522 (m), 1463 (m), 1371 (s), 1242 (w), 1211 (w), 1173 (m), 1098 (w), 1044 (m), 997 (w), 866 (w), 825 (m), 790 (m), 746 (m), 694 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.14−8.05 (m, 3 H, H_{aromatic}), 7.79−7.65 (m, 3 H, H_{aromatic}), 4.85 (t, 2 H, NCH_2, ^3J = 8.8 Hz), 3.21 (s, 3 H, CH_3), 2.35 (t, 2 H, CH_2, ^3J = 7.1 Hz), 2.03−1.93 (m, 2 H, CH_2), 1.87 (s, 6 H, 2 × CH_3), 1.69−1.29 ppm (m, 12 H, 6 × CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.5, 177.0, 171.2, 138.2, 137.2, 133.7, 131.5, 130.1, 128.7, 127.9, 127.6, 122.8, 112.4, 60.4, 55.8, 49.8, 34.0, 28.5, 26.5, 24.4, 22.7, 21.0, 16.1, 14.2 ppm. HRMS (ESI) ($C_{25}H_{34}NO_2^+$): calcd, 380.2584; found, 380.2582; Δ = −0.2 mmu.



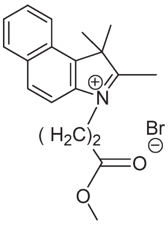
2f

*3-(10-Carboxydecyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2f**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 345 mg, 1.65 mmol) and 11-bromoundecanoic acid (437 mg, 1.65 mmol) were heated at 120 °C for 1 h, allowed to cool, stirred with diethylether (50.0 mL) for 16 h, and isolated by decanting the solvent. Yield, 640 mg (82%) of brown oil. IR (ATR): ν = 3059 (w), 2964 (w), 2925 (s), 2852 (s), 1937 (w), 1709 (s), 1624 (w), 1598 (w), 1574 (m), 1520 (m), 1463 (m), 1429 (w), 1384 (w), 1362 (w), 1350 (w), 1244 (m), 1218 (m), 1118 (w), 1023 (w), 979 (w), 862 (w), 819 (s), 747 (s), 722 (w), 694 (w), 668 (w), 640 (w), 609 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, 1 H, H_{aromatic}, ^3J = 8.4 Hz), 7.94 (d, 1 H, H_{aromatic}, ^3J = 7.8 Hz), 7.85 (d, 1 H, H_{aromatic}, ^3J = 8.6 Hz), 7.82 (d, 1 H, ^3J = 8.5 Hz) 7.54 (ddd, 1 H, H_{aromatic}, ^4J = 1.3 Hz, ^3J = 6.8 Hz, ^3J = 8.3 Hz), 7.44 (ddd, 1 H, H_{aromatic}, ^4J = 1.1 Hz, ^3J = 6.8 Hz, ^3J = 8.0 Hz), 3.40 (t, 2 H, NCH_2, ^3J = 6.9 Hz), 2.41 (s, 3 H, CH_3), 2.36 (t, 2H, CH_2, ^3J = 7.5 Hz), 1.87−1.82 (m, 2 H, CH_2), 1.71−1.63 (m, 2 H, CH_2,), 1.55 (s, 6 H, 2 × CH_3), 1.45−1.39 (m, 2 H, CH_2), 1.38−1.33 (m, 2 H, CH_2), 1.32−1.27 ppm (m, 8 H, 4 × CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.9, 178.6, 149.9, 138.4, 132.3, 129.6, 128.9, 128.6, 126.3, 124.4, 122.4, 119.6, 55.2, 34.2, 33.9, 32.8, 29.3, 29.2, 29.1, 28.6, 28.1, 24.8, 22.6, 14.9 ppm. HRMS (ESI) ($C_{26}H_{36}NO_2^+$): calcd, 394.2740; found, 394.2743; Δ = 0.3 mmu.



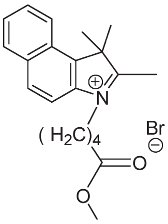
2g

*3-(11-Carboxyundecyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2g**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 450 mg, 2.15 mmol) and 12-bromododecanoate (200 mg, 0.72 mmol) were allowed to react (2.5 h) and purified analogously to 3-(9-carboxynonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2e**). Yield, 297 mg (84%) of brown solid. IR (ATR): ν = 2926 (m), 2850 (m), 2489 (w), 1779 (w), 1750(w), 1716 (s), 1634 (s), 1615 (w), 1581 (s), 1523 (s),1476 (w), 1463 (s), 1388 (m), 1317 (w), 1270 (m), 1212 (w), 1174 (m), 1113 (w), 1101 (w), 1036 (w), 1026 (w), 998 (m), 940 (w), 900 (w), 865 (m), 827 (s), 789 (m), 745 (s), 719 (m), 694 (m), 616 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.14−8.01 (m, 3 H, $H_{aromatic}$), 7.82−7.60 (m, 3 H, $H_{aromatic}$), 4.84 (t, 2 H, NCH_2, ^3J = 7.4 Hz), 3.20 (s, 3 H, CH_3), 2.31 (t, 2 H, CH_2, ^3J = 7.3 Hz), 1.86 (s, 6 H, 2 × CH_3), 1.62−1.20 ppm (m, 18 H, 9 × CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.0, 138.3, 137.2, 133.7, 131.4, 130.1, 128.7, 128.0, 127.6, 122.8, 112.3, 55.8, 33.6,0 28.7, 28.6, 28.4, 28.4, 28.3, 28.3, 28.1, 26.4, 24.4, 22.7, 16.0, 3.1, 3.0, 2.7 ppm. HRMS (ESI) ($C_{27}H_{38}NO_2^+$): calcd, 408.2897; found, 408.2895; Δ = −0.2 mmu.

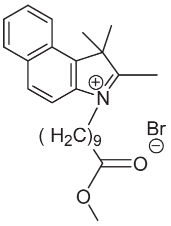


2h

*3-(2-Methoxycarbonylethyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2h**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 250 mg, 1.19 mmol) and methyl-3-bromopropionate (400 mg, 2.39 mmol) were heated at 120 °C for 1 h, allowed to cool, treated with diethylether (50.0 mL), stirred for 16 h, collected by vacuum filtration, dissolved in chloroform, precipitated with diethylether, and collected by vacuum filtration. Yield, 321 mg (49%, content 68% besides starting material according to ^1H NMR spectroscopy) of brown solid. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.10−7.98 (m, 4 H, $CH_{aromatic}$), 7.78−7.59 (m, 2 H, $CH_{aromatic}$), 5.24 (t, 2 H, NCH_2, ^3J = 5.9 Hz), 3.58 (s, 3 H, OCH_3), 3.27 (t, 2 H, CH_2COOCH_3, ^3J = 6.0 Hz), 3.24 (s, 3 H, CH_3), 1.84 ppm (s, 6 H, 2 × CH_3). HRMS (ESI) ($C_{19}H_{22}NO_2^+$): calcd, 296.1645; found, 296.1638; Δ = −0.7 mmu.

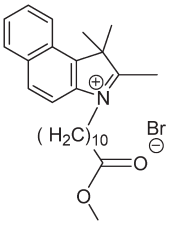


*3-(4-Methoxycarbonylbutyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2i**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 214 mg, 1.02 mmol) and methyl-5-bromopentanoate (200 mg, 1.02 mmol) were heated at 120 °C for 2 h, allowed to cool, treated with diethylether (50.0 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 253 mg (28%, content 46% besides starting material according to ^1H NMR spectroscopy) of grayish solid. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.15−8.01 (m, 4 H, $CH_{aromatic}$), 7.87−7.63 (m, 2 H, $CH_{aromatic}$), 4.97 (t, 2 H, NCH_2, ^3J = 7.4 Hz), 3.64 (s, 3 H, OCH_3), 3.25 (s, 3 H, CH_3), 2.46 (t, 2 H, ^3J = 6.8 Hz), 2.19−1.98 (m, 2 H, CH_2), 1.89 (s, 6 H, 2 × CH_3), 1.78−1.70 ppm (m, 2 H, CH_2). HRMS (ESI) ($C_{21}H_{26}NO_2^+$): calcd, 324.1958; found, 324.1949; Δ = −0.9 mmu.



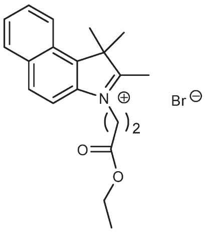
2j

*3-(9-Methoxycarbonylnonyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2j**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 947 mg, 4.52 mmol) and methyl-10-bromodecanoate (400 mg, 1.50 mmol) were allowed to react and purified analogously to 3-(4-methoxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2i**). Yield, 310 mg (18% content 40% besides starting material according to ^1H NMR spectroscopy) of grayish solid. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.14−8.00 (m, 4 H, $CH_{aromatic}$), 7.79−7.60 (m, 2 H, $CH_{aromatic}$), 4.86 (t, 2 H, NCH_2, ^3J = 7.7 Hz), 3.64 (s, 3 H, OCH_3), 3.22 (s, 3 H, CH_3), 2.27 (t, 2 H, ^3J = 7.3 Hz), 2.08−1.90 (m, 4 H, 2 × CH_2), 1.88 (s, 6 H, 2 × CH_3), 1.60−1.30 ppm (m, 10 H, 5 × CH_2). HRMS (ESI) ($C_{26}H_{36}NO_2^+$): calcd, 394.2741; found, 394.2729; Δ = −1.2 mmu.

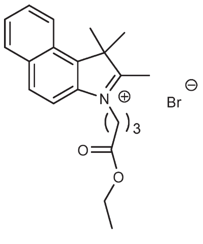


2k

*3-(10-Methoxycarbonyldecyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2k**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 1.2 g, 5.73 mmol) and methyl-11-bromoundecanoate (400 mg, 1.43 mmol) were allowed to react (1.5 h) and purified analogously to 3-(4-methoxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2i**). Yield, 270 mg (25%, content 65% besides starting material according to ^1H NMR spectroscopy) of grayish blue solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11−7.99 (m, 4 H, $CH_{aromatic}$), 7.75−7.60 (m, 2 H, $CH_{aromatic}$), 4.86 (t, 2 H, NCH_2, ^3J = 7.7 Hz), 3.64 (s, 3 H, OCH_3), 3.22 (s, 3 H, CH_3), 2.27 (t, 2 H, ^3J = 7.5 Hz), 2.01−1.93 (m, 2 H, CH_2), 1.88 (s, 6 H, 2 × CH_3), 1.61−1.54 (m, 2 H, CH_2), 1.51−1.44 (m, 2 H, CH_2), 1.40−1.32 (m, 2 H, CH_2), 1.29−1.21 ppm (m, 8 H, 4 × CH_2). HRMS (ESI) ($C_{27}H_{38}NO_2^+$): calcd, 408.2897; found, 408.2895; Δ = −0.2 mmu.

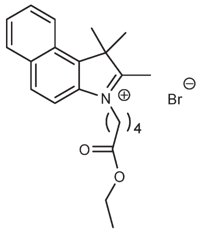


*3-(2-Ethoxycarbonylethyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2l**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 462 mg, 2.21 mmol) and ethyl-3-bromopropionate (2 g, 11 mmol) were allowed to react and purified analogously to 3-(9-carboxynonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2e**). Yield, 656 mg (62%, content 81% besides starting material according to ^{1}H NMR spectroscopy) of brown solid. IR (ATR): ν = 3381 (m), 3056 (w), 2923 (w), 2852 (w), 2350 (w), 2287 (w), 1711 (s), 1626 (m), 1588 (s), 1554 (w), 1520 (s), 1479 (w), 1423 (m), 1357 (m), 1277 (w), 1224 (w), 1168 (w), 1142 (w), 1127 (w), 1012 (m), 971 (w), 930 (w), 898 (w), 867 (w), 806 (s), 786 (m), 746 (s), 726 (w), 685 (w), 676 (w), 652 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13−8.01 (m, 4 H, CH_{aromatic}), 7.75−7.60 (m, 2 H, CH_{aromatic}), 5.23 (t, 2 H, NCH_2, ^3J = 6.0 Hz), 4.09 (q, 2 H, OCH_2CH_3, ^3J = 7.2 Hz), 3.0 (s, 3 H, CH_3), 2.41−2.39 (m, 2 H, $CH_2COOCH_2CH_3$), 1.77 (s, 6 H, 2 × CH_3), 1.14 ppm (t, 3 H, OCH_2CH_3, ^3J = 7.2 Hz). HRMS (ESI) ($C_{20}H_{24}NO_2^+$): calcd, 310.1796; found, 310.1762; Δ = −0.4 mmu.



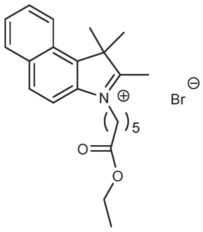
2m

*3-(3-Ethoxycarbonylpropyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2m**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 429 mg, 2.05 mmol) and ethyl-4-bromobutyrate (2 g, 10 mmol) were allowed to react (2 h) and purified analogously to 3-(9-carboxynonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2e**). Yield, 496 mg (21%, content 35% besides starting material according to ^{1}H NMR spectroscopy) of gray solid. IR (ATR): ν = 3381 (w), 3056 (m), 2350 (w), 2287 (w), 1711 (s), 1626 (m), 1588 (s), 1520 (m), 1276 (m), 971 (w), 867 (m), 786 (m), 746 (m), 726 (w), 685 (m), 676 (w), 652 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13−7.97 (m, 4 H, CH_{aromatic}), 7.76−7.58 (m, 2 H, CH_{aromatic}), 5.00 (t, 2 H, NCH_2, ^3J = 8.1 Hz), 4.08 (q, 2 H, OCH_2CH_3, ^3J = 7.2 Hz), 3.27 (s, 3 H, CH_3), 2.76 (t, 2 H, $CH_2COOCH_2CH_3$, ^3J = 6.8 Hz), 2.37−2.21 (m, 2 H, CH_2), 1.85 (s, 6 H, 2 × CH_3), 1.21 ppm (t, 3 H, OCH_2CH_3, ^3J = 7.2 Hz). HRMS (ESI) ($C_{21}H_{26}NO_2^+$): calcd, 324.1958; found, 324.1962; Δ = 0.4 mmu.



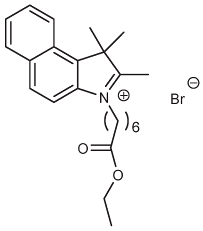
2n

*3-(4-Ethoxycarbonylbutyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2n**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 400 mg, 1.91 mmol) and ethyl-5-bromopentanoate (2 g, 9.56 mmol) were allowed to react and purified analogously to 3-(9-carboxynonyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2e**). Yield, 513 mg (26%, content 40% besides starting material according to ^{1}H NMR spectroscopy) of blue solid. IR (ATR): ν = 3381 (m), 3056 (w), 2350 (w), 2287 (w), 1711 (s), 1626 (w), 1588 (s), 1520 (m), 1277 (w), 971 (w), 898 (w), 867 (w), 786 (m), 746 (s), 726 (w), 685 (m), 676 (w), 652 (w) cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.40−8.03 (m, 4 H, CH_{aromatic}), 7.83−7.53 (m, 2 H, CH_{aromatic}), 4.61 (t, 2 H, NCH_2, ^3J = 7.2 Hz), 4.03 (q, 2 H, OCH_2CH_3, ^3J = 6.9 Hz), 2.95 (s, 3 H, CH_3), 2.10 (t, 2 H, $CH_2COOCH_2CH_3$, ^3J = 7.3 Hz), 1.99−1.83 (m, 2 H, CH_2), 1.76 (s, 6 H, 2 × CH_3), 1.73−1.66 (m, 2 H, CH_2), 1.14 ppm (t, 3 H, OCH_2CH_3, ^3J = 7.1 Hz). HRMS (ESI) ($C_{22}H_{28}NO_2^+$): calcd, 338.2115; found, 338.2118; Δ = 0.3 mmu.



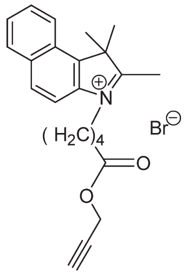
2o

*3-(5-Ethoxycarbonylpentyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2o**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 31 mg, 0.15 mmol) and ethyl-6-bromohexanoate (100 mg, 0.45 mmol) were allowed to react (1 h) and purified analogously to 3-(7-carboxyheptyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2d**). Yield, 41 mg (63%) of grayish solid. IR (ATR): ν = 3851 (w), 3420 (s), 2921 (m), 2851 (w), 1726 (s), 1622 (w), 1589 (m), 1556 (w), 1520 (m), 1477 (w), 1352 (m), 1227 (w), 1067 (w), 1014 (m), 941 (w), 899 (w), 805 (m), 786 (w), 744 (m), 728 (w), 652 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.36−8.15 (m, 3 H, CH_{aromatic}), 8.02 (d, 1 H, CH_{aromatic}, ^3J = 9.1 Hz), 7.86−7.66 (m, 2 H, CH_{arom}), 4.65 (t, 2 H, NCH_2, ^3J = 7.5 Hz), 4.07 (q, 2 H, OCH_2CH_3, ^3J = 7.2 Hz), 2.38 (t, 2 H, $CH_2COOCH_2CH_3$, ^3J = 7.0 Hz), 2.10−2.02 (m, 2 H, CH_2), 1.99 (s, 3 H, CH_3), 1.85 (s, 6 H, 2 × CH_3), 1.77−1.52 (m, 4 H, CH_2), 1.20 ppm (t, 3 H, OCH_2CH_3, ^3J = 7.1 Hz). HRMS (ESI) ($C_{23}H_{30}NO_2^+$): calcd, 352.2271; found, 352.2275; Δ = 0.4 mmu.



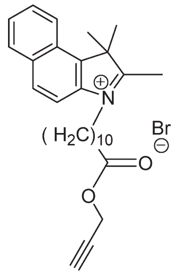
2p

*3-(6-Ethoxycarbonylhexyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2p**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 1.05 g, 5.04 mmol) and ethyl-7-bromoheptanoate (400 mg, 1.68 mmol) were heated at 120 °C for 2 h, allowed to cool, treated with diethylether (50 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 348 mg (22%, content 48% besides starting material according to ^{1}H NMR spectroscopy) of grayish solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11−8.07 (m, 4 H, CH_{aromatic}), 7.75−7.70 (m, 2 H, CH_{aromatic}), 4.88 (t, 2 H, NCH_2, ^3J = 7.3 Hz), 4.09 (q, 2 H, OCH_2CH_3, ^3J = 7.1 Hz), 3.23 (s, 3 H, CH_3), 2.28 (t, 2 H, $CH_2COOCH_2CH_3$, ^3J = 7.3 Hz), 2.03−1.99 (m, 2 H, CH_2), 1.88 (s, 6 H, 2 × CH_3), 1.65−1.59 (m, 2 H, CH_2), 1.56−1.52 (m, 2 H, CH_2), 1.46−1.40 (m, 2 H, CH_2), 1.22 ppm (t, 3 H, OCH_2CH_3, ^3J = 7.1 Hz). HRMS (ESI) ($C_{24}H_{32}NO_2^+$): calcd, 366.2428; found, 366.2426; Δ = −0.2 mmu.



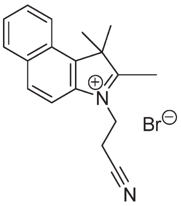
2q

*3-(4-Propargyloxycarbonylbutyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2q**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 450 mg, 1.14 mmol) and 4-bromovaleric propargylester (716 mg, 3.42 mmol) were heated at 120 °C for 2 h, allowed to cool, precipitated with diethylether (50 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 200 mg (41%) of green decomposible solid; mp 205 °C. IR (ATR): ν = 3289 (w), 3057 (m), 2966 (m), 2930(s), 2866 (m), 2123 (w), 1952 (w), 1736 (s), 1650 (s), 1621 (m), 1592 (w), 1568 (s), 1519 (s), 1463 (w), 1441 (w), 1380 (w), 1350 (w), 1242 (w), 1207 (m), 1152 (m), 1024 (w), 977 (w), 948 (w), 931 (w), 864 (m), 819 (s), 764 (s), 693 (w), 666 (w) cm^{-1}. HRMS (ESI) ($C_{23}H_{26}NO_2^+$): calcd, 348.1958; found, 348.1956; $\Delta = -0.2$ mmu.



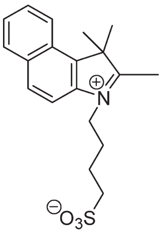
2r

*3-(10-Propargyloxycarbonyldecyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2r**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 517 mg, 2.47 mmol) and propargyl-11-bromoundecanoate[19] (250 mg, 0.82 mmol) were allowed to react (1.5 h) and purified analogously to 3-(4-methoxycarbonylbutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2i**). Yield, 148 mg (35%) of black solid. HRMS (ESI) ($C_{29}H_{38}NO_2^+$): calcd, 432.2897; found, 432.2899; $\Delta = 0.2$ mmu.



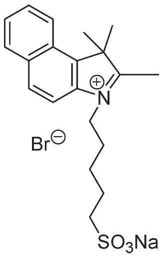
2s

*3-(2-Cyanoethyl)-1,1,2-trimethyl-1H-benz[e]indolenium Bromide (**2s**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 340 mg, 1.62 mmol) and 3-bromopropionitrile (108 mg, 0.812 mmol) were heated at 120 °C for 2 h, allowed to cool, precipitated with diethylether (50 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 311 mg (6%, content 5% besides the starting material) of black solid. IR (ATR): ν = 3398 (m), 2969 (m), 2774 (m), 2434 (w), 1708 (s), 1624 (s), 1579 (w), 1555 (w), 1520 (m), 1462 (s), 1438 (w), 1389 (w), 1354 (w), 1279 (w), 1250 (m), 1198 (w), 1128 (w), 1104 (w), 1020 (s), 984 (w), 935 (w), 886 (w), 864 (w), 815 (s), 788 (w), 748 (s), 685 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.14−8.00 (m, 4H, H_{aromat}), 7.75−7.64 (m, 2H, H_{aromat}), 5.54−5.52 (m, 2H, NCH_2), 3.51 (t, 2H, CH_2CN, ^3J = 6 Hz), 3.29 (s, 3H, CH_3), 1.96 ppm (s, 6H, 2 × CH_3); additional signals from the staring material **1**. HRMS (ESI) ($C_{18}H_{19}N_2^+$): calcd, 263.1543; found, 263.1544; $\Delta = 0.1$ mmu.



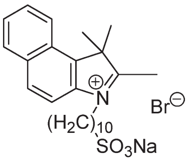
2t

*3-(4-Sufobutyl)-1,1,2-trimethyl-1H-benz[e]indole (**2t**)*[3]. 1,1,2-Trimehylbenz[*e*]indole (**1**, 1.0 g, 4.8 mmol) and 1,4-butanesultone (0.50 mL, 4.8 mmol) were heated at 130 °C for 2.5 h, allowed to cool, collected by vacuum filtration, washed with acetone, and dried at 100 °C for 3 h. Yield, 1.13 g (70%) of slightly greyish solid; mp 263 °C (ref 1, 266 °C). IR (ATR): ν = 3435 (m), 2939 (w), 1636 (w), 1584 (w), 1523 (w), 1468 (m), 1199 (s), 1034 (s), 872 (w), 824 (m), 791 (w), 758 (m), 737 (w) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 8.32 (d, 1H, H_{aromat}, ^3J = 8.5 Hz), 8.24 (d, 1H, H_{aromat}, ^3J = 8.9 Hz), 8.16 (d, 1H, H_{aromat}, ^3J = 8.2 Hz), 8.06 (d, 1H, H_{aromat}, ^3J = 9.0 Hz), 7.80 (ddd, 1H, H_{aromat}, ^4J = 1.3 Hz, ^3J = 6.9 Hz, ^3J = 8.4 Hz), 7.71 (ddd, 1H, H_{aromat}, ^4J = 1.1 Hz, ^3J = 6.9 Hz, ^3J = 8.1 Hz), 4.70- 4.64 (m, 2H, NCH_2), 2.91 (t, 2H, $CH_2SO_3^-$, ^3J = 7.1 Hz), 2.26- 2.18 (m, 2H, CH_2), 2.03- 1.94 (m, 2H, CH_2), 1.84 (s, 6H, 2 × CH_3), 1.30 ppm (s, 3H, CH_3). ^{13}C NMR (100 MHz, CD_3OD): δ = 196.6, 138.7, 137.5, 134.1, 131.3, 129.9, 128.5, 127.9, 127.5, 123.2, 112.7, 56.1, 49.9, 26.4, 23.0, 22.1, 21.2 ppm. HRMS (ESI) ($C_{19}H_{24}NO_3S$): calcd, 346.1471; found, 346.1473; $\Delta = 0.2$ mmu.



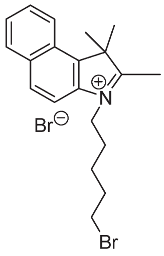
2u

*3-(5-Sulfopentyl)-1,1,2-trimethyl-1H-benz[e]indoleniumbromide Sodium Salt (**2u**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 744 mg, 3.56 mmol) and sodium 5-bromopentanesulfonate (300 mg, 1.18 mmol) were heated at 150 °C for 2 h, allowed to cool, treated with diethylether (30 mL), stirred for 16 h, collected by vacuum filtration, dissolved in a small amount of methanol, and precipitated with diethylether. Yield, 59% of bluish black solid; mp 213 °C. IR (ATR): ν = 3054 (w), 2963 (m), 2928 (m), 2866 (w), 2661 (w), 2614 (w), 2587 (w), 2456 (w), 1960 (w), 1915 (w), 1819 (w), 1782 (w), 1700 (w), 1645 (m), 1621 (m), 1570 (s), 1519 (s), 1466 (s), 1431 (m), 1377 (m), 1346 (m), 1282 (w), 1263 (w), 1242 (m), 1218 (s), 1206 (m), 1180 (m), 1036 (w), 1022 (w), 974 (m), 929 (m), 871 (s), 827 (s), 803 (s), 755 (s), 756 (s), 682 (w), 666 (m), 608 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.35−8.00 (m, 4H, H_{aromat}), 7.82−7.64 (m, 2H, H_{aromat}), 4.64 (t, 2H, NCH_2, ^3J = 7.5 Hz), 3.56 (t, 2H, CH_2SO_3H, ^3J = 6.3 Hz), 2.11−1.98 (m, 2H, CH_2), 1.82 (s, 6H, 2 × CH_3), 1.79 (s, 3H, CH_3), 1.62−1.50 ppm (m, 4H, 2 × CH_2). HRMS (ESI) ($C_{20}H_{25}NNaO_3S^+$): calcd, 328.1447; found, 328.1447; $\Delta = 0$ mmu.



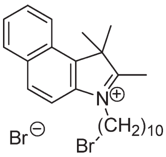
2v

*3-(10-Sulfodecyl)-1,1,2-trimethyl-1H-benz[e]indoleniumbromide Sodium Salt (**2v**).* 3-(10-Bromodecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indoleniumbromide (**2x**, 600 mg, 1.18 mmol) and sodium sulfite (50 mg, 0.39 mmol) were dissolved in a mixture of ethanol (5.0 mL) and distilled water (3.0 mL), heated to reflux for 6 h, allowed to cool, separated from the organic phase (1,10-dibromdecan), extracted with chloroform (3 × 50 mL), dried with megnesiumsulfate, and evaporated in vacuo. Yield, 165 mg (79%) of colorless solid. IR (ATR): ν = 2923 (s), 2853 (m), 1703 (m), 1521 (m), 1465 (w), 1352 (w), 1208 (m), 1035 (m), 810 (s), 750 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.09−7.91 (m, 4H, H_{aromat}), 7.77−7.64 (m, 2H, H_{aromat}), 3.93−3.90 (m, 2H, NCH_2), 3.65−3.54 (m, 2H, CH_2SO_3H), 2.38 (s, 3H, 2 × CH_3), 2.07−1.97 (m, 2H, CH_2), 1.83−1.76 (4H, 2 × CH_2), 1.55 (s, 6H, 2 × CH_3), 1.39−1.22 ppm (m, 10H, 5 × CH_2). MS (EI^+): m/z (%) 556.6 [M^+ 2HNa].



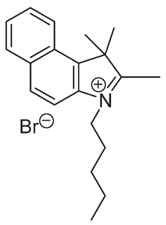
2w

*3-(5-Bromopentyl)-1,1,2-trimethyl-1H-benz[e]indoleniumbromide (**2w**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 1.0 g, 4.8 mmol) and 1,5-dibromopentane (0.22 mL, 1.6 mmol) were heated at 120 °C for 2 h, allowed to cool, treated with diethylether (30 mL), stirred for 16 h, collected by vacuum filtration, dissolved in a small amount of dichloromethane, and precipitated with diethylether. Yield, 860 mg (54%, content 44% besides the starting material by ^{1}H NMR) of brown solid; mp 123 °C. IR (ATR): ν = 3393 (s), 3058 (w), 2976 (m), 2928 (m), 2867 (w), 2714 (w), 2667 (w), 2588 (w), 2362 (m), 2336 (w), 1982 (w), 1739 (w), 1702 (w), 1632 (w), 1618 (w), 1582 (s), 1522 (s), 1464 (s), 1388 (w), 1367 (w), 1352 (w), 1279 (w), 1206 (m), 1148 (w), 1130 (w), 1039 (w), 1007 (w), 938 (w), 897 (w), 871 (w), 817 (s), 803 (s), 790 (m), 746 (s), 711 (w), 692 (w), 668 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.04−7.91 (m, 4H, H_{aromat}), 7.70−7.49 (m, 2H, H_{aromat}), 4.95 (t, 2H, NCH_2, ^{3}J = 7.3 Hz), 3.30 (s, 3H, CH_3), 3.25−3.19 (m, 4H, 2 × CH_2), 2.41−2.25 (m, 2H, CH_2), 2.17−2.03 (m, 2H, CH_2), 1.77 ppm (s, 6H, 2 × CH_3).



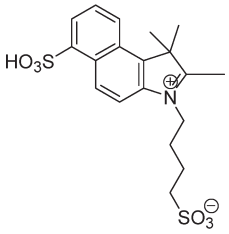
2x

*3-(10-Bromodecyl)-1,1,2-trimethyl-1H-benz[e]indoleniumbromide (**2x**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 2.0 g, 10 mmol) and 1,10-dibromodecane (0.75 mL, 3.3 mmol) were heated at 120 °C for 40 min, allowed to cool, treated with diethylether (30 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 1.3 g (32%, content 40% besides the starting material); mp 109 °C. IR (ATR): ν = 3394 (s, br), 3056 (w), 2977 (w), 2926 (s), 2854 (m), 2717 (w), 2665 (w), 2616 (w), 2591 (w), 2455 (w), 2038 (w), 1824 (w), 1633 (w), 1316 (w), 1582 (s), 1523 (m), 1465 (s), 1391 (w), 1368 (w), 1352 (w), 1334 (w), 1281 (w), 1216 (m), 1175 (w), 1147 (w), 1130 (w), 1040 (w), 1007 (w), 982 (w), 932 (w), 896 (w), 870 (w), 817 (m), 790 (w), 746 (s), 692 (w), 659 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.14−7.98 (m, 4H, H_{aromat}), 7.76−7.58 (m, 2H, H_{aromat}), 4.93−4.82 (m, 2H, NCH_2), 3.29 (s, 3H, CH_3), 2.10−1.84 (m, 2H, CH_2), 1.86 (s, 6H, 2 × CH_3), 1.84−1.76 (m, 4H, 2 × CH_2), 1.70−1.20 ppm (m, 12H, 6 × CH_2); there are also the signals of the starting material in the spectrum. HRMS (ESI) ($C_{25}H_{35}BrN^+$): calcd, 428.1947; found, 428.1948; Δ = 0.1 mmu.



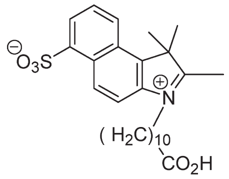
2y

*1,1,2-Trimethyl-3-pentyl-1H-benz[e]indoleniumbromide (**2y**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 690 mg, 3.31 mmol) and 1-bromopentane (0.20 mL, 1.6 mmol) were heated at 120 °C for 1.5 h, allowed to cool, treated with diethylether (20 mL), stirred for 16 h, and collected by vacuum filtration. Yield, 182 mg (24%, content 80% besides the starting material according to ^{1}H NMR) of brown solid, applied for the subsequent condensation without further purification; mp 241 °C. IR (ATR): ν = 3398 (w), 3052 (w), 2929 (w), 2869 (w), 2709 (w), 2588 (w), 1819 (w), 1643 (m), 1584 (s), 1524 (m), 1464 (s), 1394 (m), 1218 (w), 1204 (w), 1148 (w), 1007 (w), 846 (w), 802 (s), 744 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15−8.01 (m, 4H, H_{aromat}), 7.75−7.62 (m, 2H, H_{aromat}), 4.88 (t, 2H, NCH_2, ^{3}J = 7.7 Hz), 3.23 (s, 3H, CH_3), 2.05−1.96 (m, 2H, CH_2), 1.89 (s, 6H, 2 × CH_3), 1.71−1.68 (m, 2H, CH_2), 1.56−1.40 (m, 2H, CH_2), 0.92 ppm (t, 3H, CH_2CH_3, ^{3}J = 7.0 Hz); there are additional signals from the starting material. HRMS (ESI) ($C_{20}H_{26}N^+$): calcd, 280.2060; found, 280.2057; Δ = −0.3 mmu.



5a

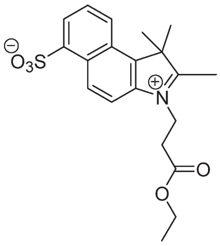
*3-(4-Sulfobutyl)-1,1,2-trimethyl-1H-sulfobenz[e]indole (**5a**).* 3-(4-Sufobutyl)-1,1,2-trimethyl-1*H*-benz[*e*]indole (**2f**, 300 mg, 0.868 mmol), nitrobenzene (5.0 mL), and fuming sulfuric acid (0.11 mL, 0.87 mmol, SO_3 content 65%) were allowed to react analogously to **5b** (2 days of stirring at room temperature). Yield, 200 mg (46%) of black, viscous oil, applied for the subsequent condensation without further purification. HRMS (ESI) ($C_{19}H_{24}NO_6S_2^+$): calcd, 426.1040; found, 426.1039; Δ = −0.1 mmu.



5c

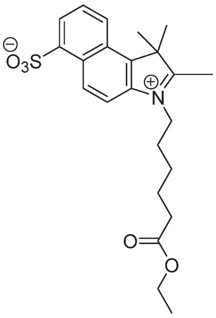
*3-(10-Carboxyldecyl)-1,1,2-trimethyl-1H-sulfobenz[e]indole (**5c**).* 3-(10-Carboxydecyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium bromide (**2f**, 300 mg, 0.632 mmol), nitrobenzene (5.0 mL), and fuming sulfuric acid (0.08 mL, 0.63 mmol, SO_3 content 65%) were allowed to react analogously to 1,1,2-trimethyl-1*H*-sulfobenz[*e*]indole (**4**, 3 d). Yield, 300 mg (85%) of black, viscous oil, applied for the subsequent condensation without further purification. ^{1}H NMR (200 MHz,

CD_3OD): δ = 8.41−8.01 (m, 4H, H_{aromat}), 7.87−7.66 (m, 1H, H_{aromat}), 4.63 (t, 2H, NCH_2, ^3J = 7.3 Hz), 3.35 (s, 3H, CH_3), 2.28 (t, 2H, $CH_2CO_2CH_3$, ^3J = 7.3 Hz), 2.69−1.93 (m, 2H, CH_2), 1.82 (s, 6H, 2 × CH_3), 1.64−1.30 ppm (m, 14H, 7 × CH_2). HRMS (ESI) ($C_{26}H_{34}NO_5S^-$): calcd, 472.2169; found, 472.2159; Δ = −1 mmu.



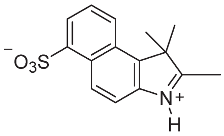
5e

*3-(2-Ethoxycarbonylethyl)-1,1,2-trimethyl-1H-sulfobenz[e]indole (**5e**).* 3-(2-Ethoxycarbonylethyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium-bromide (**2l**, 300 mg, 0.768 mmol), nitrobenzene (5.0 mL) and fuming sulfuric acid (0.10 mL, 0.77 mmol, SO_3 content 65%) were allowed to react analogously to **5b**. Yield, 250 mg (69%) of black, viscous oil, applied for the subsequent condensation without further purification. ^1H NMR (200 MHz, CD_3OD): δ = 8.37−8.03 (m, 4H, H_{aromat}), 7.84−7.66 (m, 1H, H_{aromat}), 4.96−4.87 (m, 2H, NCH_2), 4.22−4.20 (m, 2H, OCH_2CH_3), 3.32−3.13 (m, 2H, $CO_2CH_2CH_3$), 2.95−2.85 (m, 3H, OCH_2CH_3), 1.82 ppm (s, 6H, 2 × CH_3). The protons of the methyl group in position 2 exchange with the solvent.



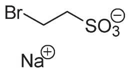
5g

*3-(5-Ethoxycarbonylpentyl)-1,1,2-trimethyl-1H-sulfobenz[e]indole (**5g**).* 3-(5-Ethoxycarbonylpentyl)-1,1,2-trimethyl-1*H*-benz[*e*]indolenium-bromide (**2o**, 230 mg, 0.532 mmol), nitrobenzene (5.0 mL) and fuming sulfuric acid (0.06 mL, 0.53 mmol, SO_3 content 65%) were allowed to react analogously to **5b**. Yield, 111 mg (41%) of black, viscous oil, applied for the subsequent condensation without further purification. ^1H NMR (200 MHz, CD_3OD): δ = 8.39−8.29 (m, 2H, H_{aromat}), 8.18−8.01 (m, 2H, H_{aromat}), 7.87−7.74 (m, 1H, H_{aromat}), 4.64 (t, 2H, NCH_2, ^3J = 7.6 Hz), 4.20−4.17 (m, 2H, OCH_2CH_3), 2.95−2.85 (m, 3H, OCH_2CH_3), 2.37 (t, 2H, $CH_2CO_2CH_2CH_3$, ^3J = 6.9 Hz), 2.10−1.95 (m, 2H, CH_2), 1.81 (s, 6H, 2 × CH_3), 1.74−1.50 ppm (m, 4H, 2 × CH_2). The protons of the methyl group in position 2 exchange with the solvent. HRMS (ESI) ($C_{23}H_{30}NO_5S^+$): calcd, 432.1839; found, 432.1484; Δ = 35.5 mmu.

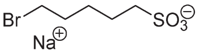


4

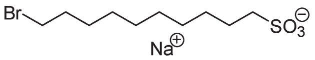
*1,1,2-Trimethyl-1H-sulfobenz[e]indole (**4**).* 1,1,2-Trimethylbenz[*e*]indole (**1**, 1.0 g, 5.0 mmol) were dissolved in nitrobenzene (5.0 mL), treated cautiously dropwise with ice cooling with fuming sulfuric acid (0.65 mL, 5.0 mmol, SO_3 content 65%, temperature increase until 20 °C, cooling until the end of the evolution of smoke), allowed to warm to room temperature, stirred for 4 h, separated from the nitrobenzene by decanting and subsequent steam distillation until odorless, and evaporated in vacuo. Yield, 1.00 g (69%) of black, viscous oil, applied for the subsequent condensation without further purification. HRMS (ESI) ($C_{15}H_{14}NO_3S^-$): calcd, 288.0700; found, 288.0698; Δ = −0.2 mmu.



*Sodium **2**-Bromoethansulfonate*[21]. 1,2-Dibromoethane (6.2 mL, 72 mmol) and sodium sulfite (3 g, 24 mmol) were heated to reflux for 6 h in a mixture of ethanol (25 mL) and distilled water (20 mL), allowed to cool, extracted with chloroform (3 × 25 mL), dried with magnesium sulfate, and evaporated in vacuo. Yield, 8.3 g (55%) of colorless solid; mp 289 °C. IR (ATR): ν = 3600 (w), 3528 (w), 3408 (s), 2980 (w), 2946 (w), 2087 (w), 1635 (w), 1615 (s), 1435 (m), 1411 (m), 1294 (m), 1263 (w), 1202 (m), 1168 (m), 1112 (w), 1041 (s) 794 (w), 779 (w), 750 (w), 674 (w), 617 (w) cm^{-1}. HRMS (ESI) ($C_2H_4BrO_3S^-$): calcd, 186.9070; found, 186.9070; Δ = 0 mmu.



*Sodium **5**-Bromopentanesulfonate.* 1,5-Dibromopentane (16.4 g, 71 mmol), sodium sulfite (3 g, 24 mmol), ethanol (25 mL), and distilled water (20 mL) were allowed to react analogously to sodium 2-bromoethansulfonate. Yield, 7.4 g (41%) of colorless solid. IR (ATR): ν = 3485 (m), 3411 (w), 2978 (w), 2930 (m), 2908 (w), 2895 (w), 2867 (w), 2851 (w), 1636 (w), 1616 (w), 1487 (w), 1466 (m), 1410 (w), 1390 (w), 1329 (w), 1314 (w), 1293 (w), 1262 (w), 1224 (m), 1207 (s), 1180 (s), 1044 (s), 988 (w), 938 (w), 823 (w), 804 (w), 792 (w), 729 (w), 618 (w) cm^{-1}. HRMS (ESI) ($C_5H_{11}BrNaO_3S^+$): calcd, 252.9504; found, 252.9820; Δ = 31.6 mmu.



*Sodium **10**-Bromdecanesulfonate*[22]. 1,10-Dibromodecane (7.5 g, 25 mmol), sodium sulfite (1.4 g, 11 mmol), ethanol (25 mL), and distilled water (20 mL) were allowed to react analogously to sodium 2-bromoethansulfonate. Yield, 1.8 g (23%) of colorless solid; mp 342 °C. IR (ATR): ν = 3541 (s), 3481 (s), 2916 (s), 2874 (m), 2853 (s), 2095 (w), 1627 (m), 1472 (m), 1307 (w), 1281 (w), 1250 (w), 1230 (m), 1197 (m), 1178 (s), 1055 (m), 1044 (m), 968 (w), 796 (m), 721 (w), 640 (w), 608 (m) cm^{-1}. HRMS (ESI) ($C_{10}H_{21}BrNaO_3S^+$): calcd, 323.0287; found, 323.0602; Δ = 31.5 mmu.

Staining of the Porcine Lens Capsule. Porcine eyes with a postmortem time of approximately 3 h were obtained for the evaluation of the staining effect. After the cornea was removed, the iris was carefully removed, and the zonules were exposed. Then, the lens was prepared, and great care was taken not to affect the lens capsule. The lenses were then placed in BSS. Then, 2−3 drops of the respective dye concentration was applied on the lens surface. After a few seconds, the dye was washed out using BSS, and the staining effect was assessed using the following scale: excellent (+++), good (++), fair (+), or absent (−). Photographs were taken from each stained lens.

Studies of Toxicity by Means of Established Models of Cell Structure: MTT Assay. ARPE-19 cell and RPE cell material, respectively, were kept

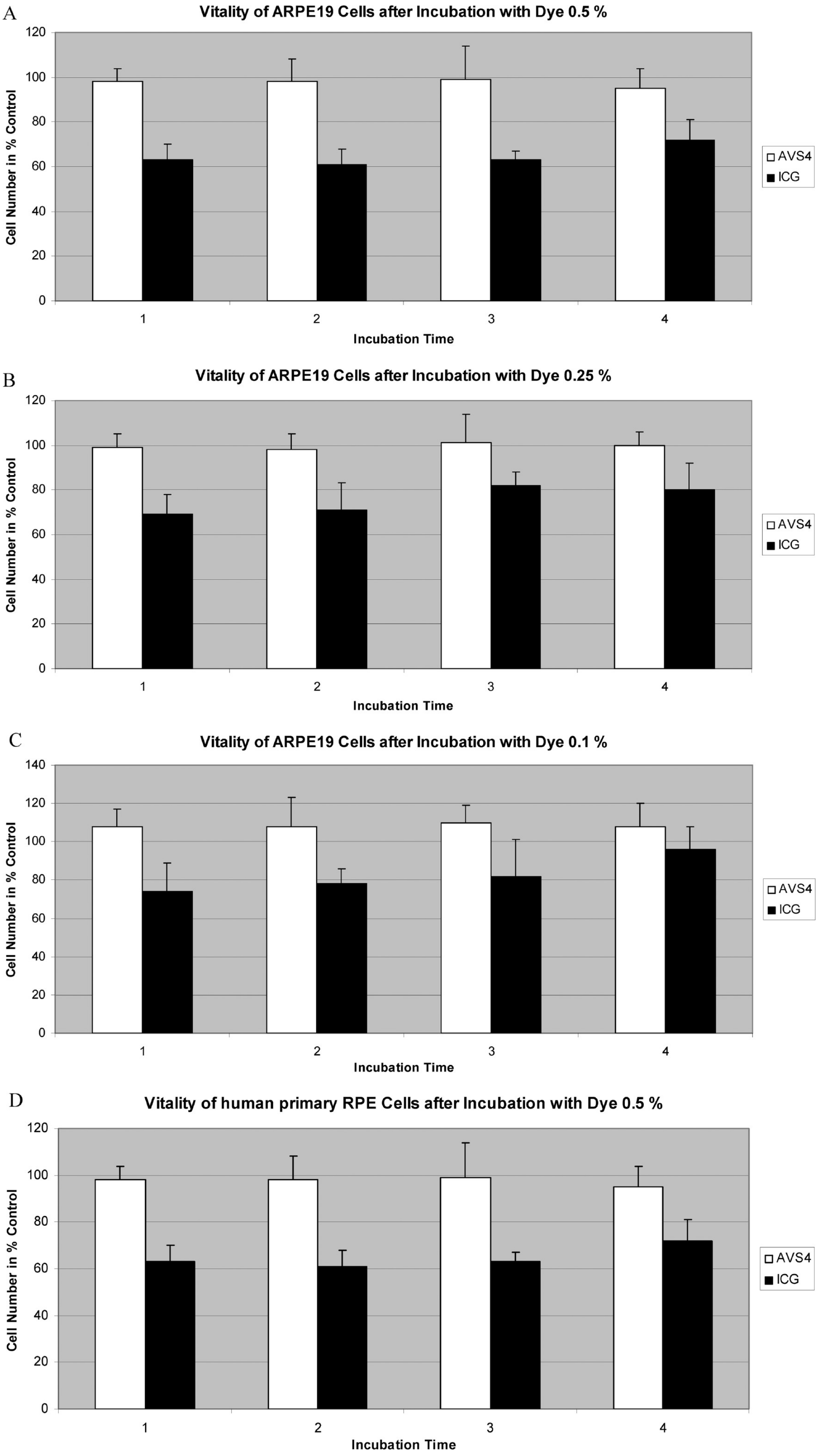


Figure 4. Continued

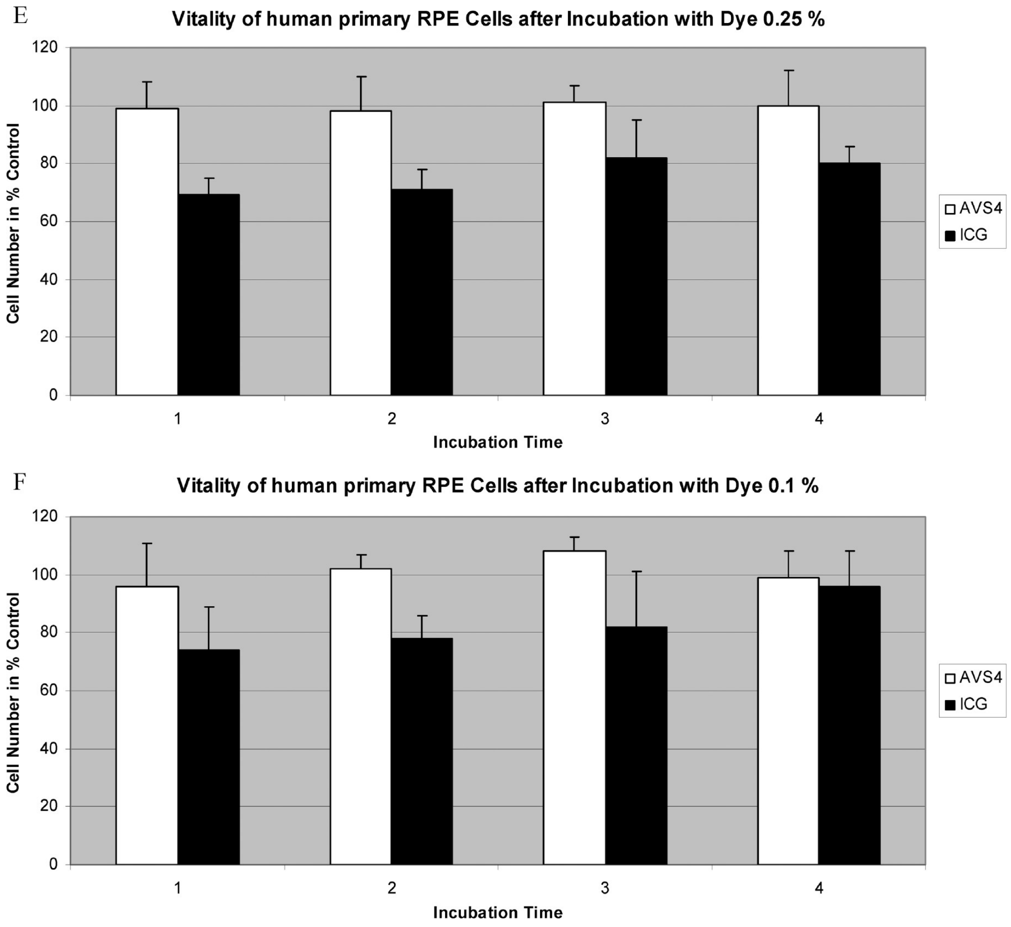


Figure 4. Number of cells of the type ARPE-19 and primary RPE, rescpectively, measured by means of a colorimetric test (MTT) after the treatment with dyes; incubation time varied from 30, 60, and 120 to 300 s. ARPE-19: (A) 0.5, (B) 0.25, and (C) 0.1% of dye **3t**. RPE: (D) 0.5, (E) 0.25, and (F) 0.1% of dye **3t**. ICG served as a reference dye in the same concentrations and exposure times. Compound **3t** as a triple test and three times repeated. Control tests were performed without any addition of dyes and with the addition of hydrogen peroxide (not presented). The presented results are means of three triplicate tests in relation to the control experiments; error bars, SEM. The observed variations are statistically insignificant.

under serum-free conditions for 24 h for the investigation of the impact of dyes. After they were grown to confluency (100%), the cells were washed with BSS plus solution for three times and then incubated with 700 μL of BSS plus solution containing 0.5, 0.25, and 0.1% 3,3′-di-(4-sulfobutyl)-1,1,1′,1′-tetramethyl-di-1*H*-benz[*e*]indocarbocyanine (**4**) each for 30, 60, 120, and 300 s. The comparably long incubation times are necessary for the detection of comparably weak toxicity, although they are far beyond the clinical applications of the dyes. ICG (0.5, 0.25, and 0.1%; exposure times 30, 60, 120, and 300 s) was used as a reference since this dye is still used in vitreoretinal surgery and also represents a cyanine dye. The excess of dye was removed by three washing steps of the cells with BSS plus solution preceding the proliferation assay. After 24 h of incubation with serum-containing media, the cell proliferation assay was performed. Control experiments were carried out with BSS plus without any additives and with the addition of H_2O_2 (200 μL/mL).

The tetrazolium dye reduction assay [MTT; 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] was applied for the determination of the amount of cellular survival. The MTT test according to Mosmann was modified as was reported in ref 20. The medium was removed, and the cells were treated with PBS and 1000 μL/well MTT solution (1.5 mL of MTT stock solution, 2 mg/mL in PBS, and 28.5 mL of DMEM), RPE cells were incubated at 37 °C for 1 h, the formed crystals of formazane in dimethylsulfoxide (DMSO) were dissolved (1000 μL/well), and the UV/vis absorption was measured with a scanning multiwell spectrophotometer at 550 nm (Molecular Probes, Garching, Germany). The results were related to an averaged control proliferation. The experiments were repeated three times in 3-fold tests. ARPE-19 cells of the same series incubated in BSS were used for control. The results for various dye concentrations were statistically analyzed by means of SPSS (Mann–Whitney U test).

The applied MTT test is well-established for the determination of the cell activity and depends on the colorimetric determination of a blue formazane (550 nm) as the product. The absorption of the latter overlaps partially with the spectrum of the investigated dyes. As a consequence, control experiments were performed for the estimation of possible interference in the test. Monolayers of cells were incubated with the dye; however, the read-out of the absorption was carried out without application of MTT. No influence was found of the treatment with dyes compares with the BSS control experiments. These control experiments were repeated three times.

A comparison of the survival of ARPE-19 and RPE cells, respectively, in BSS after 30, 60, 120, and 300 s indicated for the time of incubation that the cell vitality is statistically not significantly influenced by the addition of 0.1, 0.25, and 0.5% of the dye 3,3′-di-(4-sulfobutyl)-1,1,1′,1′-tetramethyl-di-1*H*-benz[*e*]indocarbocyanine (**4**), respectively; see Figure 4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Staining of pig's eye, stability of naphthocyanine dyes, NMR spectra, and HPLC analyze.

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ABBREVIATIONS USED

LLI, lamina limitans interna; ICG, indocyanine green; NIR, near-infrared; BSS, balanced salt solution where BSS plus is a commercial name; MTT, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide; RP 18, reversed phase coated silica by 18 carbon chains; SEM, standard error of the mean; ARPE 19, a human adult retinal pigment epithelial cell line; RPE, RPE 19 cells are a commercially available cell line [American Type Culture Collection (ATCC)]; HRMS, high-resolution mass spectrum

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