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ORIGINAL PAPER

Thiol-functionalized anthraquinones: mass spectrometry and electrochemical studies

Paweł Niedziałkowski · Tadeusz Ossowski ·
Radosław Majewski · Zdzisława Nowakowska ·
Grzegorz Schroeder

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Abstract In this work, the synthesis of various thiol-functionalized anthraquinone compounds is presented. The studied compounds were characterized by mass spectrometry and the main fragmentation pathways are discussed. The compounds studied formed stable self-assembled monolayers (SAMs) in the gold surface. The parameters for the reduction processes in the gold surface of the studied new anthraquinones were determined by cyclic voltammetry tests.

Keywords Anthraquinones · Mass spectrometry · Cyclic voltammetry

Introduction

Anthraquinone derivatives play a very important role in medicine as the basic unit for the design of medical drugs [1]. Anthraquinone is usually connected to sugars, amines, peptides, and others molecules forming specific combinations of chemical and biological activity. This group of compounds can be used as a potential transcription factor because they show DNA interaction binding and recognition of specific sentences of DNA binding domains [2, 3]. Peptide derivatives of anthraquinone [4, 5] show activity as histochemical reagents for detection of TTP I activity [6, 7].

P. Niedziałkowski (✉) · T. Ossowski · R. Majewski
Faculty of Chemistry, University of Gdańsk,
Sobieskiego 18/19, 80-952 Gdańsk, Poland
e-mail: pawel@chem.univ.gda.pl

Z. Nowakowska · G. Schroeder
Faculty of Chemistry, Adam Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland

From this point of view, synthesis of connections of anthraquinone and peptides is an important part of investigation currently. Chemical properties like coordination, redox activity, and spectroscopic properties are the key problem for understanding the medical (anticancer) activity of anthraquinones. Anthraquinone derivatives are often used as model compounds for studying mechanisms of biologically important redox processes involving anthracyclines, including peroxidation mediated by metal ions and superoxide generation in the cell [8–10]. Anthraquinone derivatives can also be used for the detection of complementary nucleic acids in DNA [11].

In this paper, the synthesis of various thiol-functionalized anthraquinone compounds forming self-assembled monolayers (SAMs) in the gold surface and their characterization by mass spectrometry and electrochemical methods were studied.

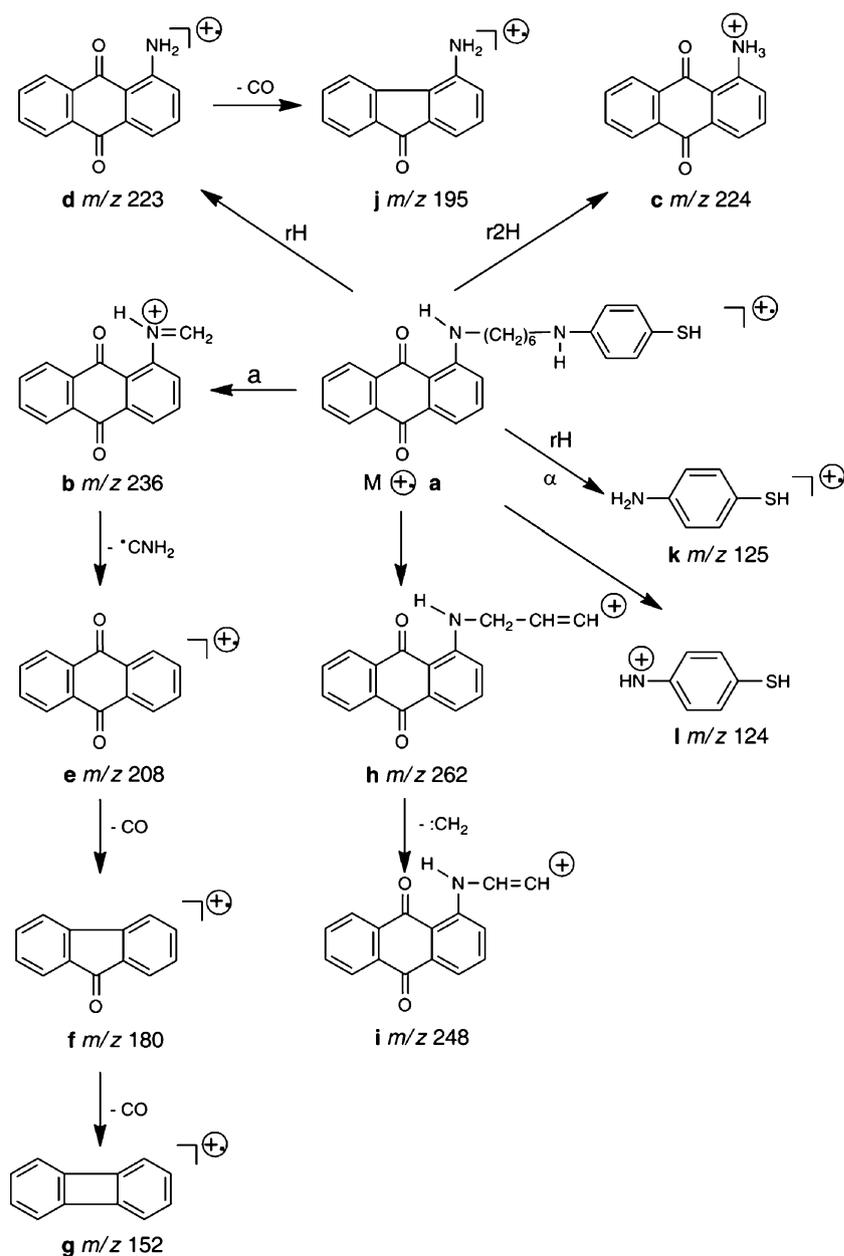
Results and discussion

Eight derivatives of anthraquinone were synthesized as compounds with nucleophilic and redox groups. The thiol-functionalized anthraquinones are characterized by two types of different-length linkers, the first only with an aliphatic chain $(\text{CH}_2)_n$ and the second with $(\text{CH}_2)_n\text{NHC}_6\text{H}_4$ groups. The studied compounds formed self-assembled monolayers (SAMs) by terminal $-\text{SH}$ groups in the gold surface. The chain length determined the redox properties in gold materials.

MS studies

The purpose of this investigation was to elucidate the EI–MS fragmentations of eight new derivatives of anthraquinone.

Fig. 1 Main fragmentation pathways of 1-[6-(4-mercaptophenylamino)hexylamino]anthraquinone (**10**)



The fragmentation pathways of the molecular ions of the compounds investigated were detected by using B²/E linked-scan spectra. As an example, the fragmentation pathway proposed for 1-[6-(4-mercaptophenylamino)hexylamino]anthraquinone (**10**) is shown in Fig. 1, and its fragmentation behavior could be extended to the other compounds.

Examination of the mass spectra of compounds **5–12** reveals no signal of the molecular ion of compounds **5** and **9**, and very small relative abundance of ion **a** of **6** and **10**, as well as an increase in its abundance with increasing length of the *n*-alkyl side chain to ten methylene groups.

For all compounds studied, ions **b** are formed directly from the molecular ions, as a result of α -cleavage of the structure with the radical site localized on the nitrogen atom of the 1-aminoanthraquinone moiety. For compounds **9–12**, the α -cleavage of the C_{sp3}–C_{sp3} bond next to the nitrogen atom of the 4-mercaptoaniline moiety was also observed, and the ion **m** at *m/z* = 138 was obtained. This type of fragmentation gives ions of lower abundance (1.0–20.1% r.a.) than that of ions **b**.

Decomposition of the molecular ions also proceeds via a rearrangement of two hydrogen atoms to the nitrogen atom attached to the anthraquinone moiety and cleavage of the

N–C_{sp3} bond. This fragmentation provides even-electron ion **c** at $m/z = 224$. Consequently, the α -cleavage of the N–C_{sp3} bond with one hydrogen atom rearrangement leads to the odd-electron 1-aminoanthraquinone ion **d** at $m/z = 223$. In the next step of decomposition, this ion loses a molecule of a CO, and the ion **j** at $m/z = 195$ is formed.

In the EI–MS spectra of **5–12**, two other signals appear at $m/z = 180$ and 152 , which can be assigned to the fragmentary ions **f** and **g**, respectively. The loss of a neutral CO molecule from the odd-electron anthraquinone ion **e** ($m/z = 208$) leads to the formation of fluorenone ion **f**, which loses the second molecule of CO to give the highly excited *o*-biphenylene ion **g**. The prime driving force for such eliminations is the stability of the product ion **g** [12]. According to the B²/E linked scan spectra the fragment ion **h** at $m/z = 262$ was formed directly from the molecular ions by cleavage of the C_{sp3}–C_{sp3} bond with simultaneous elimination of a H₂ molecule. In the next step of mass fragmentation, the inductive cleavage of the C–C bond in this ion eliminates a CH₂ fragment giving the even-electron fragment ion **i** at $m/z = 248$. Among 1-(mercaptoalkyl-amino)anthraquinones **5–8** only the spectrum of compound **1** shows high relative abundance of ions **h** and **i**.

The loss of H₂S is a probable fragmentation mode in primary thiols to give olefinic ions of mass M–34. The first

step of elimination of the H₂S molecule is the rearrangement of the hydrogen atom from the alkyl chain to the sulfur atom of the mercapto group, and the next is inductive cleavage of the C_{sp3}–S bond. For **5**, this very abundant process gives the base peak in the spectrum. In the case of **6–8** the relative abundance of the [M–H₂S]⁺ is lower than 3%.

In contrast to the EI spectra of **5–8**, in the spectra of **9–12** the [M–H₂S]⁺ ions were not observed. However, for **11** and **12**, the ejection of the neutral sulfur atom was observed with the relative abundance of 5.4 and 11.2%, respectively.

For **9–12**, the formation of the odd-electron fragment ion **k** at $m/z = 125$ proceeds by the transfer of a hydrogen atom from the alkyl chain to the nitrogen atom attached to the 4-mercaptobenzyl ring. In the next step of the fragmentation, a cleavage of the C_{sp3}–N bond occurs. The EI–MS data of anthraquinone derivatives **5–12** are collected in Table 1.

MALDI-TOF MS

In the presented study, the MALDI-TOF method was applied to confirm the structure of the investigated compounds. The MALDI-TOF mass spectra of the obtained derivatives indicate that these compounds do not form dimers.

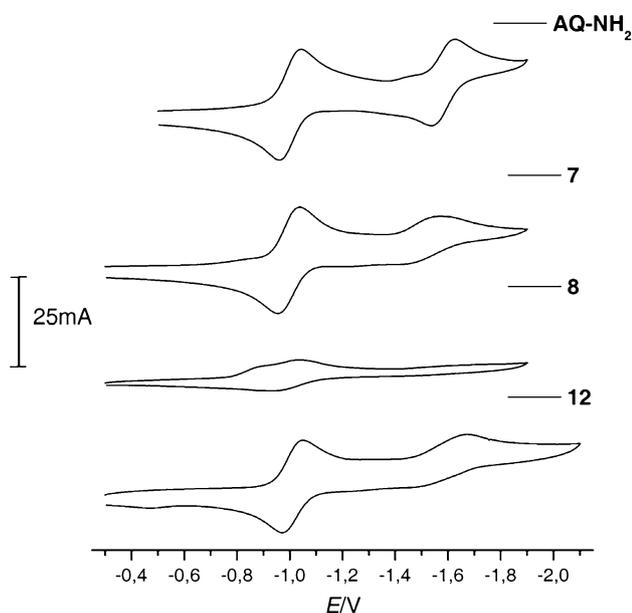
Table 1 Selected mass spectral data (m/z and peak abundance in %) for **5–12**

Ion	Elemental composition	m/z	Relative abundance %							
			5	6	7	8	9	10	11	12
M ⁺	C ₁₇ H ₁₅ NO ₂ S	297	–	–	–	–	–	–	–	–
	C ₂₀ H ₂₁ NO ₂ S	339	–	2.4	–	–	–	–	–	–
	C ₂₂ H ₂₅ NO ₂ S	367	–	–	20.6	–	–	–	–	–
	C ₂₄ H ₂₉ NO ₂ S	395	–	–	–	27.8	–	–	–	–
	C ₂₃ H ₂₀ N ₂ O ₂ S	388	–	–	–	–	–	–	–	–
	C ₂₆ H ₂₆ N ₂ O ₂ S	430	–	–	–	–	–	4.4	–	–
	C ₂₈ H ₃₀ N ₂ O ₂ S	458	–	–	–	–	–	–	33.1	–
	C ₃₀ H ₃₄ N ₂ O ₂ S	486	–	–	–	–	–	–	–	51.3
b	C ₁₅ H ₁₀ NO ₂	236	20.8	11.8	100	100	3.2	21.0	100	100
c	C ₁₄ H ₁₀ NO ₂	224	8.0	6.8	11.5	13.6	–	6.6	22.6	28.7
d	C ₁₄ H ₉ NO ₂	223	32.9	100	22.1	18.2	–	15.4	60.3	38.9
e	C ₁₄ H ₈ O ₂	208	15.4	2.2	8.6	9.9	–	5.2	10.3	14.4
f	C ₁₃ H ₈ O	180	18.6	2.5	5.1	6.1	–	2.3	6.2	9.8
g	C ₁₂ H ₈	152	23.5	3.1	8.7	8.5	–	3.0	8.5	12.7
h	C ₁₇ H ₁₂ NO ₂	262	40.8	1.5	3.9	1.9	1.0	3.2	7.1	29.5
i	C ₁₆ H ₁₀ NO ₂	248	17.9	1.0	2.0	1.5	37.6	64.2	7.6	5.2
j	C ₁₃ H ₉ NO	195	8.0	21.0	5.1	4.2	1.1	3.3	12.1	11.2
k	C ₆ H ₇ NS	125	–	–	–	–	37.0	51.6	48.5	54.5
l	C ₆ H ₆ NS	124	–	–	–	–	100	100	24.2	40.0
m	C ₇ H ₈ NS	138	–	–	–	–	1.0	3.7	8.2	20.1
n	C ₅ H ₆ N	80	–	–	–	–	29.7	31.2	14.5	19.8

Table 2 Formal potentials E_1^0 and E_2^0 and differences between cathodic and anodic peak potentials for both reduction steps ΔE_{p1} and ΔE_{p2} versus Ag/AgCl calculated from cyclic voltammetric curves obtained for all derivatives

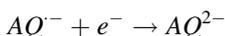
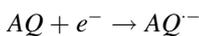
Compound	E_1^0/V	$\Delta E_{p1}/mV$	E_2^0/V	$\Delta E_{p2}/mV$	E_{pc2}/V	E_{pa3}/V
AQ-NH ₂	-1.010	88	-1.600	90	-	-
5	-1.013	78	-	-	-1.574	-
6	-1.013	78	-	-	-1.692	-
7	-0.995	83	-	-	-1.565	-
8	-0.993	98	-	-	-	-
9	-1.067	65	-	-	-	-
10	-1.006	63	-	-	-	-
11	-1.020	73	-	-	-1.657	-0.495
12	-1.008	68	-	-	-1.667	-0.476

For derivatives **5–7** and **11–12** and the second reduction step, only cathodic peak potentials E_{pc2} are given. For derivatives **11–12**, an additional anodic peak E_{pa3} is present. GC electrode scan rate 0.1 V/s

**Fig. 2** Cyclic voltammetry of 1-aminoanthraquinone and compounds **7**, **8**, and **12** on a glassy carbon electrode in DMF solution. 0.1 M TBAP versus Ag/AgCl, scan rate 0.1 V/s

Electrochemical studies

The parameters for the two reduction processes of the anthraquinones determined from cyclic voltammetric experiments are given in Table 2. All quinone derivatives like 1-aminoanthraquinone (AQ-NH₂) in nonaqueous solution undergo two reversible one-electron steps. The first step leads to formation of a radical anion and the second reduction step to a dianion [13].



Voltammetric curves of 1-aminoanthraquinone and compounds **7**, **8**, and **12** are demonstrated in Fig. 2;

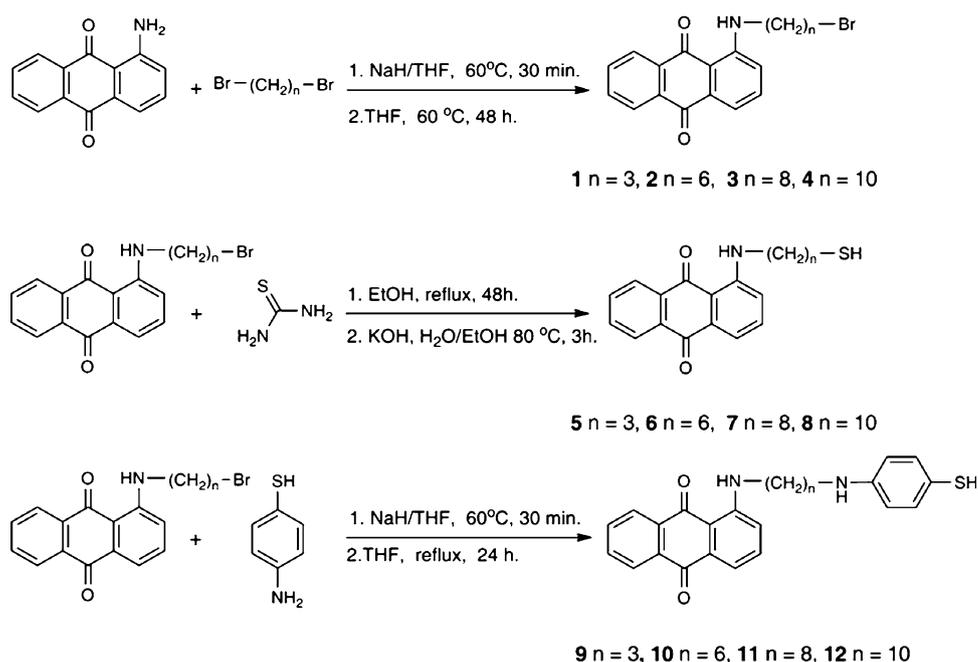
Scheme 1 whereas redox potentials obtained for all compounds are gathered in Table 2. For the obtained compounds, the first reduction step is indeed fully reversible or quasi reversible in case of compound **8** but for derivatives **5**, **6**, and **7**, the second step is irreversible, which indicates the EC mechanism. The electrochemical reaction is followed by a chemical reaction and the obtained new product is inactive electrochemically. Compounds **11** and **12** behave a little differently than **5–7**: an additional anodic peak (E_{pa3}) is present. So, the product of the follow-up reaction is electrochemically active. This behavior is similar to that of 3,5-di-*tert*-butyl-1,2-benzoquinone reported in the literature [14]. Lack of the second reduction step can be observed for derivatives **8**, **9**, and **10**, but we cannot confirm that not one but two electrons are involved in the reduction process for two particular compounds.

Experimental

1,3-Dibromopropane, 1,6-dibromohexane, and 1,8-dibromooctane were purchased from Merck, 1,10-dibromodecane was obtained from Lancaster, thiourea was from POCh (Gliwice, Poland). All solvents were purified and dried using standard methods. THF was distilled from sodium and benzophenone.

Thin layer chromatography (TLC) was performed on precoated plates (Merck TLC aluminum sheets silica 60 F₂₅₄) with detection by UV light. NMR spectra were recorded on a Varian Mercury-400BB (400 MHz) spectrometer using TMS as reference signal. Low-resolution mass spectra were recorded on an AMD 402 two-sector mass spectrometer (AMD Intectra, Germany) of B/E geometry. Elemental compositions of the ions were determined with an error of less than 5 ppm in relation to perfluorokerosene (Fluka, Switzerland) at a resolving

Scheme 1



power of 10,000. Metastable ions were recorded on the same instrument using linked scans (B^2/E). The compounds were introduced into the mass spectrometer using a direct insertion probe in the EI mode (70 eV) with an accelerating voltage of 8 kV, a source temperature of 200°C and an inlet temperature of 70–150°C. MALDI mass spectra were performed on a Biflex III MALDI-TOF mass spectrometer. IR spectra were recorded on a Bruker IFS66 spectrometer using KBr pellets. Elemental analysis data were recorded on a Carlo-Erba CHNS-O EA1108 elemental analyzer. Their results agreed favorably with the calculated values.

Electrochemical measurements

In all electrochemical experiments, *N,N*-dimethylformamide (99.8%) was used as the solvent. Tetrabutylammonium perchlorate served as supporting electrolyte. Cyclic voltammetric (CV) curves were obtained using the three-electrode system provided by an Autolab PGSTAT 30 (Eco Chemie BV, The Netherlands) potentiostat. All curves obtained were corrected for the background. A glassy carbon (GC) electrode of radius $r = 1.5$ mm served as the working electrode. Each time before use, the electrodes were briefly polished with 0.1 m Al_2O_3 powder on a wet pad. The differences in cathodic and anodic peak potentials ΔE_{p1} and ΔE_{p2} are given as a measure of the reversibility of the systems. The formal potentials E_1^0 and E_2^0 were calculated as the means of the corresponding cathodic and anodic peak potentials. For the second reduction step of compounds **5–7** and **11–12**, the formal potentials could not be calculated, thus only the cathodic peak potentials E_{pc2} are given.

General procedure for the synthesis of 1-(bromoalkylamino)anthracene-9,10-diones **1–4**

To a stirred solution of 1.5 g 1-aminoanthracene-9,10-dione (6.71 mmol) in 10 cm³ of dry THF was added dropwise 2.13 g sodium hydride (60% in mineral oil, 53.3 mmol) in 100 cm³ of THF. The mixture was stirred at 60°C. After 30 min, the appropriate dibromoalkane (13.40 mmol) in 15 cm³ of THF was slowly added to the reaction mixture and stirred at 60°C for 48 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 , the solution was washed with water (3×100 cm³), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2).

1-(3-Bromopropylamino)anthracene-9,10-dione (**1**, $C_{17}H_{14}NO_2Br$)

Yield 1.97 g (85.3%); red solid; m.p.: 111–113°C; TLC: $R_f = 0.90$ (CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.27$ – 2.34 (p, 2H, CH_2 – CH_2 – CH_2), 3.57–3.60 (t, 2H, NH – CH_2 – CH_2 , $J = 6.4$ Hz), 4.02–4.04 (t, 2H, CH_2 – CH_2 – Br , $J = 5.4$ Hz), 7.03–7.06 (dd, 1H, H-2 Ar, $J = 8.8$ Hz, $J = 1.4$ Hz), 7.53–7.57 (t, 1H, H-3 Ar, $J = 8.0$ Hz), 7.62–7.64 (d, 1H, H-3 Ar, $J = 7.2$ Hz), 7.61–7.74 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 7.77–7.80 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 8.24–8.26 (dd, 1H, H-5 Ar, $J = 7.8$ Hz, $J = 1.2$ Hz), 8.29–8.30 (dd, 1H, H-8 Ar, $J = 7.2$ Hz, $J = 0.8$ Hz), 9.90 (s, 1H, NH – CH_2 – CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.12$, 29.61, 43.27 (3 CH_2), 113.86, 115.19, 118.42, 126.91, 126.04,

129.04, 131.15, 133.89, 134.12, 134.72, 135.31, 150.72 (12C, Ar), 183.89, 184.65 (2 C=O, Ar) ppm; MALDI-TOF MS: $m/z = 346.1$ (M+H)⁺; IR (film): $\bar{\nu} = 3,304, 2,959, 2,929, 1,727, 1,668, 1,632, 1,593, 1,463, 1,274, 1,123, 1,072, 741, 710$ cm⁻¹.

1-(6-Bromohexylamino)anthracene-9,10-dione

(2, C₂₀H₂₀NO₂Br)

Yield 1.460 g (84.5%); red solid; m.p.: >300°C; $R_f = 0.91$ (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.22$ – 1.28 (m, 2H, CH₂–CH₂–CH₂–Br), 1.53 – 1.56 (p, 2H, NH–CH₂–CH₂–CH₂, $J = 3.6$ Hz), 1.79 – 1.94 (m, 4H, Br–CH₂–CH₂, NH–CH₂–CH₂), 3.34 – 3.38 (t, 2H, NH–CH₂–CH₂, $J = 7.2$ Hz), 3.42 – 4.46 (t, 2H, CH₂–CH₂–Br, $J = 7.2$ Hz), 7.06 – 7.08 (dd, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.6$ Hz), 7.54 – 7.58 (t, 1H, H-3 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 7.60 – 7.62 (dd, 1H, H-4 Ar, $J = 7.2$ Hz, $J = 1.2$ Hz), 7.69 – 7.73 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 7.75 – 7.79 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz); 8.23 – 8.26 (dd, 1H, H-5 Ar, $J = 8.8$ Hz, $J = 1.2$ Hz), 8.27 – 8.30 (dd, 1H, H-8 Ar, $J = 7.8$ Hz, $J = 1.2$ Hz), 9.76 (s, 1H, NH–CH₂–CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 27.14, 28.31, 28.95, 29.27, 38.14, 44.01$ (6CH₂), $113.11, 116.48, 118.03, 126.89, 127.01, 132.86, 133.20, 133.16, 134.37, 134.88, 135.35, 151.87$ (12C, Ar), $183.12, 184.01$ (2 C=O, Ar) ppm; MALDI-TOF MS: $m/z = 388.2$ (M+H)⁺; IR (KBr): $\bar{\nu} = 3,419, 3,305, 2,924, 2,854, 1,666, 1,637, 1,606, 1,544, 1,453, 1,281, 1,165, 1,070, 1,007, 878, 737, 707$ cm⁻¹.

1-(8-Bromooctylamino)anthracene-9,10-dione

(3, C₂₂H₂₄NO₂Br)

Yield 2.53 g (91.2%); red oil; $R_f = 0.91$ (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ – 1.54 (m, 8H, NH–CH₂–CH₂–CH₂–CH₂, CH₂–CH₂–CH₂–CH₂–Br), 1.74 – 1.81 (p, 2H, CH₂–CH₂–Br, $J = 6.8$ Hz, $J = 7.6$ Hz), 1.83 – 1.91 (p, 2H, NH–CH₂–CH₂, $J = 6.8$ Hz, $J = 7.4$ Hz), 3.31 – 3.36 (q, 2H, NH–CH₂–CH₂, $J = 6.2$ Hz), 3.40 – 4.44 (t, 2H, CH₂–CH₂–Br, $J = 6.8$ Hz), 7.05 – 7.07 (dd, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.2$ Hz), 7.53 – 7.56 (t, 1H, H-3 Ar, $J = 8.0$ Hz, $J = 1.4$ Hz), 7.58 – 7.60 (dd, 1H, H-4 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 7.67 – 7.73 (dt, 1H, H-6 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 7.75 – 7.79 (dt, 1H, H-7 Ar, $J = 7.9$ Hz, $J = 1.6$ Hz), 8.23 – 8.25 (dd, 1H, H-5 Ar, $J = 7.6$ Hz, $J = 1.2$ Hz), 8.27 – 8.29 (dd, 1H, H-8 Ar, $J = 7.8$ Hz, $J = 1.4$ Hz), 9.75 (s, 1H, NH–CH₂–CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 23.31, 29.59, 30.61, 32.99, 34.14, 38.98, 43.18, 67.49$ (8CH₂), $113.01, 115.71, 118.06, 126.80, 129.02, 132.07, 133.01, 133.25, 134.05, 134.88, 135.44, 151.94$ (12C, Ar), $184.00, 185.04$ (2 C=O, Ar) ppm; MALDI-TOF MS: $m/z = 415.2$ (M+H)⁺; IR (KBr): $\bar{\nu} = 3,423, 2,932, 2,841, 1,670, 1,645, 1,600, 1,548, 1,384, 1,287, 1,167, 1,065, 1,011, 829, 801, 732, 711$ cm⁻¹.

1-(10-Bromodecylamino)anthracene-9,10-dione

(4, C₂₄H₂₈NO₂Br)

Yield 3.12 g (78.7%); red oil; $R_f = 0.70$ (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.21$ – 1.52 (m, 12H, NH–CH₂–CH₂–CH₂–CH₂, CH₂–CH₂–CH₂–CH₂–CH₂–Br), 1.67 – 1.87 (m, 4H, NH–CH₂–CH₂, CH₂–CH₂–Br), 4.20 – 4.35 (m, 4H, NH–CH₂–CH₂, CH₂–CH₂–Br), 7.04 – 7.06 (d, 1H, H-2 Ar, $J = 8.0$ Hz), 7.50 – 7.56 (dd, 1H, H-3 Ar, $J = 6.4$ Hz, $J = 1.4$ Hz), 7.57 – 7.59 (dd, 1H, H-4 Ar, $J = 3.2$ Hz, $J = 0.8$ Hz), 7.67 – 7.73 (dt, 1H, H-6 Ar, $J = 7.4$ Hz, $J = 1.6$ Hz), 7.73 – 7.77 (dt, 1H, H-7 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 8.22 – 8.24 (dd, 1H, H-5 Ar, $J = 7.2$ Hz, $J = 1.6$ Hz), 8.26 – 8.28 (d, 1H, H-8 Ar, $J = 7.6$ Hz), 9.76 (s, 1H, NH–CH₂–CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 23.18, 23.98, 27.35, 28.34, 29.90, 29.50, 33.02, 38.97, 43.20, 68.36$ (10CH₂), $113.05, 115.70, 118.05, 126.84, 126.86, 131.06, 132.70, 133.05, 133.27, 134.08, 135.28, 152.03$ (12C, Ar); $184.00, 185.12$ (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 444.0$ (M+H)⁺; IR (KBr): $\bar{\nu} = 3,305, 2,958, 2,928, 1,728, 1,660, 1,630, 1,593, 1,463, 1,380, 1,269, 1,123, 1,072, 740, 709$ cm⁻¹.

General procedure for the synthesis of 1-(mercaptoalkylamino)anthracene-9,10-diones 5–8

A solution of 1-(bromoalkylamino)anthracene-9,10-dione (1.45 mmol) and 580 mg thiourea (7.62 mmol) in 50 cm³ of anhydrous ethanol was heated under reflux for 24 h. The mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. Potassium hydroxide (2.03 g, 36.32 mmol) dissolved in a mixture of argon-purged water and ethanol (5:1) was added to the residue and the reaction mixture was heated at 80°C for 3 h. The solvent was removed under vacuum. After acidifying with 1 M HCl, 250 cm³ of CH₂Cl₂ were added and the organic layer was washed with water (3 × 100 cm³). The solution was dried over anhydrous MgSO₄, filtered, and the solvent was evaporated to give the crude product which was purified by column chromatography (SiO₂, CH₂Cl₂:MeOH = 5:0.1).

1-(3-Mercaptopropylamino)anthracene-9,10-dione

(5, C₁₇H₁₅NO₂S)

Yield 388 mg (90.0%); m.p.: 240–241°C; $R_f = 0.5$ (CH₂Cl₂:MeOH = 5:0.1); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.57$ (s, 1H, SH), 2.16 – 2.09 (p, 2H, CH₂–CH₂–CH₂), 3.47 – 3.51 (q, 2H, NH–CH₂–CH₂, $J = 6.6$ Hz, $J = 5.6$ Hz), 4.01 – 4.05 (q, 2H, CH₂–CH₂–Br, $J = 4.6$ Hz, $J = 2.4$ Hz), 7.03 – 7.06 (dd, 1H, H-2 Ar, $J = 8.6$ Hz, $J = 0.8$ Hz), 7.53 – 7.57 (dt, 1H, H-3 Ar, $J = 8.1$ Hz, $J = 1.2$ Hz), 7.62 – 7.64 (dd, 1H, H-4 Ar, $J = 7.2$ Hz, $J = 1.2$ Hz), 7.70 – 7.74 (dt, 1H, H-6 Ar, $J = 8.2$ Hz, $J = 1.6$ Hz), 7.76 – 7.80 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 8.24 – 8.26 (dd, 1H, H-5 Ar,

$J = 7.6$ Hz, $J = 0.8$ Hz), 8.29–8.30 (dd, 1H, H-8 Ar, $J = 6.8$ Hz, $J = 0.8$ Hz), 9.90 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 23.40, 29.12, 43.19$ (3 CH_2); 114.94, 115.65, 119.21, 126.84, 127.06, 133.07, 133.38, 134.08, 134.68, 135.21, 135.51, 151.90 (12C, Ar); 182.90, 185.65 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 298.4$ (M+H) $^+$; IR (KBr): $\bar{\nu} = 3,431, 2,923, 2,851, 1,665, 1,629, 1,623, 1,593, 1,509, 1,302, 1,272, 1,070, 996, 915, 828, 802, 734, 708$ cm^{-1} .

1-(6-Mercaptohexylamino)anthracene-9,10-dione

(6, $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}$)

Yield 378 mg (86.0%); m.p.: 189–190°C; $R_f = 0.48$ (CH_2Cl_2 :MeOH = 5:0.1); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.50\text{--}1.56$ (m, 5H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$, $\text{CH}_2\text{-SH}$), 1.73–1.80 (m, 4H, $\text{Br-CH}_2\text{-CH}_2$, $\text{NH-CH}_2\text{-CH}_2$), 2.68–2.73 (q, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.2$ Hz), 3.31–3.35 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-SH}$, $J = 6.4$ Hz, $J = 4.4$ Hz), 7.03–7.06 (dd, 1H, H-2 Ar, $J = 8.6$ Hz, $J = 1.6$ Hz), 7.51–7.55 (dd, 1H, H-3 Ar, $J = 7.8$ Hz, $J = 1.4$ Hz), 7.57–7.59 (dd, 1H, H-4 Ar, $J = 7.2$ Hz, $J = 1.6$ Hz), 7.68–7.72 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.6$ Hz), 7.73–7.78 (dt, 1H, H-7 Ar, $J = 7.5$ Hz, $J = 1.6$ Hz), 8.22–8.24 (dd, 1H, H-5 Ar, $J = 7.6$ Hz, $J = 1.2$ Hz), 8.26–8.28 (dd, 1H, H-8 Ar, $J = 7.8$ Hz, $J = 1.0$ Hz), 9.75 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.0, 28.40, 29.19, 29.27, 39.19, 43.17$ (6 CH_2); 113.15, 117.53, 118.04, 126.91, 127.03, 133.09, 133.25, 134.10, 134.89, 134.95, 135.48, 151.99 (12C, Ar); 182.98, 185.18 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 340.3$ (M+H) $^+$; IR (KBr): $\bar{\nu} = 3,429, 3,268, 2,925, 2,852, 1,671, 1,629, 1,592, 1,507, 1,268, 1,069, 992, 805, 734, 707$ cm^{-1} .

1-(8-Mercaptooctylamino)anthracene-9,10-dione

(7, $\text{C}_{22}\text{H}_{25}\text{NO}_2\text{S}$)

Yield 215 mg (66.8%); m.p.: 156–157°C; $R_f = 0.47$ (CH_2Cl_2 :MeOH = 5:0.1); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.25\text{--}1.79$ (m, 11H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-SH}$), 2.65–2.70 (q, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.6$ Hz, $J = 7.2$ Hz), 3.30–3.35 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-SH}$, $J = 6.8$ Hz, $J = 5.2$ Hz), 7.04–7.06 (dd, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.6$ Hz), 7.52–7.56 (dd, 1H, H-3 Ar, $J = 8.0$ Hz, $J = 1.4$ Hz), 7.57–7.59 (dd, 1H, H-4 Ar, $J = 7.2$ Hz, $J = 1.2$ Hz), 7.68–7.72 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.6$ Hz), 7.74–7.78 (dt, 1H, H-7 Ar, $J = 7.4$ Hz, $J = 1.6$ Hz), 8.22–8.24 (dd, 1H, H-5 Ar, $J = 7.4$ Hz, $J = 1.6$ Hz), 8.26–8.28 (dd, 1H, H-8 Ar, $J = 7.8$ Hz, $J = 1.2$ Hz), 9.74 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 22.18, 28.35, 30.60, 33.02, 34.11, 38.98, 43.20, 65.33$ (8 CH_2); 113.03, 115.67, 118.04, 126.82, 127.87, 131.05, 133.02, 133.25, 134.06, 134.89, 135.42, 151.99 (12C, Ar); 183.92, 185.05 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 368.3$ (M+H) $^+$; IR (KBr): $\bar{\nu} = 3,274, 2,926, 2,852, 1,664, 1,660,$

1,630, 1,592, 1,506, 1,407, 1,272, 1,070, 1,004, 806, 737, 710 cm^{-1} .

1-(10-Mercaptodecylamino)anthracene-9,10-dione

(8, $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{S}$)

Yield 215 mg (46.0%); m.p.: 127–128°C; $R_f = 0.43$ (CH_2Cl_2 :MeOH = 5:0.1); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.25\text{--}1.79$ (m, 13H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-SH}$), 2.64–2.71 (p, 2H, $\text{CH}_2\text{-CH}_2\text{-SH}$, $J = 6.8$ Hz, $J = 7.2$ Hz, $J = 7.6$ Hz), 3.30–3.37 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 6.8$ Hz, $J = 6.4$ Hz, $J = 5.6$ Hz), 4.20–4.25 (q, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 5.8$ Hz, $J = 5.4$ Hz), 4.27–4.31 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-SH}$, $J = 7.2$ Hz, $J = 5.4$ Hz), 7.05–7.07 (dd, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.2$ Hz), 7.52–7.56 (t, 1H, H-3 Ar, $J = 6.4$ Hz), 7.58–7.60 (dd, 1H, H-4 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 7.68–7.72 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.6$ Hz), 7.74–7.78 (dt, 1H, H-7 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 8.22–8.25 (dd, 1H, H-5 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 8.27–8.29 (dd, 1H, H-8 Ar, $J = 7.6$ Hz, $J = 1.2$ Hz), 9.73 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 23.19, 23.99, 27.35, 28.25, 29.15, 29.56, 34.01, 39.18, 42.54, 58.19$ (10 CH_2); 113.25, 116.01, 118.33, 126.41, 129.00, 131.61, 132.70, 133.64, 133.91, 134.57, 135.18, 150.55 (12C, Ar); 183.15, 185.61 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 396.5$ (M+H) $^+$; IR (KBr): $\bar{\nu} = 3,277, 1,728, 1,668, 1,630, 1,593, 1,509, 1,406, 1,271, 1,124, 1,072, 1,040, 737, 710$ cm^{-1} .

General procedure for the synthesis of 1-[(4-mercapto-phenylamino)alkylamino]anthracene-9,10-diones 9–12

Sodium hydride (60% in mineral oil, 190 mg, 4.77 mmol) in 20 cm^3 of THF was slowly dropped into a stirred solution of 4-aminobenzenethiol (1.59 mmol) in 50 cm^3 of dry THF during 30 min. After 30 min of stirring at room temperature, the reaction mixture was heated to 60°C for the next 30 min. To the reaction mixture was then slowly added 1-(bromoalkylamino)anthracene-9,10-dione (1.75 mmol) dissolved in 20 cm^3 of dry THF. The mixture was heated under reflux for 24 h. The solution was filtered, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2 , CH_2Cl_2).

1-[3-(4-Mercaptophenylamino)propylamino]anthracene-9,10-dione (9, $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$)

Yield 260 mg (42.5%); m.p.: >300°C; $R_f = 0.51$ (CH_2Cl_2 :MeOH = 5:0.2); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.64$ (s, 1H, SH), 2.18–2.11 (p, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$, $J = 7.6$ Hz), 3.46–3.50 (q, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 6.6$ Hz, $J = 5.6$ Hz), 4.02–4.05 [q, 2H, $\text{CH}_2\text{-CH}_2\text{-NH(Ar')}$], $J = 4.6$ Hz, $J = 2.4$ Hz), 6.49–6.51 (d, 2H, Ar', $J = 8.0$ Hz), 6.58–7.60 (dd, 2H, Ar', $J = 6.6$ Hz, $J = 2.2$ Hz), 7.04–7.06 (d, 1H, H-2 Ar, $J = 8.0$ Hz),

7.53–7.55 (t, 1H, H-3 Ar, $J = 8.0$ Hz), 7.61–7.63 (dd, 1H, H-4 Ar, $J = 7.2$ Hz, $J = 1.2$ Hz), 7.70–7.74 (dt, 1H, H-6 Ar, $J = 8.2$ Hz, $J = 1.6$ Hz), 7.76–7.80 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 1.4$ Hz), 8.24–8.26 (dd, 1H, H-5 Ar, $J = 7.6$ Hz, $J = 1.8$ Hz), 8.27–8.30 (dd, 1H, H-8 Ar, $J = 6.8$ Hz, $J = 1.6$ Hz), 9.78 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 29.89, 43.25, 43.68$ (3CH_2); 112.16, 114.98, 115.50, 115.32, 119.12, 124.64, 125.74, 126.23, 133.27, 133.87, 134.18, 134.38, 134.87, 135.58, 135.72, 137.71, 147.35, 151.03 (18 C, Ar); 184.61, 185.86 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 389.4$ ($\text{M}+\text{H}^+$); IR (KBr): $\bar{\nu} = 3,416, 3,332, 3,208, 3,021, 1,889, 1,622, 1,590, 1,490, 1,421, 1,274, 1,175, 1,084, 821, 673$ cm^{-1} .

1-[6-(4-Mercaptophenylamino)hexylamino]anthracene-9,10-dione (10, C₂₆H₂₆N₂O₂S)

Yield 345 mg (50.5%); m.p.: $>300^\circ\text{C}$; $R_f = 0.47$ ($\text{CH}_2\text{Cl}_2:\text{MeOH} = 5:0.1$); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.20\text{--}1.69$ (m, 5H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$, SH), 1.79–1.86 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.2$ Hz, $J = 7.6$ Hz), 3.08–3.16 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.4$ Hz), 3.32–3.37 (q, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.4$ Hz, $J = 4.8$ Hz), 3.72–3.85 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$, $J = 7.2$ Hz), 6.49–6.50 (d, 2H, Ar' , $J = 8.0$ Hz), 6.58–7.61 (dd, 2H, Ar' , $J = 6.6$ Hz, $J = 1.6$ Hz), 7.06–7.08 (d, 1H, H-2 Ar, $J = 8.0$ Hz), 7.53–7.55 (t, 1H, H-3 Ar, $J = 8.0$ Hz), 7.70–7.61 (d, 1H, H-4 Ar, $J = 7.2$ Hz), 7.69–7.73 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.6$ Hz), 7.75–7.79 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 6.4$ Hz, $J = 1.2$ Hz), 8.24–8.26 (d, 1H, H-5 Ar, $J = 7.6$ Hz), 8.27–8.29 (d, 1H, H-8 Ar, $J = 7.2$ Hz), 9.78 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.05, 27.17, 29.04, 29.54, 43.05, 43.82$ (6CH_2); 113.11, 115.28, 115.60, 115.84, 118.09, 125.95, 126.45, 126.88, 126.94, 133.15, 133.60, 134.18, 134.60, 135.26, 135.55, 138.57, 142.82, 152.03 (18C, Ar); 184.07, 185.25 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 431.5$ ($\text{M}+\text{H}^+$); IR (film): $\bar{\nu} = 3,462, 3,370, 3,213, 3,024, 2,929, 2,854, 1,660, 1,620, 1,592, 1,492, 1,271, 1,175, 1,089, 822, 754, 734, 709$ cm^{-1} .

1-[8-(4-Mercaptophenylamino)octylamino]anthracene-9,10-dione (11, C₂₈H₃₀N₂O₂S)

Yield 375 mg (51.5%); m.p.: $260\text{--}261^\circ\text{C}$; $R_f = 0.45$ ($\text{CH}_2\text{Cl}_2:\text{MeOH} = 5:0.1$); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.22\text{--}1.62$ (m, 9H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$, SH), 1.72–1.80 [p, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$], 2.73–2.80 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$), 3.09–3.12 (t, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 6.8$ Hz), 3.32–3.37 (q, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$, $J = 7.2$ Hz, $J = 5.6$ Hz, $J = 5.2$ Hz), 6.48–6.50 (d, 2H, Ar' , $J = 8.8$ Hz), 6.57–7.60 (dd, 2H, Ar' , $J = 9.0$ Hz, $J = 2.2$ Hz), 7.07–7.05 (d, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.6$ Hz), 7.52–7.56 (t, 1H, H-3 Ar, $J = 7.8$ Hz, $J = 1.4$ Hz), 7.57–7.59 (dd, 1H, H-4 Ar,

$J = 7.2$ Hz, $J = 1.6$ Hz), 7.68–7.72 (dt, 1H, H-6 Ar, $J = 7.6$ Hz, $J = 1.2$ Hz), 7.73–7.78 (dt, 1H, H-7 Ar, $J = 7.4$ Hz, $J = 1.6$ Hz), 8.23–8.25 (dd, 1H, H-5 Ar, $J = 7.6$ Hz, $J = 1.6$ Hz), 8.27–8.28 (dd, 1H, H-8 Ar, $J = 6.4$ Hz, $J = 1.2$ Hz), 9.74 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.27, 29.28, 29.42, 43.15, 45.13, 76.90, 77.22, 77.53$ (8CH_2); 111.88, 115.62, 115.87, 116.12, 118.06, 124.82, 125.21, 126.85, 126.93, 132.10, 132.94, 134.12, 134.75, 135.12, 135.50, 138.51, 141.65, 150.78 (18C, Ar); 183.46, 184.91 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 459.3$ ($\text{M}+\text{H}^+$); IR (film): $\bar{\nu} = 3,375, 3,020, 2,926, 2,853, 1,722, 1,664, 1,626, 1,593, 1,507, 1,473, 1,271, 1,175, 1,091, 1,070, 820, 802, 755, 734, 709$ cm^{-1} .

1-[10-(4-Mercaptophenylamino)decylamino]anthracene-9,10-dione (12, C₃₀H₃₄N₂O₂S)

Yield 389 mg (50.3%); m.p.: $>300^\circ\text{C}$; $R_f = 0.58$ ($\text{CH}_2\text{Cl}_2:\text{MeOH} = 5:0.1$); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.24\text{--}1.79$ [m, 13H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$, SH], 1.73–1.81 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.6$ Hz, $J = 7.2$ Hz), 1.82–1.83 (p, 2H, $\text{NH-CH}_2\text{-CH}_2$, $J = 7.2$ Hz, $J = 6.8$ Hz), 3.31–3.42 [m, 4H, $\text{NH-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}_2\text{-NH}(\text{Ar}')$], 6.48–6.50 (d, 2H, Ar' , $J = 8.0$ Hz), 6.58–7.60 (d, 2H, Ar' , $J = 8.4$ Hz), 7.04–7.07 (dd, 1H, H-2 Ar, $J = 8.4$ Hz, $J = 1.2$ Hz), 7.51–7.55 (t, 1H, H-3 Ar, $J = 7.2$ Hz, $J = 8.4$ Hz), 7.58–7.60 (dd, 1H, H-4 Ar, $J = 7.4$ Hz, $J = 1.2$ Hz), 7.68–7.72 (dt, 1H, H-6 Ar, $J = 7.4$ Hz, $J = 1.4$ Hz), 7.74–7.78 (dt, 1H, H-7 Ar, $J = 7.6$ Hz, $J = 1.2$ Hz, $J = 1.6$ Hz), 8.23–8.25 (dd, 1H, H-5 Ar, $J = 7.6$ Hz, $J = 1.8$ Hz), 8.27–8.29 (dd, 1H, H-8 Ar, $J = 9.2$ Hz, $J = 1.6$ Hz), 9.74 (s, 1H, $\text{NH-CH}_2\text{-CH}_2$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 26.48, 27.49, 29.52, 29.94, 32.57, 38.43, 43.19, 44.59, 76.12, 76.49$ (10CH_2); 112.84, 115.12, 115.49, 115.91, 119.01, 125.41, 126.55, 126.95, 127.32, 132.56, 133.35, 134.17, 134.59, 135.18, 135.70, 137.38, 150.09, 154.29 (18C, Ar); 184.49, 185.85 (2 C=O, Ar) ppm; MS (MALDI-TOF): $m/z = 487.5$ ($\text{M}+\text{H}^+$); IR (film): $\bar{\nu} = 3,459, 3,367, 3,209, 2,924, 2,853, 2,599, 1,886, 1,619, 1,592, 1,492, 1,463, 1,284, 1,175, 1,193, 823, 731, 711$ cm^{-1} .

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