Synthesis, Structure, and Optical Properties of Terminally Sulfur-Functionalized Core-Substituted Naphthalene-Bisimide Dyes

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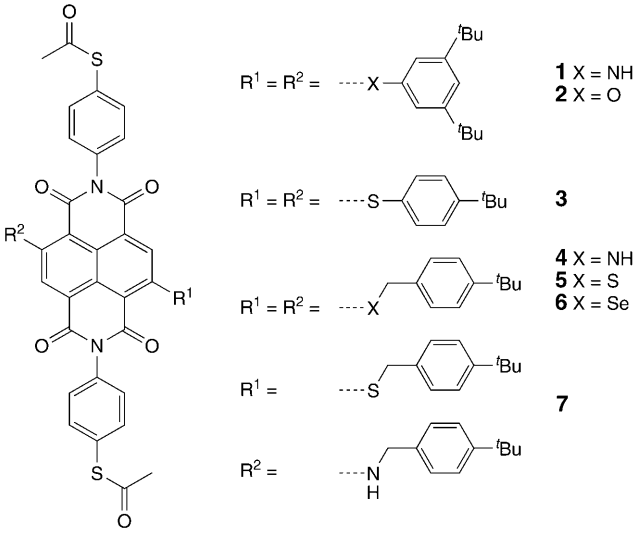
The synthesis, characterization, and optical properties of a series of new 2,6-disubstituted naphthalene-bisimide dyes as molecular rods comprising terminal AcS groups is reported. The first series of dyes (**1**–**3**), comprising phenylhetero (Ph-X) core substituents, cover a broad range of the VIS spectrum, ranging from yellow (**2**) over red (**3**) to blue (**1**). The second series of dyes contains benzylhetero (Bn-X) core substituents (**4**–**7**). For the same heteroatom connecting the substituent to the naphthalene core, both series were found to display comparable colors. For the second series, the colors were blue (**4**), red (**5**), and violet (**6**, **7**). The Ph-X-substituted dyes **1**–**3** are nonfluorescent, in contrast to the Bn-X-substituted compounds **4**–**7**. This rich variety of optical features that can be adjusted by rather small alterations of the core substituents makes these structurally very comparable molecular rods ideal candidates for optically triggered molecular-transport investigations. Also, thanks to the terminal AcS groups, these compounds can be placed between nobel-metal electrodes for optically triggered transport experiments.

Introduction. – In the last few years, several terminally sulfur (S)-functionalized molecules have been successfully immobilized on a single-molecule level between two electrodes, and correlations between their molecular structures and electronic-transport properties have been revealed to some extent [1][2]. A current challenge is to extend such molecular-electronic-transport arrangements with an additional signal capable of triggering the current through the molecular structure. First examples of a single-molecule device responding to an electrochemical trigger have already been reported [3–5]. Alternatively, light may also serve as an external trigger of the electronic current. While molecular switches [6] and shuttles [7] between different electrodes have already been reported, our current focus is to combine electronic excitation of the immobilized molecule with electronic transport. In particular, we strive towards the investigation of optically triggered currents through single molecules, and of single-molecule electroluminescence. Against this background, our interest in rod-like and terminally S-functionalized dye molecules becomes reasonable.

Herein, we report the synthesis, structural analysis, and optical properties of a series of core-substituted naphthalene-bisimide dyes, *i.e.*, the rod-like compounds **1**–**7**, comprising terminal acetyl (Ac)-protected S-atoms.

2. Results and Discussion. – 2.1. *General Strategy.* An ideal dye structure for the envisaged experiments has to fulfill several requirements. For single-molecule experi-

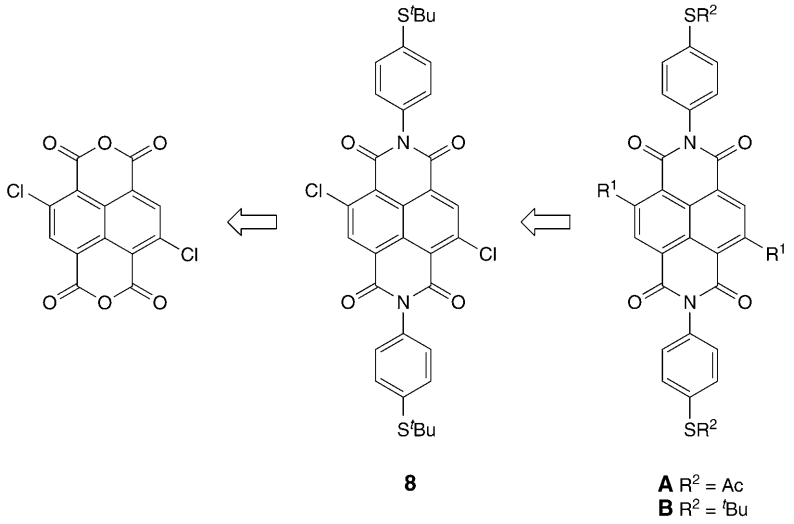


ments in mechanically controlled break junctions (MCB) and junctions based on electromigration, rigid rod-like structures with terminal Ac-protected S-atoms proved to be ideally suited [8][9]. The distance between both terminal S-atoms should be *ca.* 2 nm. Furthermore, the optical properties of the molecular structure should be adjustable to the equipment of the experiment station. In particular, dye structures providing different absorption and emission properties as a function of lateral substituents, without changing the rigid rod-type backbone, are of great interest. Finally, processability, solubility, and, of course, ready chemical access are crucial requirements.

During the search for an ideally suited basic dye structure, we became aware of the studies of *Würthner* and co-workers on core-substituted naphthalene bisimides as fluorophores [10] and as H-bond-directed surface-structure motives [11]. Already the size and the structural symmetry of the naphthalene-bisimide dye were very appealing. In particular, the molecules' symmetry should be reflected in transport investigations, as has been shown for oligo(phenylene-ethynyl) rods [8]. Furthermore, its color is reported to be tunable by the core substituent [10]. Moreover, the fluorescence of the dye seems to depend to some extent on the core substituents. In particular, naphthalene-bisimide dyes with phenylamine substituents are reported to be nonfluorescent [10]. This is a particular interesting feature for optoelectronic, molecule-based devices, as it allows tracking the origin of an observed effect by comparison experiments of two very similar molecules that differ strongly in only one particular optical property. Altogether, the naphthalene-bisimide subunit appeared ideally suited for the envisaged experiments. However, the compounds had to be terminally substituted by AcS groups to become immobilizable between two metallic electrodes.

2.2. *Synthesis.* The retro-synthetic approach to the desired core unit **A** is shown in *Scheme 1*. To provide processability, in particular solubility and chemical stability of the intermediates, the terminal S-atoms were introduced as (*tert*-butyl)sulfanyl groups. The condensation of 4-[(*tert*-butyl)sulfanyl]benzen-1-amine and 2,6-dichloronaphtha-

Scheme 1. *Synthetic Strategy to Access Terminally Acetylsulfanyl-Functionalized Naphthalene-Bisimide Dyes*



lene bisanhydride should provide the chlorinated naphthalene bisimide derivative **8**. Nucleophilic substitution of the Cl-atoms by O-, N-, S-, or Se nucleophiles should then provide access to a variety of dye structures **B** of varying colors. To keep the shape of the series of dyes comparable and to integrate the option to quench the fluorescence, only heteroatom-linked phenyl (Ph) and benzyl (Bn) groups were considered as core substituents. To guarantee solubility of the target dye structures, these Ph and Bn groups had to carry additional peripheral ^{t}Bu groups. Finally, exchange of the ^{t}Bu by Ac groups at both terminal S-atoms would provide a series of core-substituted naphthalene-bisimide dyes **A**.

All here reported dyes were prepared from the common precursor **8**, *i.e.*, *N*,*N*′-bis{[4-(*tert*-butyl)sulfanyl]phenyl}-2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisimide[1]), the synthesis of which is displayed in *Scheme 2*. Both starting compounds for the synthesis of **8** are known [12][13]. While 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride (**9**) was synthesized according to a literature procedure [13], the synthesis of 4-[(*tert*-butyl)sulfanyl]aniline (**10**) [12] has been slightly modified. First, the F-atom of commercially available 1-fluoro-4-nitrobenzene (**11**) was substituted by a ^{t}BuS group by treatment with 1.2 equiv. of sodium 2-methylpropane-2-thiolate in anhydrous DMF for 1 h. The mixture was not heated since this nucleophilic aromatic substitution is exothermic and initially heats the reaction mixture considerably. After workup and column chromatography, compound **12** was isolated in 91% yield as a light-yellow solid. Subsequently, the NO_2 group of **12** was reduced with Sn in HCl/EtOH to afford **10** as a yellowish solid in 95% yield. Next, the bisanhydride **9** was treated with 3.5 equiv. of the aniline **10** in AcOH at 110°. Neither the starting bisan-

[1]) For systematic names, see *Exper. Part.*

hydride **9** nor the resulting target compound **8** were soluble under these reaction conditions. However, immediately after the addition of the aniline **10**, the suspended bisanhydride **9** completely dissolved, and product **8** started to precipitate as a brown solid, which was isolated by filtration in 67% yield. During the synthesis of **8**, a side product was formed, which gave rise to a signal at *m*/*z* 808.74 in the MALDI-TOF mass spectrum. This compound, which was formed in considerable amounts, was formed by substitution of one of the Cl-atoms of the naphthalene core of **8** with **10** as the nucleophile, which points at the reactivity of the Cl-atoms towards nucleophilic substitution. Finally, to overcome the poor solubility of **8**, its Cl-atoms were substituted by Ph-X and Bn-X groups (X = NH, O, S, Se) comprising additional peripheral ^{t}Bu groups to prevent the molecules from forming hardly soluble stacks. This gave rise to compounds **13**–**20** (see *Scheme 2* and *Scheme 4* below).

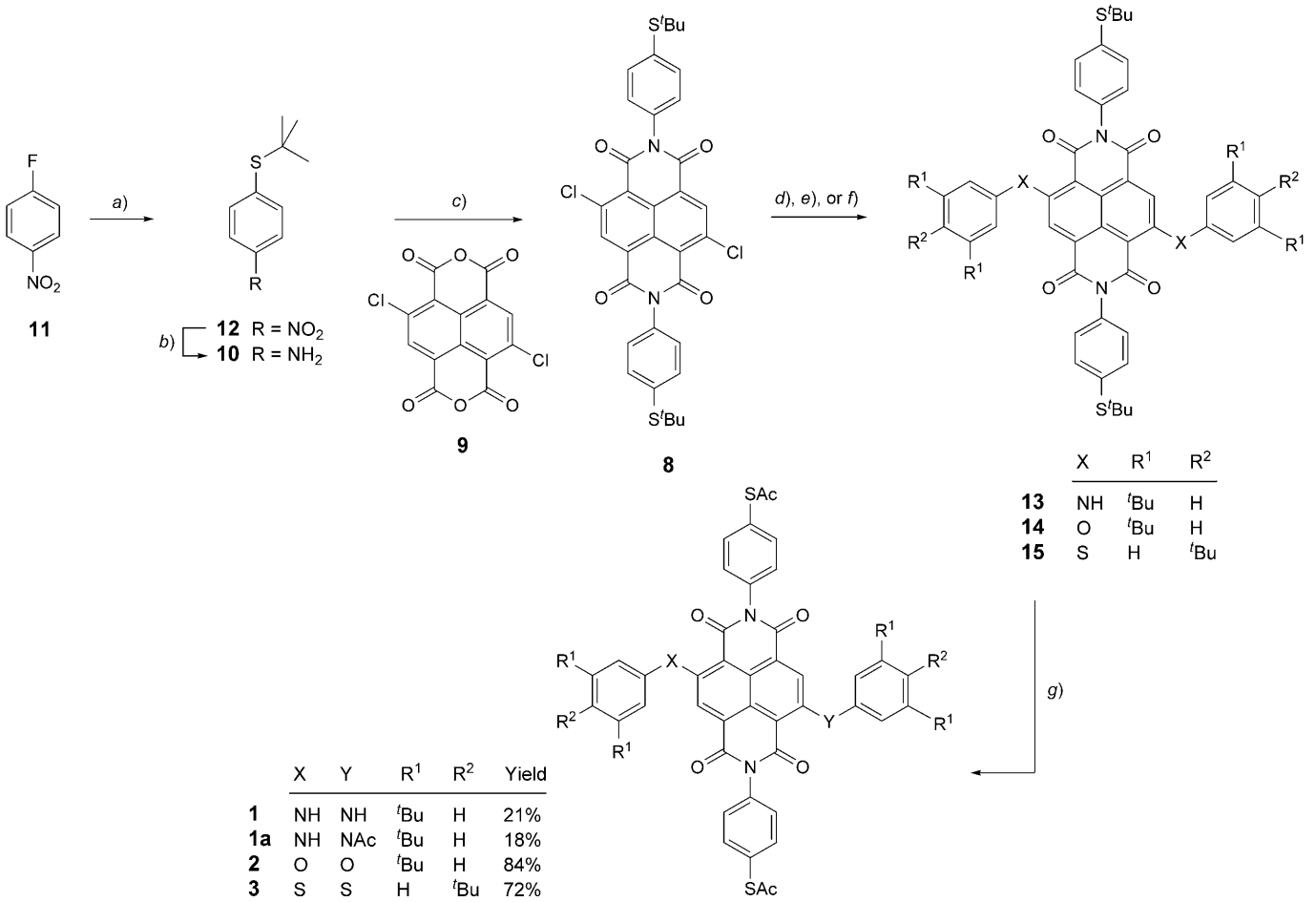
Our first attempts were focused on dye structures comprising peripheral Ph-X substituents. Thus, ^{t}Bu-substituted anilines, phenols, and thiophenols were considered as nucleophiles for the core functionalization of the naphthalene bisimide. While 3,5-di(*tert*-butyl)aniline and 4-(*tert*-butyl)thiophenol are commercially available, 3,5-di(*tert*-butyl)phenol was synthesized in 96% yield by hydrolysis of commercially available 3,5-di(*tert*-butyl)phenyl trifluoromethanesulfonate according to a literature procedure [14].

As displayed in *Scheme 2*, the Ph-substituted dyes comprising terminal ^{t}BuS groups were synthesized by the method of *Vollmann et al.* [13]. The dichloro precursor **8** was treated with an excess of the corresponding nucleophile in DMF as a nonprotic polar solvent. The synthesis of the dark-blue [3,5-di(*tert*-butyl)phenyl]amino-substituted dye **13** was accomplished in 70% yield with 6 equiv. of the aniline at 120° for 16 h. The role of 3,5-di(*tert*-butyl)aniline in this nucleophilic substitution is twofold: on one hand, it serves as the nucleophile proper, on the other hand, it acts as a base to catch the liberated HCl during the reaction.

The 3,5-di(*tert*-butyl)phenoxy- and the [4-(*tert*-butyl)phenyl]sulfanyl-substituted dyes **14** and **15**, respectively, could be prepared at lower temperature (60°) in the presence of 3 equiv. of the corresponding nucleophiles as well as K_2CO_3 as base. To keep the reaction temperature as low as possible (*ca.* 60°) turned out to be crucial for an efficient synthesis of the desired dyes, as decomposition of both the starting material **8** and the products was observed at elevated temperatures under these conditions. After chromatographic purification, the intense-yellow and red dyes **14** and **15** were isolated in 63 and 76% yield, respectively.

According to the strategy described above, the three Ph-substituted dyes **13**–**15** with terminal ^{t}BuS groups were transformed to the target dye structures **1**–**3** with AcS groups. Following a reported procedure [15], compounds **13**–**15** were treated with BBr_3 in CH_2Cl_2/toluene/AcCl. Compound **1** was isolated in 21% yield as a dark-blue solid. Acetylation of the [3,5-di(*tert*-butyl)phenyl]amino substituents was observed as a side reaction, which rationalized, to some extent, the rather low yield. Compound **1a**, a dark-violet side product containing an additional Ac group at one of the peripheral amino substituents, was isolated in 18% yield after column chromatography, and was fully characterized. Furthermore, the formation of 4-methylacetophenone was observed under the reaction conditions. As this compound is also formed in absence of the dye molecules, it is most likely formed by a *Friedel–Crafts* acylation of the co-sol-

Scheme 2

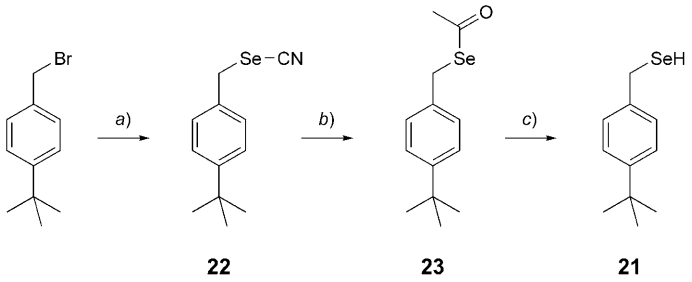


a) Na^{t}BuS, DMF, 1 h; 91%. *b*) Sn/HCl, EtOH, r.t., 1 h; 95%. *c*) 3.5 equiv. of **10**, AcOH, 110°, 30 min; 67%. *d*) 3,5-di(*tert*-butyl)aniline, DMF, 120°, 16 h; 70%. *e*) 3,5-di(*tert*-butyl)phenol, DMF, K_2CO_3, 60°, 2 h; 63%. *f*) 4-(*tert*-butyl)thiophenol, DMF, K_2CO_3, 60°, 1 h; 76%. *g*) BBr_3, AcCl, CH_2Cl_2, toluene, r.t., *ca.* 1 h.

vent toluene by AcCl, with BBr_3 acting as *Lewis* acid. Finally, the dyes **2** and **3**, which cannot be further acetylated, were isolated in yields of 84% and 72% as yellow and red solids, respectively.

For the syntheses of dyes **4**–**7**, the precursors required to introduce the peripheral substituents, [4-(*tert*-butyl)phenyl]methanamine, [4-(*tert*-butyl)phenyl]methanol, and [4-(*tert*-butyl)phenyl]methanethiol, were commercially available. To expand the series, [4-(*tert*-butyl)phenyl]methaneselenol (**21**) was synthesized according to *Scheme 3*. Commercially available 1-(bromomethyl)-4-(*tert*-butyl)benzene was treated with 2 equiv. of potassium selenocyanate in anhydrous MeCN at room temperature to afford the selenocyanate **22** as a colorless solid in 96% yield [16][17]. Reduction of **22** with 2 equiv. of $Li[Et_3BH]$ in THF at $-78°$, followed by quenching with an excess of Ac_2O at $-78°$, resulted in the Ac-protected selenol **23** as a colorless oil [18]. The Ac group of **23** was then cleaved according to a reported procedure [19] by treatment with excess AcCl in anhydrous, degassed MeOH at $-78°$ to afford **21** as a crude, colorless oil, which was used without characterization and purification in the following synthetic steps.

Scheme 3



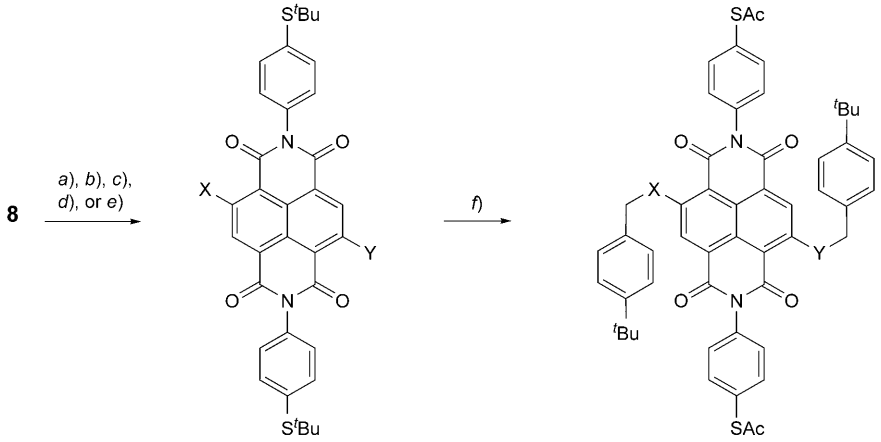
a) KSeCN, MeCN, r.t., 16 h; 96%. *b*) 1. $Li[Et_3BH]$, THF, $-78°$, 15 min; 2. Ac_2O, $-78° \rightarrow$ r.t.; 84%. *c*) AcCl, MeOH, $-78° \rightarrow$ r.t.

As displayed in *Scheme 4*, comparable reaction conditions as described above for the Ph-X-substituted dyes enabled the assembly of Bn-X-functionalized analogues comprising ^{t}Bu-protected terminal S-atoms.

Treatment of the dichloro precursor **8** in anhydrous 1,3-dimethylimidazolidinone (DMI) with an excess of [4-(*tert*-butyl)phenyl]methanamine at 90° gave the desired precursor **16** as a blue solid in 42% yield after chromatographic purification and recrystallization from i-PrOH. The monosubstituted intermediate was identified by MALDI-TOF-MS (M^+ at m/z 790.6488) as a major side product. The choice of DMI as solvent for this reaction turned out to be crucial. In our first attempts, we used DMF instead of DMI, and substitution of the Cl-atoms of **8** by Me_2NH, most likely arising from decomposing DMF, was observed.

After numerous standard procedures had failed with respect to the synthesis of **17**, a suspension of **8** in CH_2Cl_2 was treated with a large excess of the freshly prepared Na alcoholate of [4-(*tert*-butyl)phenyl]methanol. After 3 h at ambient temperature, aqueous extraction and purification, the desired naphthalene-bisimide derivative **17** was obtained as a yellow-brownish solid in poor yield (18%).

Scheme 4



		X	Y
	16	4-^{t}BuC$_6$H$_4$CH$_2$NH	= X
f)	**17**	4-^{t}BuC$_6$H$_4$CH$_2$O	= X
	17a	OH	OH
	18	4-^{t}BuC$_6$H$_4$CH$_2$S	= X
	19	4-^{t}BuC$_6$H$_4$CH$_2$Se	= X
g)	**20**	4-^{t}BuC$_6$H$_4$CH$_2$NH	Cl
	20a	4-^{t}BuC$_6$H$_4$CH$_2$NH	4-^{t}BuC$_6$H$_4$CH$_2$S

	X	Y	Yield
4	NH	NH	53%
5	S	S	65%
6	Se	Se	59%
7	NH	S	61%

a) 4-^{t}BuC$_6$H$_4$CH$_2$NH$_2$; DMI, 90°, 4 h; 42%. *b*) 4-^{t}BuC$_6$H$_4$CH$_2$O$^-$ Na$^+$, CH_2Cl_2, r.t., 3 h; 18%. *c*) 4-^{t}BuC$_6$H$_4$CH$_2$SH, DMF, K_2CO_3, 50°, 45 min; 79%. *d*) 4-^{t}BuC$_6$H$_4$CH$_2$SeH, DMF, K_2CO_3, r.t., 45 min; 24%. *e*) 4-^{t}BuC$_6$H$_4$CH$_2$NH$_2$, DMI, 40°, 8 h; 61%. *f*) BBr_3, AcCl, CH_2Cl_2, toluene, r.t., *ca.* 1 h. *g*) 4-^{t}BuC$_6$H$_4$CH$_2$SH, K_2CO_3, DMF, 50°, 1 h; 73%.

For the synthesis of the benzylsulfanyl-substituted precursor **18**, even milder reaction conditions had to be applied than for the phenylsulfanyl precursor **15** due to the higher reactivity of alkylthiolates compared to arylthiolates. The dichloro precursor **8** was, thus, treated with [4-(*tert*-butyl)phenyl]methanethiol in anhydrous, degassed DMF with K_2CO_3 as base at 50° for 45 min. Compound **18** was isolated in 79% yield as a strongly fluorescent red-violet solid after chromatographic purification. Thereby, the product yield decreased considerably with increasing reaction temperature.

Organoselenocyanates like **22** have been reported as precursors of selenolates upon reaction with reducing agents like $NaBH_4$ [20] or on alkaline hydrolysis with hydroxides [21] or K_2CO_3 [22]. However, naphthalene bisimides are also susceptible to reducing agents [23][24] and strong hydroxides [25]. In our first attempt, compound **22** and **8** in anhydrous, degassed DMF were treated with K_2CO_3 to generate the benzylic selenolate *in situ*. However, only traces of the desired dye precursor **19** were obtained after workup. In the next attempt, the starting materials were dissolved in THF, and $NaBH_4$ was tested for the formation of the benzylic selenolate. However, under these conditions, the desired product was isolated in only 5% yield. Competing reactions, either reaction between the formed selenolate and organoselenocyanate [26] to

form the diselenide, or nucleophilic substitution of the Cl-atoms of **8** by cyano nucleophiles, may account for this. To improve the yield of **19**, the free selenol **21** was prepared (see *Scheme 3*) and used for the nucleophilic substitution. When a mixture of **8** and K_2CO_3 in DMF was treated with an excess of **21**, the desired dye precursor **19** was isolated in 24% yield after purification as a dark-red solid. Whether the rather poor yield is due to the high reactivity of the selenolates or because of the powerful reducing properties of selenols was not further investigated [27][28].

A similar protocol as described above for the Ph-X-substituted compounds was next applied for the replacement of the ^{t}Bu group by Ac protecting groups. Thus, precursor **16** was treated with BBr_3 in CH_2Cl_2, and then exposed to AcCl in toluene for 1 h to afford the desired target dye **4** as a blue solid in 53% yield after chromatographic purification. Similar as described above for **1**, acetylation of the amino substituent of **4** was observed as a side reaction (M^+ at m/z 971.51). However, this additionally acetylated side product was not isolated and further characterized.

Applying similar reaction conditions for the group exchange of the BnO-substituted dye precursor **17** did not provide the desired compound. When a solution of **17** in CH_2Cl_2, AcCl, and toluene was treated with BBr_3 in CH_2Cl_2 at room temperature, a dark-red solid precipitated. During aqueous workup and extraction with CH_2Cl_2, the organic phase turned yellow, and after column chromatography, the 2,6-dihydroxy compound **17a**, still comprising the ^{t}BuS groups, was isolated as the main product in 36% yield (*Scheme 4*). As BBr_3 is known to cleave benzyl ethers [29], debenzylation and the resulting considerable decrease in solubility were not surprising. Next, we tried to remove the ^{t}Bu groups with catalytic amounts of Br_2 in AcCl and toluene [30]. However, a large number of compounds of varying polarities were formed, but not the desired reaction product. However, for the benzylsulfanyl and -seleno precursors **18** and **19**, respectively, the BBr_3 replacement protocol applied for the formation of **4** provided the desired Ac-protected dye structures. The target dye **5** was isolated in 65% yield as a red solid, and the benzylseleno-substituted dye **6** was obtained in 59% yield as a violet solid.

Finally, we were interested in the noncentrosymmetric dye **7** with mixed substituents (*Scheme 4*). First, one of the Cl-atoms of **8** was substituted with the benzylamine. Thus, **8** was treated with 2 equiv. of [4-(*tert*-butyl)phenyl]methanamine in DMI at 40°. The role of the second equivalent of amine was to capture the protons evolved during the reaction. The desired monosubstituted dye precursor **20** was isolated as a red solid in 61% yield. Its remaining Cl-atom was then replaced by exposure to [4-(*tert*-butyl)-phenyl]methanethiol in the presence of K_2CO_3 in DMF at 50°, which afforded the nonsymmetric precursor **20a** in 73% yield as a violet solid. The choice of the order of introduction of the two side groups turned out to be crucial, as the increased reactivity of the benzylsulfanylate as a nucleophile results almost exclusively in the doubly substituted precursor **18**, even upon treatment with excess **8**. Subsequent replacement of the ^{t}Bu moieties of **20a** by AcS groups was finally achieved by the same protocol as applied for the synthesis of **1**–**6** (BBr_3 in CH_2Cl_2/AcCl/toluene), which afforded **7** as a violet solid after purification in 61% yield. Again, additional acetylation of the benzylamino substituent was observed as side reaction, as detected by MALDI-TOF-MS (M^+ at m/z 974.75).

2.3. *Structure Elucidation*. Compounds **1**–**7** were found to be reasonably soluble in nonprotic solvents like toluene or THF, and well-soluble in chlorinated organic solvents such as CH_2Cl_2 or $CHCl_3$. Their structures, including those of the precursors, were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, MALDI-TOF-MS, elemental analysis, and, in the case of **1**, also by single-crystal X-ray-diffraction analysis (*Fig. 1*). Crystals were obtained by slow diffusion of EtOH into a CH_2Cl_2 solution of **1**. Interestingly, only samples containing considerable amounts of 4-methylacetophenone gave single crystals suitable for X-ray analysis. Compound **1** was found to crystallize with two independent, inversion-symmetric molecules and one molecule of 4-methylacetophenone in the triclinic space group $P\bar{1}$[2]). Some of the *t*Bu groups are disordered and have been refined with split positions concerning the Me units. The intramolecular S···S distance in **1** is 1.88(3) nm. The benzene rings of the 4-(AcS)-C_6H_4 groups are nearly perpendicular to the central naphthalene bisimide core, the torsion angles C(5)–C(6)–N(1)–C(9) and C(5)–C(6)–N(1)–C(13) amounting to 109.24(7)° and 72.03(8)°, respectively.

2.4. *Optical Properties*. 2.4.1. *Dyes* **1**–**3**. The UV/VIS absorption spectra of dyes **1**–**3** in CH_2Cl_2 at room temperature are shown in *Fig. 2*. As expected from their different colors, the variation of the heteroatom connecting the naphthalene bisimide core and the Ph substituents results in considerably different absorption spectra. Their UV/VIS spectra are divided in three groups of absorption bands. While the short-wavelength peaks between 250 and 315 nm and the color-determining longest-wavelength absorptions between 400 and 700 nm depend considerably on the substituents in positions 2 and 6 of the naphthalene-bisimide core, the central absorption bands, with maxima below 380 nm, are barely affected by the peripheral substituents. The observation that these bands are independent of the core substituents and remain outside the VIS range has already been reported as the origin of the high brilliancy of 2,6-disubstituted naphthalene bisimides [10].

The short-wavelength absorption maxima at 315 nm (**1**) or 256 nm (**2**) were found to be shifted bathochromically with increasing strength of the electron-donating character of the core substituents. The same tendency, with even stronger shifts, was observed for the longest-wavelength absorptions, which consist of a broad maximum with a shoulder towards shorter wavelength. The maxima are at 462 nm for the phenoxy-substituted dye **2**, and at 626 nm for **1** with its two phenylamino substituents. The strong effect of the electron-donor substituents on the absorption properties was attrib-

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[2]) Crystallographic data: formula: $C_{58}H_{58}N_4O_6S_2 \cdot C_9H_{10}O$, lattice parameters: $a = 1042.7(2)$, $b = 1579.0(3)$, $c = 1987.5(4)$ pm, $\alpha = 112.05(3)$, $\beta = 95.66(3)$, $\gamma = 92.28(3)°$, $V = 3007.6(11) \cdot 10^6$ pm^3; triclinic, space group $P\bar{1}$, $Z = 2$; $\rho_{calc} = 1.193$ g cm^{-1}; $\mu(\text{Mo}K_\alpha) = 0.144$ mm^{-1}, STOE IPDS2, MoK_α-radiation, $\lambda = 0.71073$ Å; $T = 180$ K; $2\theta_{max} = 45°$; 10053 reflections measured, 6751 independent reflections ($R_{int} = 0.0608$), 5070 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2, 810 parameters. S, O, N, and C were refined anisotropically, H-atoms were calculated at ideal positions. Three *t*Bu groups were refined with split positions, no H-atoms were fitted to these groups. $R1 = 0.0807$; $wR2 = 0.2254$ (all data); Gof: 1.016; maximum peak 0.247 e Å^{-3}. CCDC-606900 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, at www.ccdc.cam.ac.uk/conts/retrieving.html or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

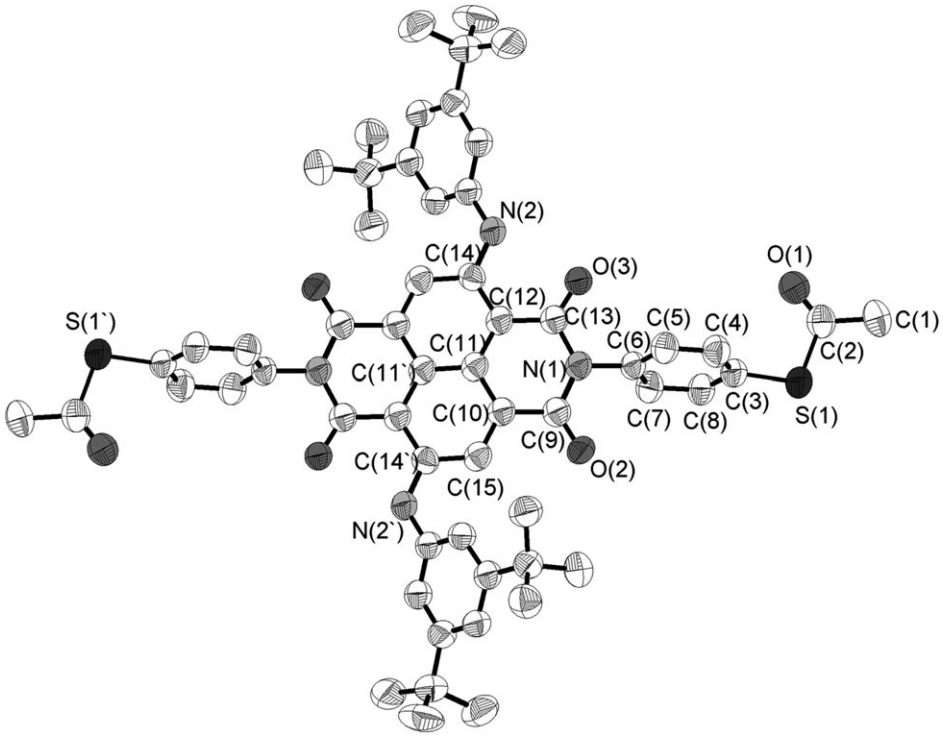

Fig. 1. *X-Ray single-crystal structure of* **1** (ORTEP representation, thermal ellipsoids set at the 40%-probability level). H-atoms have been omitted for clarity; only one orientation of the disordered *t*Bu groups is shown. Selected bond lengths (in pm) and bond angles (in °): C(1)–C(2) 149.6(6), C(2)–O(1) 119.7(5), C(2)–S(1) 178.4(5), S(1)–C(3) 176.6(4), C(3)–C(4) 138.1(6), C(4)–C(5) 138.8(5), C(5)–C(6) 133.8(6), C(6)–C(7) 140.6(5), C(7)–C(8) 139.6(5), C(8)–C(3) 135.9(6), C(6)–N(1) 146.7(4), N(1)–C(9) 138.1(5), C(9)–O(2) 121.2(5), C(9)–C(10) 148.3(5), C(10)–C(11) 140.4(5), C(11)–C(12) 142.0(5), C(12)–C(13) 145.9(5), C(13)–O(3) 122.5(5), C(13)–N(1) 140.2(5), C(12)–C(14) 140.8(5), C(14)–N(2) 137.0(5), C(10)–C(15) 137.0(6), C(15)–C(14′) 142.0(5), C(11)–C(11′) 141.4(7); C(2)–S(1)–C(3) 102.7(2), C(9)–N(1)–C(13) 126.4(3).

uted to the electronic $S_0 \rightarrow S_1$ transition, which has been assumed to arise from interactions between the electron-donor substituents and the C=O functional groups [10].

The short- and the long-wavelength maxima of **3** at 295 nm and 519 nm, respectively, are both clearly shifted bathochromically compared to **2**, pointing at an increased electron-donating character of the phenylsulfanyl substituent compared with the phenoxy substituents in **2**.

2,6-Arylamino-substituted naphthalene-bisimide dyes have been reported to be nonfluorescent, and intramolecular bonding of the amino H-atom to the adjacent C=O group is considered as the major pathway for radiationless deactivation of the excited state [10], in analogy to numerous commercial UV absorbers [31]. Therefore, the lack of a detectable fluorescence signal for **1** was not surprising. However, also the phenoxy- and phenylsulfanyl-substituted dyes **2** and **3**, without the possibility of H-bonding, were found to be nonfluorescent. We assume that the high-lying HOMO

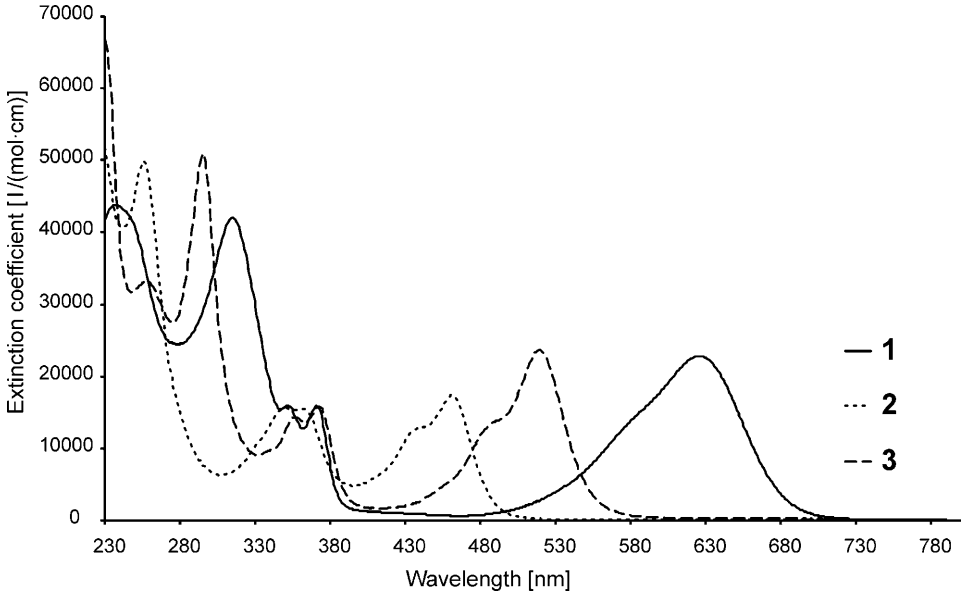

Fig. 2. *UV/VIS Spectra of* **1**–**3** (*ca.* 10 μM) *in* CH_2Cl_2 *at room temperature*

of the electron-donor substituents is quenching the excited state by electron transfer into the singly occupied former HOMO of the chromophore as an alternative pathway for radiationless deactivation. Details of the intramolecular-quenching mechanism are currently under investigation with suitable model compounds.

Considering the electron-donor Ph-X substituents as the origin of the radiationless deactivation of the excited state, our interest moved towards naphthalene-bisimide dyes comprising benzyl substituents. By altering the structure from Ph-X to Bn-X substituents, shape, size and solubility of the dye molecule should remain to a large extend comparable, but the peripheral π-substituents are separated electronically, and the hypothesized quenching mechanism may be suppressed.

2.4.2. *Dyes* **4**–**7**. The electronic-absorption spectra of the benzyl-substituted dyes **4**–**6** are shown in *Fig. 3*. At a first glance, they are very similar to those of the corresponding phenyl derivatives (see *Fig. 2*). Again, there are three absorption regions, one at short wavelength (280–310 nm), a second set of bands with maxima below 380 nm, and, finally, a color-determining longest-wavelength region that strongly depends on the core substituents. Again, the longest-wavelength absorptions were found to be broad, their shoulder to shorter wavelength being slightly more pronounced. The longest-wavelength absorption of **4** (610 nm) is shifted hypsochromically compared to the analogue **1** (626 nm). The longest-wavelength absorptions of both **5** (528 nm) and **3** (519 nm) are comparable. In case of the seleno congener **6**, the maximum lies at 553 nm, in between the maxima of the S- and N-analogues **5** and **4**, respectively, as expected from its violet color. While the short-wavelength absorption of dyes **1**–**3** follows in their order that of their longest-wavelength absorption, this order is no longer maintained for the series **4**–**6**, with maxima at 283, 297, and 308 nm, respectively.

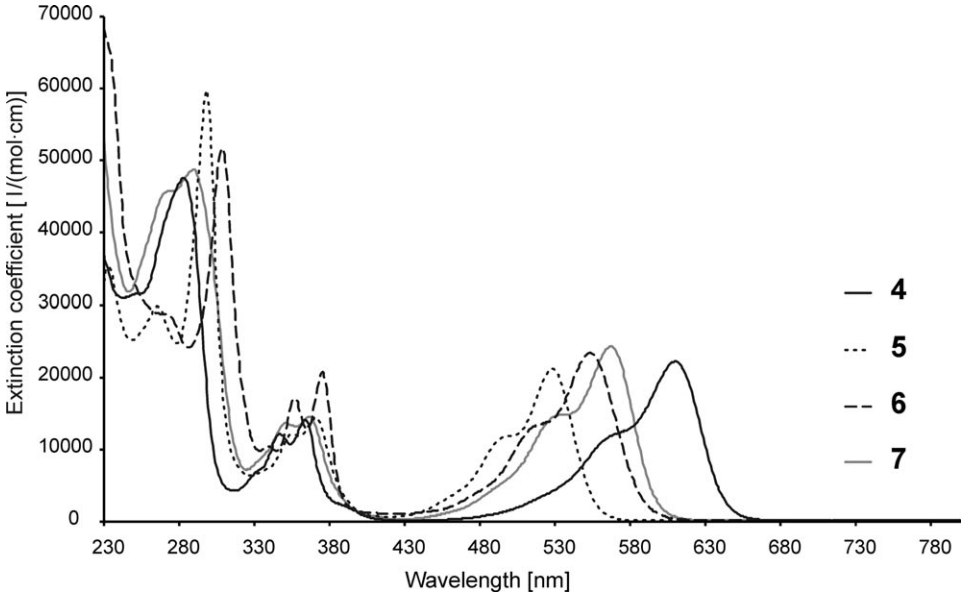

Fig. 3. *UV/VIS Spectra of* **4**–**7** (*ca.* 10 μM) *in* CH_2Cl_2 *at room temperature*

Of particular interest were the photoluminescence properties of these new series of dyes (*Fig. 4*). Strong fluorescence properties had already been observed during the reaction and upon chromatographic purification of **4** and **5** (excitation at 254 nm upon TLC analysis), but not for the benzylseleno compound **6**. Qualitative investigation by fluorescence spectroscopy displayed, indeed, an intense fluorescence signal for **4** upon excitation at 610 nm (*Fig. 4*). Even with a very diluted sample of **4** (0.177 μM) and minimal excitation energy, a strong fluorescence signal with a maximum at 642 nm was recorded. This intense fluorescence signal further challenges the proposed radiationless deactivation of the excited state by H-bonding with the C=O group, as the benzylamine core substituents of **4** also provide H-atoms required for the suggested mechanism. Similar observations have been reported before for alkylamine-substituted naphthalene bisimides [10].

The benzylthio-substituted dye **5** displayed a fluorescence maximum at 558 nm upon excitation at 528 nm. However, the intensity of the signal was weaker than that observed for **4**: both the sample concentration (13.1 μM) and the excitation energy had to be increased. By further increasing the excitation energy, a fluorescence signal at 594 nm was even observed for a solution of the benzylseleno-substituted dye **6** (11.1 μM) upon excitation at 553 nm. The considerably reduced intensity of the fluorescence signal of **6** compared to those of the analogues **4** and **5** can be rationalized by an internal heavy-atom effect of the Se substituents, as reported for example for chalcogeno-xanthylium dyes [32]. The *Stoke* shifts of **4**–**6** were 32–42 nm, which is slightly larger than those reported for comparable chromophores comprising alkyl-X substituents in 2- and 6-position [10].

The rather weak fluorescence properties of the Se-substituted dye **6**, with its longest-wavelength absorption maximum between those of the S- and N-substituted ana-

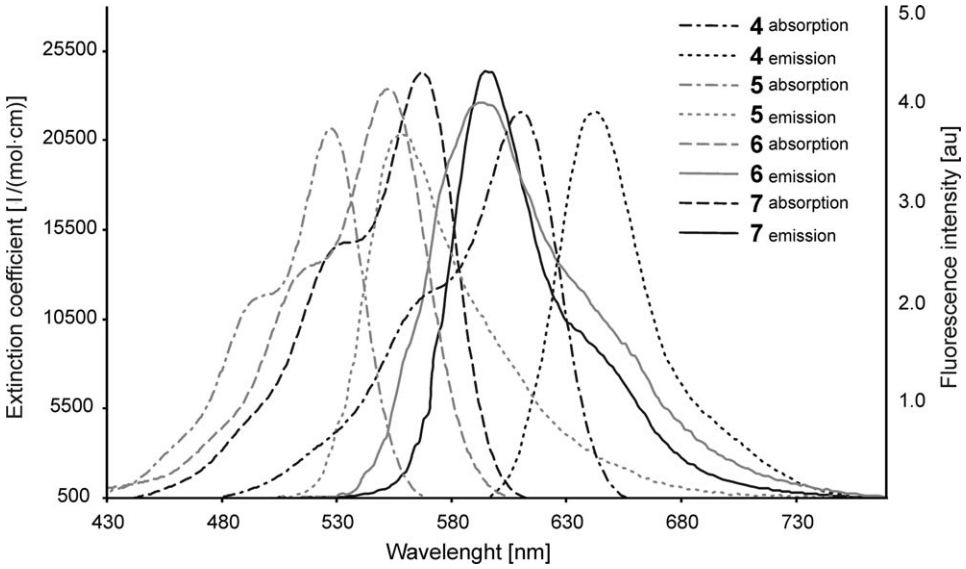

Fig. 4. *UV/VIS Absorption and fluorescence spectra of* **4**–**7** *in* CH_2Cl_2 *at room temperature.* The fluorescence signals are normalized to the intensities of the absorption maxima. Concentrations of the samples (and excitation wavelengths) in fluorescence experiments: **4**: 0.177 μM (610 nm); **5**: 13.1 μM (528 nm); **6**: 11.1 μM (553 nm); **7**: 0.186 μM (567 nm).

logues, inspired the design of compound **7**, comprising both a [(*tert*-butyl)phenyl]amino and a [(*tert*-butyl)phenyl]sulfanyl substituent. The substitution pattern of **7** should provide absorption and emission bands at comparable wavelengths as in the case of **6**, but the lack of Se should increase the fluorescence intensity.

The UV/VIS spectrum of **7** was found to be comparable to those of the other members of the Bn series (see *Fig. 3* above). As intended, the longest-wavelength absorption of **7** at 567 nm lies in between those of **4** and **5**. Furthermore, the position of the absorption maximum is comparable to that of the Se dye **6** (552 nm). The nonsymmetric dye **7** showed a very strong fluorescence signal at 596 nm upon excitation at 567 nm (*Fig. 4*). As anticipated, **7** displays with 596 nm a fluorescence signal at comparable wavelength as the Se compound **6** (594 nm), but with considerably increased intensity, almost comparable to that observed for **1**.

Conclusions. – A series of rod-type dyes, **1**–**7**, with terminal AcS groups comprising a 2,6-disubstituted naphthalene-bisimide chromophore, were synthesized and analyzed. Due to peripheral ^{t}Bu groups at the Ph or Bn substituents, respectively, the dyes display reasonable solubility in organic solvents. The choice of the hetero-atoms at C(2) and C(6) of the naphthalene-bisimide core allow one to adjust the longest-wavelength absorption and, thus, the compound color over a wide range of the visible spectrum. Furthermore, the chemical nature of the core substituents enables one to tailor the fluorescence properties of these compounds. While rods with phenyl-heteroatom substituents are nonfluorescent, those with benzyl-heteroatoms are fluorescent. The molecular-rod motive containing two anchor groups for metal electrodes at both ends with this

broad range of addressable optical properties has been designed for optically triggered transport investigations in metal–molecule hybrid setups. While experiments along this idea are currently performed, the structural motive is further extented to enable single-molecule-electroluminescence experiments and optically triggered directional transport in molecule–metal hybrid structures.

We are grateful for financial support by the *Swiss National Science Foundation* and the *German Ministry of Education and Research*. We are thankful to *Valerie Chaurin* for her support in fluorescence investigations. We also thank *Thomas Carell* for fruitful discussions.

Experimental Part

General. All chemicals were used as received; solvents were of anal. quality, used without further purification, and dried by standard procedures; in particular, THF was distilled from Na/benzophenone, and CH_2Cl_2 was distilled over CaH [33]. Anh. 1,3-dimethylimidazolidinone (DMI) was purchased from *Fluka*, and anh. DMF and MeCN were from *Aldrich*. TLC: *Merck* silica gel *60* F_{254} plates. Column chromatography (CC): *Merck* silica gel *60* (0.040–0.063 mm). Melting points (m.p.) were measured on a *Büchi B-540* apparatus; uncorrected. UV/VIS Spectra: *Varian Carry-500Scan* spectrophotometer, with 1-cm quartz cuvettes, at r.t.; λ_{max} in nm (ε in l $mol^{-1}cm^{-1}$). Fluorescence spectra: *Shimadzu RF-5301 PC* spectrofluorometer, with 1-cm quartz cuvettes, at r.t. ^{1}H- and ^{13}C-NMR Spectra: *Bruker Ultra-Shield-300* apparatus, at 300 and 75 MHz, resp.; δ in ppm, J in Hz; all spectra were recorded at 25°, unless noted otherwise. MALDI-TOF-MS: *PerSeptive Biosystems Voyager-DE-PRO* time-of-flight mass spectrometer; EI-MS: *Finnigan MAT-95Q* mass spectrometer; in m/z (rel. %). Elemental analyses: *ThermoQuest FlashEA 1112-N* protein analyzer.

1-(1,1-Dimethylethyl)sulfanyl-4-nitrobenzene (**12**). Prepared as reported in [34]. Briefly, a mixture of 4-fluoro-1-nitrobenzene (11.1 g, 0.079 mol) and sodium 2-methyl-2-propanethiolate (14.3081 g, 0.1276 mol) in anh. DMF (200 ml) was stirred for 1 h at r.t. The mixture was poured into brine and extracted with Et_2O. After evaporation of the solvents of the org. phase, the crude product was purified by filtration through a short column of SiO_2 eluting with hexane/CH_2Cl_2 2:1. Yield: 15.1938 g (91%). Yellowish solid. M.p. 39–40° (lit. m.p. 39.5–40.5° [12]). ^{1}H-NMR ($CDCl_3$): 1.29 (*s*, 3 Me); 7.63 (*d*, ^3J=8.7, 2 H); 8.12 (*d*, ^3J=8.7, 2 H). ^{13}C-NMR ($CDCl_3$): 31.14 (Me); 47.58 (Me*C*); 123.37, 136.90, 142.39, 147.76. EI-MS: 211.1 (13, M^+), 155.0 (12, $[M-C_4H_8]^+$), 57.1 (100, $C_4H_9^+$).

4-[(1,1-Dimethylethyl)sulfanyl]benzene-1-amine (**10**). To a soln. of **12** (7.4451 g, 0.035 mol) in EtOH (150 ml), conc. HCl (4 ml) and Sn powder (8.3083 g, 0.07 mol) were added in one portion, which gave rise to an exothermic reaction. The mixture was stirred for 1 h without cooling. After neutralization with NaOH, extraction with toluene, and evaporation of the solvents, the crude product was purified by CC (SiO_2; hexane/CH_2Cl_2 2:1). Yield: 6.0492 g (95%). Yellowish solid. M.p. 69–70° (lit. m.p. 71–72° [12]). ^{1}H-NMR ($CDCl_3$): 1.23 (*s*, 3 Me); 3.80 (*s*, NH_2); 6.59 (*d*, ^3J=8.4, 2 H); 7.28 (*d*, ^3J=8.4, 2 H). ^{13}C-NMR ($CDCl_3$): 30.72; 45.32; 114.93; 120.49; 138.77; 147.16. EI-MS: 181.1 (17, M^+), 125.0 (100, $[M-C_4H_8]^+$).

*4,9-Dichloro-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8-(2*H*,7*H*)-tetrone* (**8**). 2,6-Dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride (**9**) (4.0695 g, 0.0121 mol) was suspended in glacial AcOH (300 ml) and heated at 110°. Then, 3.5 equiv. of **10** was added, and the mixture was kept at 110° for another 30 min. After the addition of **10**, a soln. was obtained, out of which a brownish solid started to precipitate. The precipitate was filtered off and washed repeatedly with hot AcOH to afford **8** (5.3528 g) in 67% yield. Brown solid. M.p. >410°. UV/VIS (CH_2Cl_2): 401 (13300), 380 (12200), 358 (20700), 340 (15000), 250 (57800). ^{1}H-NMR ($C_2D_2Cl_4$, 100°): 1.47 (*s*, 6 Me); 7.34 (*d*, ^3J=7.8, 4 H); 7.79 (*d*, ^3J=8.1, 4 H); 8.88 (*s*, 2 H). MALDI-TOF-MS: 663.6268 (M^+, $C_{34}H_{28}Cl_2N_2O_4S_2^+$; calc. 662.0862). Anal. calc. for $C_{34}H_{28}Cl_2N_2O_4S_2$ (663.63): C 61.54, H 4.25, N 4.22; found: C 60.25, H 4.31, N 4.20. Due to the very poor solubility of the material, we were not able to record its ^{13}C-NMR spectrum.

3,5-Bis(1,1,dimethylethyl)phenol. Prepared according to [14]. To a soln. of 3,5-bis(1,1-dimethylethyl)phenyl trifluoromethanesulfonate (4.236 g, 0.0125 mol) in 1,4-dioxane (50 ml), $Bu_4N^+OH^-$ (20% soln. in H_2O; 32.94 ml, 0.025 mol) was added, and the mixture was stirred for 1 h at r.t. Approximately half of the 1,4-dioxane was removed under reduced pressure, and the mixture was poured into H_2O and extracted with CH_2Cl_2. The combined org. layers were dried and concentrated, and the residue was purified by CC (SiO_2; hexane/CH_2Cl_2 1:1). Yield: 2.4714 g (96%). Colorless solid. M.p. 89–91° (lit. m.p. 89.5–90° [35]). ^{1}H-NMR ($CDCl_3$): 1.31 (*s*, 6 Me); 4.40 (br. *s*, OH); 6.70 (*d*, ^4J = 1.5, 2 H); 7.01 (*t*, ^4J = 1.5, 1 H). ^{13}C-NMR ($CDCl_3$): 31.53; 34.99; 109.79; 115.08; 152.75; 155.01. EI-MS: 206.2 (24, M^+), 191.2 (100, $[M-CH_3]^+$), 57.1 (51, $C_4H_9^+$).

*4,9-Bis{[3,5-bis(1,1-dimethylethyl)phenyl]amino}-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone* (**13**). A mixture of **8** (0.5575 g, 0.84 mmol) and 3,5-bis(1,1-dimethylethyl)benzen-1-amine (1.035 g, 5.04 mmol) in anh. DMF (10 ml) was kept at 120° for 16 h. After evaporation of the solvent, the residue was purified by CC (SiO_2; hexane/CH_2Cl_2 1:2). Yield: 0.5851 g (70%). Blue solid. M.p. 370–372°. ^{1}H-NMR ($CDCl_3$): 1.34 (*s*, 12 Me); 1.39 (*s*, 6 Me); 7.17 (*s*, 4 H); 7.32 (*s*, 2 H); 7.34 (*d*, ^3J = 8.4, 4 H); 7.74 (*d*, ^3J = 8.1, 4 H); 8.66 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.20; 31.53; 35.09; 46.44; 102.93; 118.68; 120.28; 121.18; 122.72; 126.38; 128.87; 133.99; 135.74; 137.54; 138.32; 148.01; 152.76; 162.72; 166.54. MALDI-TOF-MS: 1000.7866 (M^+, $C_{62}H_{72}N_4O_4S_2^+$; calc. 1000.4990). Anal. calc. for $C_{62}H_{72}N_4O_4S_2$ (1001.39): C 74.36, H 7.25, N 5.59; found: C 74.42, H 7.23, N 5.63.

*4,9-Bis{[3,5-bis(1,1-dimethylethyl)phenyl]oxy}-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo-[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone* (**14**). A mixture of **8** (1.0192 g, 1.5 mmol), 3,5-bis(1,1-dimethylethyl)phenol (0.9506 g, 4.61 mmol), and K_2CO_3 (0.6371 g, 4.61 mmol) in anh. DMF (10 ml) was kept at 60° for 2 h. The mixture was poured into H_2O and extracted with CH_2Cl_2. The combined org. phases were concentrated under reduced pressure, and the residue was purified by CC (SiO_2; hexane/CH_2Cl_2 1:2). Yield: 0.9482 g (63%). Yellow solid. M.p. 345–347°. ^{1}H-NMR ($CDCl_3$): 1.30 (*s*, 12 Me); 1.31 (*s*, 6 Me); 6.99 (*d*, ^4J = 1.5, 4 H); 7.25–7.33 (*m*, 6 H); 7.68 (*d*, ^3J = 8.4, 4 H); 8.37 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.01; 31.36; 35.15; 46.31; 112.21; 114.99; 120.06; 123.26; 124.66; 127.60; 128.84; 133.74; 135.28; 138.21; 153.62; 153.78; 160.36; 160.83; 161.99. MALDI-TOF-MS: 1003.8168 (M^+, $C_{62}H_{70}N_2O_6S_2^+$; calc. 1002.4670). Anal. calc. for $C_{62}H_{70}N_2O_6S_2$ (1003.36): C 74.22, H 7.03, N 2.79; found: C 74.25, H 6.95, N 2.89.

*4,9-Bis{[4-(1,1-dimethylethyl)phenyl]sulfanyl}-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo-[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone* (**15**). A mixture of **8** (0.1520 g, 0.229 mmol), 4-(1,1-dimethylethyl)benzenethiol (0.1143 g, 0.687 mmol), and K_2CO_3 (0.095 g, 0.687 mmol) in anh., degassed DMF (10 ml) was kept at 60° for 1 h. The mixture was poured into H_2O and extracted with CH_2Cl_2. The combined org. phases were collected and concentrated under reduced pressure, and the resulting residue was separated by CC (SiO_2; hexane/CH_2Cl_2 1:2). Yield: 0.1618 g (76%). Red solid. M.p. > 410°. ^{1}H-NMR ($CDCl_3$): 1.35 (*s*, 12 Me); 7.27 (*d*, ^3J = 8.4, 4 H); 7.53 (*d*, ^3J = 8.7, 4 H); 7.57 (*d*, ^3J = 8.7, 4 H); 7.70 (*d*, ^3J = 8.1, 4 H); 8.31 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.18; 31.32; 35.10; 46.52; 118.48; 124.28; 125.88; 126.09; 127.76; 128.81; 130.48; 134.31; 135.13; 135.76; 138.40; 150.97; 154.40; 162.29; 163.50. MALDI-TOF-MS: 923.1648 (M^+, $C_{54}H_{54}N_2O_4S_4^+$; calc. 922.2961). Anal. calc. for $C_{54}H_{54}N_2O_4S_4$ (923.27): C 70.25, H 5.89, N 3.03; found: C 70.43, H 5.89, N 3.16.

S,S′-*[(4,9-Bis{[3,5-bis(1,1-dimethylethyl)phenyl]amino}-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*]-[3,8]phenanthroline-2,7-diyl)dibenzene-4,1-diyl] Diethanethioate* (**1**) *and* S,S′-*[(4-{Acetyl[3,5-bis(1,1-dimethylethyl)phenyl]amino}-9-{[3,5-bis(1,1-dimethylethyl)phenyl]amino}-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)dibenzene-4,1-diyl] Diethanethioate* (**1a**). To a soln. of **13** (0.4327 g, 0.432 mmol) in CH_2Cl_2 (100 ml), toluene (40 ml), and AcCl (40 ml), a soln. of BBr_3 in CH_2Cl_2 (4 ml) was added at 0°. The mixture was stirred for 1 h at r.t. Then, the violet soln. was poured into ice-water, and the org. residue was extracted with CH_2Cl_2 and purified by CC (SiO_2; CH_2Cl_2) to afford **1** (0.088 g, 21%) and **1a** (0.08 g, 18%).

Data of **1**. Blue solid. M.p. 358–361°. UV/VIS (CH_2Cl_2): 626 (22700), 371 (15800), 352 (15800), 315 (41900), 237 (43700). ^{1}H-NMR ($CDCl_3$): 1.32 (*s*, 12 Me); 2.46 (*s*, 2 Me); 7.15 (*d*, ^4J = 1.8, 4 H); 7.28 (*t*, ^4J = 1.8, 2 H); 7.39 (*d*, ^3J = 8.4, 4 H); 7.63 (*d*, ^3J = 8.4, 4 H); 8.73 (*s*, 2 H); 11.06 (*s*, 2 NH). ^{13}C-NMR ($CDCl_3$): 30.45; 31.53; 35.12; 102.98; 118.22; 120.14; 121.23; 122.81; 126.39; 129.33; 129.61; 135.12;

136.14; 137.57; 147.76; 152.77; 162.66; 166.51; 192.88. MALDI-TOF-MS: 972.2391 (M^+, $C_{58}H_{60}N_4O_6S_2^+$; calc. 972.3949). Anal. calc. for $C_{58}H_{60}N_4O_6S_2$ (973.25): C 71.58, H 6.21, N 5.76; found: C 71.43, H 6.09, N 5.81.

Data of **1a**. Violet solid. M.p. 315–316°. ^{1}H-NMR ($CDCl_3$): 1.31 (*s*, 6 Me); 1.34 (*s*, 6 Me); 2.07 (*s*, AcN); 2.46 (*s*, 2 AcS); 7.16 (*s*, 2 H); 7.32 (*s*, 2 H); 7.34–7.45 (*m*, 7 H); 7.57–7.69 (*m*, 4 H); 8.46 (*s*, 1 H); 8.73 (*s*, 1 H); 11.63 (*s*, NH). ^{13}C-NMR ($CDCl_3$): 23.52; 30.44; 31.47; 35.10; 35.13; 100.75; 118.58; 121.14; 122.35; 122.66; 123.10; 124.67; 128.75; 128.84; 129.17; 129.44; 129.51; 129.67; 133.18; 135.05; 135.22; 135.93; 136.08; 136.62; 140.20; 141.92; 150.62; 153.02; 153.06; 162.20; 162.30; 162.48; 166.34; 172.25 (NC=O); 192.77; 192.89; one signal masked. FAB-MS: 1015.4 (M^+, $C_{60}H_{62}N_4O_7S_2^+$; calc. 1014.4).

S,S′-*[(4,9-Bis{[3,5-bis(1,1-dimethylethyl)phenyl]oxy}-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*]-[3,8]phenanthroline-2,7-diyl)dibenzene-4,1-diyl] Diethanethioate* (**2**). To a soln. of **14** (0.7598 g, 0.757 mmol) in CH_2Cl_2 (70 ml), toluene (14 ml), and AcCl (50 ml), a soln. of BBr_3 in CH_2Cl_2 (7 ml) was added dropwise at r.t. The mixture was stirred for 30 min at r.t., poured into ice-water, and extracted with CH_2Cl_2. The combined org. phases were collected and concentrated at reduced pressure. The resulting residue was separated by CC (SiO_2; CH_2Cl_2). Yield: 0.6217 g (84%). Yellow solid. M.p. 355–357°. UV/VIS (CH_2Cl_2): 462 (17300), 437 (12700), 362 (15500), 350 (15700), 256 (54100). ^{1}H-NMR ($CDCl_3$): 1.30 (*s*, 12 Me); 2.43 (*s*, 2 Me); 6.99 (*d*, ^4J = 1.8, 4 H); 7.32 (*s*, 2 H); 7.38 (*d*, ^3J = 8.4, 4 H); 7.57 (*d*, ^3J = 8.1, 4 H); 8.38 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 30.39; 31.43; 35.22; 112.62; 114.75; 120.08; 123.62; 124.92; 127.74; 129.23; 129.64; 135.06; 135.72; 153.83; 153.85; 160.30; 160.89; 162.07; 193.01. MALDI-TOF-MS: 975.3077 (M^+, $C_{58}H_{58}N_2O_8S_2^+$; calc. 974.3629). Anal. calc. for $C_{58}H_{58}N_2O_8S_2$ (975.22): C 71.43, H 5.99, N 2.87; found: C 71.52, H 5.96, N 2.99.

S,S′-*[(4,9-Bis{[4-(1,1-dimethylethyl)phenyl]sulfanyl}-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*]-[3,8]phenanthroline-2,7-diyl)dibenzene-4,1-diyl] Diethanethioate* (**3**). To a soln. of **15** (0.1444 g, 0.156 mmol) in CH_2Cl_2 (15 ml), toluene (3 ml), and AcCl (10 ml), a soln. of BBr_3 in CH_2Cl_2 (1.5 ml) was added at r.t. The mixture was stirred for 30 min at r.t., poured into ice-water, and extracted with CH_2Cl_2. The combined org. phases were collected, and concentrated at reduced pressure. The resulting residue was separated by CC (SiO_2; CH_2Cl_2). Yield: 0.1006 g (72%). Red solid. M.p. 367–369°. UV/VIS (CH_2Cl_2): 519 (23800), 486 (13400), 373 (15900), 356 (14500), 295 (51000), 258 (33300). ^{1}H-NMR ($CDCl_3$): 1.35 (*s*, 6 Me); 2.45 (*s*, 2 Me); 7.35 (*d*, ^3J = 8.4, 4 H); 7.50–7.56 (*m*, 8 H); 7.59 (*d*, ^3J = 8.4, 4 H); 8.25 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 30.42; 31.37; 35.15; 118.53; 124.28; 125.85; 126.30; 127.76; 129.63; 129.65; 130.50; 135.15; 135.62; 135.83; 151.14; 154.53; 162.13; 163.38; 192.78. Anal. calc. for $C_{50}H_{42}N_2O_6S_4$ (895.14): C 67.09, H 4.73, N 3.13; found: C 66.90, H 4.83, N 3.34. MALDI-TOF-MS: 895.3359 (M^+, $C_{50}H_{42}N_2O_6S_4^+$; calc. 894.1920).

[4-(1,1-Dimethylethyl)phenyl]methyl Selenocyanate (**22**). To a soln. of 1-(bromomethyl)-4-(1,1-dimethylethyl)benzene (7.416 g, 0.0326 mol) in anh. MeCN (10 ml), potassium selenocyanate (9.4079 g, 0.0653 mol) was added in one portion at 0°. The mixture was stirred for 16 h at r.t., poured into ice-water, and extracted with Et_2O. The combined org. phases were collected, and the solvents were removed at reduced pressure. The resulting colorless residue was recrystallized from hexane to afford 7.8692 g (96%) of the title compound. Colorless crystals. M.p. 93–94°. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 3 Me); 4.31 (*s*, CH_2); 7.31 (*d*, ^3J = 8.1, 2 H); 7.40 (*d*, ^3J = 8.4, 2 H). ^{13}C-NMR ($CDCl_3$): 31.33; 32.83; 34.78; 102.27; 126.20; 128.85; 132.32; 151.97. EI-MS: 253.1 (0.1, M^+), 147.1 (100, $[M-SeCN]^+$), 132.1 (38.9), 117.1 (21.2), 91.0 (7.7). Anal. calc. for $C_{12}H_{15}NSe$ (252.22): C 57.15, H 5.99, N 5.55; found: C 57.04, H 6.13, N 5.60.

Se-*{[4-(1,1-Dimethylethyl)phenyl]methyl} Ethaneselenoate* (**23**). To a soln. of **22** (2.3875 g, 9.5 mmol) in anh., degassed THF, maintained at −78° under N_2 atmosphere, was added dropwise a 1M soln. of *Super-Hydride*® in THF (19 ml, 19 mmol). After 15 min, the reaction was quenched with 10 equiv. of degassed Ac_2O (9 ml, 95 mmol) at −78°. The mixture was allowed to warm to r.t. over 1 h, poured into ice-water, and extracted with Et_2O. The combined org. phases were collected and concentrated at reduced pressure. The resulting residue was separated by CC (SiO_2; hexane/CH_2Cl_2). Yield: 2.1368 g (83.5%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 1.36 (*s*, 3 Me); 2.46 (*s*, 3 Me); 4.20 (*s*, CH_2); 7.27 (*d*, ^3J = 8.4, 2 H); 7.36 (*d*, ^3J = 8.4, 2 H). ^{13}C-NMR ($CDCl_3$): 28.98; 31.39; 34.50; 34.51; 125.58; 128.59; 136.04; 149.87; 197.48. EI-MS: 270.1 (4.2, M^+), 147.1 (100, $[M-C_2H_3OSe]^+$), 132.1 (19.5), 117.1 (11.0).

[4-(1,1-Dimethylethyl)phenyl]methaneselenol (**21**). To a soln. of **23** (0.6570 g, 2.44 mmol) in anh., degassed MeOH (15 ml) was slowly added at −78° an excess of AcCl (1 ml) under N_2 atmosphere.

The mixture was kept at this temp. for 30 min, and then allowed to warm to r.t. over a period of 2 h under N_2 atmosphere. Removal of the volatile products at reduced pressure provided the crude title compound as a colorless oil, which was dissolved in anh., degassed DMF, and directly used in the following steps without purification.

*4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}amino)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}-benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H,7H*)-tetrone* (**16**). A soln. of **8** (0.5237 g, 0.789 mmol) and 4-(1,1-dimethylethyl)benzen-1-amine (0.5153 g, 3.16 mmol) in DMI (5 ml) was kept at 90° for 4 h. After evaporation of the solvents, the crude mixture was purified by CC (SiO_2; CH_2Cl_2) and recrystallization from i-PrOH. Yield: 0.3029 g (42%). Blue solid. M.p. >410°. ^{1}H-NMR ($CDCl_3$): 1.30 (*s*, 6 Me); 1.38 (*s*, 6 Me); 4.62 (*d*, ^3J=5.7, 4 H); 7.29 (*d*, ^3J=8.4, 8 H); 7.35 (*d*, ^3J=8.4, 4 H); 7.72 (*d*, ^3J=8.4, 4 H); 8.30 (*s*, 2 H); 9.61 (*t*, ^3J=5.7, 2 NH). ^{13}C-NMR ($CDCl_3$): 31.21; 31.43; 34.68; 46.52; 47.13; 102.49; 119.34; 122.03; 126.07; 126.46; 127.43; 128.84; 134.13; 134.l9; 135.81; 138.44; 149.55; 151.00; 163.12; 166.41. MALDI-TOF-MS: 915.8814 (M^+, $C_{56}H_{60}N_4O_4S_2^+$; calc. 916.4051). Anal. calc. for $C_{56}H_{60}N_4O_4S_2$ (917.23): C 73.33, H 6.59, N 6.11; found: C 73.44, H 6.40, N 6.19.

*4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}oxy)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}-benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H,7H*)-tetrone* (**17**). To a suspension of **8** (0.3250 g, 0.49 mmol) in anh. CH_2Cl_2 (25 ml), sodium [4-(1,1-dimethylethyl)phenyl]methanolate (1 ml) – prepared by dissolving Na (1.08 g, 4.71 mmol) in [4-(1,1-dimethylethyl)phenyl]methanol (5 ml, 3.14 mmol) – was added. The mixture was stirred for 3 h at r.t., poured into H_2O, and extracted with CH_2Cl_2. After removal of the solvents, the residue was purified by CC (SiO_2; CH_2Cl_2). Yield: 0.0788 g (17.5%). Yellow-brownish solid. M.p. *ca.* 330° (dec.). ^{1}H-NMR ($CDCl_3$): 1.28 (*s*, 6 Me); 1.37 (*s*, 6 Me); 5.49 (*s*, 2 CH_2); 7.30 (*d*, ^3J=8.4, 4 H); 7.38 (*d*, ^3J=8.4, 4 H); 7.49 (*d*, ^3J=8.4, 4 H); 7.71 (*d*, ^3J=8.4, 4 H); 8.59 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.24; 31.42; 34.77; 46.50; 71.96; 111.76; 120.61; 124.36; 126.00; 127.38; 127.62; 128.99; 132.04; 134.04; 135.62; 138.35; 151.72; 160.29; 160.95; 162.60. MALDI-TOF-MS: 916.7705 (M^+, $C_{56}H_{58}N_2O_6S_2^+$; calc. 918.3731).

*2,7-Bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}-4,9-dihydroxybenzo[*lmn*][3,8]phenanthroline-1,3,6,8-(2*H,7H*)-tetrone* (**17a**). To a solution of **17** (0.035 g, 0.038 mmol) in CH_2Cl_2 (10 ml), toluene (10 ml), and AcCl (5 ml), a soln. of BBr_3 in CH_2Cl_2 (0.2 ml) was added dropwise at r.t. A red solid started to precipitate. The mixture was stirred for 30 min at r.t., poured into ice-water, and extracted with CH_2Cl_2, which resulted in a color change from red to yellow. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2). Yield: 0.0086 g (36%). Yellow solid. M.p. >410°. ^{1}H-NMR ($CDCl_3$): 1.38 (*s*, 6 Me); 7.31 (*d*, ^3J=8.1, 4 H); 7.76 (*d*, ^3J=8.1, 4 H); 8.39 (*s*, 2 H); 12.14 (*s*, 2 OH). MALDI-TOF-MS: 627.4142 (M^+, $C_{34}H_{30}N_2O_6S_2^+$; calc. 626.1540). Due to the very poor solubility of the material, we were not able to record its ^{13}C-NMR spectrum.

*4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}sulfanyl)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H,7H*)-tetrone* (**18**). A soln. of **8** (0.6456 g, 0.973 mmol), [4-(1,1-dimethylethyl)phenyl]methanethiol (0.7018 g, 3.89 mmol), and K_2CO_3 (0.4034 g, 2.92 mmol) in anh., degassed DMF (10 ml) was kept at 50° for 45 min. The solvent was evaporated, and the crude mixture was purified by CC (SiO_2; hexane/CH_2Cl_2 1:1 → 1:6). Yield: 0.7336 g (79%). Red-violet solid. M.p. 308–309°. ^{1}H-NMR ($CDCl_3$,): 1.29 (*s*, 6 Me); 1.37 (*s*, 6 Me); 4.33 (*s*, 2 CH_2); 7.28–7.34 (*m*, 10 H); 7.37 (*d*, ^3J=8.4, 4 H); 7.70 (*d*, ^3J=8.7, 4 H); 8.76 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.18; 31.38; 34.67; 37.18; 46.47; 118.72; 123.87; 125.12; 125.94; 128.62; 128.91; 129.27; 131.09; 134.20; 134.94; 138.31; 149.54; 151.09; 162.18; 163.16. MALDI-TOF-MS: 948.5477 (M^+, $C_{56}H_{58}N_2O_4S_4^+$; calc. 950.3274). Anal. calc. for $C_{56}H_{58}N_2O_4S_4$ (951.32): C 70.70, H 6.14, N 2.94; found: C 70.64, H 6.21, N 3.11.

*4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}selanyl)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H,7H*)-tetrone* (**19**). To a soln. of **21** (0.5544 g, 2.44 mmol) in anh., degassed DMF (10 ml), K_2CO_3 (0.3372 g, 2.44 mmol) and **8** (0.2348 g, 0.354 mmol) were added. The color of the mixture turned to green. The mixture was stirred for 45 min at r.t., poured into H_2O, and extracted with CH_2Cl_2. The solvent was evaporated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2). Yield: 0.0891 g (24%). Dark-red solid. M.p. 272–274°. ^{1}H-NMR ($CDCl_3$): 1.28 (*s*, 6 Me); 1.37 (*s*, 6 Me); 4.29 (*s*, 2 CH_2); 7.30 (*d*, ^3J=8.4, 6 H); 7.34 (*d*, ^3J=8.4, 6 H); 7.71 (*d*, ^3J=8.4, 4 H); 8.83 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 31.07 ($SeCH_2$); 31.30; 31.42; 34.69; 46.48; 121.31; 123.53;

125.96; 126.33; 128.91; 129.27; 131.21; 132.19; 134.53; 135.03; 138.19; 147.53; 150.76; 162.42; 163.95. Anal. calc. for $C_{56}H_{58}N_2O_4S_2Se_2$ (1045.12): C 64.36, H 5.59, N 2.68; found: C 64.12, H 5.63, N 2.89. MALDI-TOF-MS: 1044.4933 (M^+, $C_{56}H_{58}N_2O_4S_2Se_2^+$; calc. 1044.2187).

*4-Chloro-9-({[4-(1,1-dimethylethyl)phenyl]methyl}amino)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]-phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone* (**20**). A soln. of **8** (0.6406 g, 0.965 mmol) and 4-(1,1-dimethylethyl)benzene-1-amine (0.3152 g, 1.93 mmol) in DMI (10 ml) was kept at 40° for 8 h. The mixture was poured in H_2O, and the precipitate was collected by filtration. The filtrate was concentrated at reduced pressure, and purified by CC (SiO_2, CH_2Cl_2). Yield: 0.4633 g (61%). Red solid. M.p. 230–233°. ^{1}H-NMR ($CDCl_3$): 1.29 (*s*, 3 Me); 1.37 (*s*, 3 Me); 1.38 (*s*, 3 Me); 4.70 (*d*, ^3J=5.7, 2 H); 7.24–7.33 (*m*, 6 H); 7.37 (*d*, ^3J=7.8, 2 H); 7.71 (*d*, ^3J=7.5, 2 H); 7.73 (*d*, ^3J=7.5, 2 H); 8.41 (*s*, 1 H); 8.64 (*s*, 1 H); 10.27 (*t*, ^3J=5.6, NH). ^{13}C-NMR ($CDCl_3$): 31.16; 31.21; 31.38; 34.69; 46.54; 47.25; 100.60; 121.52; 121.89; 122.43; 124.36; 126.24; 127.40; 127.91; 128.69; 128.75; 128.85; 133.08; 133.97; 134.28; 134.30; 135.14; 135.24; 135.43; 138.39; 138.41; 151.40; 152.04; 161.30; 161.95; 162.09; 166.10. MALDI-TOF-MS: 790.6488 (M^+, $C_{45}H_{44}ClN_3O_4S_2^+$; calc. 789.2456). Anal. calc. for $C_{45}H_{44}ClN_3O_4S_2$ (790.43): C 68.38, H 5.61, N 5.32; found: C 68.79, H 5.67, N 5.40.

*4-({[4-(1,1-Dimethylethyl)phenyl]methyl}amino)-9-({[4-(1,1-dimethylethyl)phenyl]methyl}sulfanyl)-2,7-bis{4-[(1,1-dimethylethyl)sulfanyl]phenyl}benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone* (**20a**). To a solution of **20** (0.406 g, 0.514 mmol) in anh., degassed DMF (10 ml), [4-(1,1-dimethylethyl)-phenyl]methanethiol (0.1852 g, 1.03 mmol), and K_2CO_3 (0.1423 g, 1.03 mmol) were added. The mixture was kept at 50° for 1 h, and then poured into H_2O, and extracted with CH_2Cl_2. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; hexane/CH_2Cl_2 7:3 → 0:1). Yield: 0.3515 g (73%). Blue-violet solid. M.p. 299–302°. ^{1}H-NMR ($CDCl_3$): 1.28 (*s*, 3 Me); 1.29 (*s*, 3 Me); 1.34 (*s*, 3 Me); 1.37 (*s*, 3 Me); 4.30 (*s*, SCH_2); 4.64 (*d*, ^3J=5.1, NCH_2); 7.26–7.39 (*m*, 12 H); 7.68 (*d*, ^3J=8.7, 2 H); 7.74 (*d*, ^3J=8.4, 2 H); 8.32 (*s*, 1 H); 8.75 (*s*, 1 H); 10.01 (*t*, ^3J=5.4, NH). ^{13}C-NMR ($CDCl_3$): 31.12; 31.17; 31.35; 31.38; 34.63; 34.65; 36.98; 46.46; 46.48; 47.24; 100.45; 119.31; 120.12; 121.20; 123.09; 125.79; 126.12; 126.32; 126.93; 127.64; 128.14; 128.82; 128.87; 129.28; 131.41; 133.17; 133.94; 134.08; 135.04; 135.45; 138.34; 138.45; 144.49; 150.81; 150.93; 151.24; 162.21; 162.73; 163.37; 165.97. MALDI-TOF-MS: 932.6744 (M^+, $C_{56}H_{59}N_3O_4S_3^+$; calc. 933.3662). Anal. calc. for $C_{56}H_{59}N_3O_4S_3$ (934.28): C 71.99, H 6.37, N 4.50; found: C 72.23, H 6.41, N 4.45.

S,S′*-{[4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}amino)-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo-[*lmn*][3,8]phenanthroline-2,7-diyl]dibenzene-4,1-diyl} Diethanethioate* (**4**). To a soln. of **16** (0.4168 g, 0.454 mmol) in CH_2Cl_2 (100 ml), toluene (40 ml), and AcCl (40 ml), a soln. of BBr_3 in CH_2Cl_2 (4 ml) was added dropwise at 0°. The mixture was stirred for 1 h at r.t, poured into ice-water, and extracted with CH_2Cl_2. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2/AcOEt). Yield: 0.2122 g (53%). Blue solid. M.p. 281–283°. UV/VIS (CH_2Cl_2): 610 (22000), 563 (11100), 364 (14000), 347 (12100), 283 (47500). Fluorescence spectrum (CH_2Cl_2): λ_{max} 642 nm. ^{1}H-NMR ($CDCl_3$, 45°): 1.28 (*s*, 6 Me); 2.47 (*s*, 2 Me); 4.58 (*d*, ^3J=5.1, 4 H); 7.26 (*d*, ^3J=8.4, 4 H); 7.32 (*d*, ^3J=8.4, 4 H); 7.40 (*d*, ^3J=8.4, 4 H); 7.58 (*d*, ^3J=8.4, 4 H); 8.12 (*s*, 2 H); 9.46 (*t*, ^3J=5.1, 2 NH). ^{13}C-NMR ($CDCl_3$, 45°): 30.39; 31.44; 34.68; 47.32; 102.16; 119.01; 121.75; 126.07; 126.27; 127.75; 129.29; 129.78; 133.89; 135.10; 136.23; 149.30; 151.09; 162.81; 166.16; 192.80. MALDI-TOF-MS: 887.7246 (M^+, $C_{52}H_{48}N_4O_6S_2^+$; calc. 888.3010). Anal. calc. for $C_{52}H_{48}N_4O_6S_2$ (889.09): C 70.25, H 5.44, N 6.30; found: C 70.12, H 5.44, N 6.31.

S,S′*-{[4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}sulfanyl)-1,3,6,8-tetrahydro-1,3,6,8-tetraoxoben-zo[*lmn*][3,8]phenanthroline-2,7-diyl]dibenzene-4,1-diyl} Diethanethioate* (**5**). To a soln. of **18** (0.1260 g, 0.132 mmol) in CH_2Cl_2 (25 ml), toluene (5 ml), and AcCl (10 ml), a soln. of BBr_3 in CH_2Cl_2 (0.5 ml) was added dropwise at 0°. The mixture was stirred for 1 h at r.t., poured into H_2O, and extracted with CH_2Cl_2. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2/AcOEt 1:0 → 20:1). Yield: 0.0801 g (65%). Red solid. M.p. 313–315°. UV/VIS (CH_2Cl_2): 528 (21100), 493 (11500), 370 (14400), 355 (12000), 297 (59800), 265 (29900). Fluorescence spectrum (CH_2Cl_2): λ_{max} 558 nm. ^{1}H-NMR ($CDCl_3$, 50°): 1.29 (*s*, 6 Me); 2.46 (*s*, 2 Me); 4.37 (*s*, 2 CH_2); 7.33 (*d*, ^3J=8.4, 4 H); 7.36–7.42 (*m*, 8 H); 7.61 (*d*, ^3J=8.7, 4 H); 8.87 (*s*, 2 H). ^{13}C-NMR ($C_2D_2Cl_4$):

30.62; 31.37; 34.61; 37.17; 118.95; 124.10; 125.46; 126.12; 128.89; 129.16; 129.53; 129.60; 130.83; 135.14; 135.25; 149.36; 151.27; 162.16; 163.22; 193.31. MALDI-TOF-MS: 921.3207 (M^+, $C_{52}H_{46}N_2O_6S_4^+$; calc. 922.2233). Anal. calc. for $C_{52}H_{46}N_2O_6S_4$ (923.18): C 67.65, H 5.02, N 3.03; found: C 67.48, H 5.07, N 3.12.

S,S′-*{[4,9-Bis({[4-(1,1-dimethylethyl)phenyl]methyl}selanyl)-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl]dibenzene-4,1-diyl} Diethanethioate* (**6**). To a soln. of **19** (0.0666 g, 0.064 mmol) in CH_2Cl_2 (10 ml), toluene (4 ml), and AcCl (4 ml), a soln. of BBr_3 in CH_2Cl_2 (0.2 ml) was added dropwise at 0°. The mixture was stirred for 1 h at r.t., poured into H_2O, and extracted with CH_2Cl_2. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2). Yield: 0.0387 g (59%). Pink solid. M.p. 320–322°. UV/VIS (CH_2Cl_2): 553 (23400), 515 (13000), 375 (20700), 357 (17100), 308 (51700). Fluorescence spectrum (CH_2Cl_2): λ_{max} 594 nm. ^{1}H-NMR ($C_2D_2Cl_4$, 50°): 1.32 (*s*, 6 Me); 2.52 (*s*, 2 Me); 4.34 (*s*, 2 CH_2); 7.38 (*s*, 8 H); 7.43 (*d*, ^3J = 7.8, 4 H); 7.65 (*d*, ^3J = 7.8, 4 H); 8.90 (*s*, 2 H). ^{13}C-NMR ($C_2D_2Cl_4$, 50°): 32.18; 32.67; 33.03; 36.23; 123.00; 125.25; 127.69; 128.13; 130.77; 131.26; 131.34; 132.94; 133.58; 136.69; 136.97; 149.04; 152.49; 163.92; 165.53; 194.67. MALDI-TOF-MS: 1016.4682 (M^+, $C_{52}H_{46}N_2O_6S_2Se_2^+$; calc. 1016.1145). Anal. calc. for $C_{52}H_{46}N_2O_6S_2Se_2$ (1016.98): C 61.41, H 4.56, N 2.75; found: C 61.23, H 4.61, N 2.96.

S,S′-*{[4-({[4-(1,1-Dimethylethyl)phenyl]methyl}amino)-9-({[4-(1,1-dimethylethyl)phenyl]methyl}sulfanyl)-1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl]dibenzene-4,1-diyl} Diethanethioate* (**7**). To a soln. of **20a** (0.2352 g, 0.252 mmol) in CH_2Cl_2 (20 ml), toluene (5 ml), and AcCl (10 ml), a soln. of BBr_3 in CH_2Cl_2 (1 ml) was added dropwise at 0°. The mixture was stirred for 1 h at r.t., poured into H_2O, and extracted with CH_2Cl_2. The combined org. phases were concentrated at reduced pressure, and the residue was purified by CC (SiO_2; CH_2Cl_2/AcOEt 1:0 → 20:1). Yield: 0.1380 g (60.5%). Violet solid. M.p. 298–299°. UV/VIS (CH_2Cl_2): 567 (24300), 529 (14500), 366 (14600), 351 (13600), 289 (48700), 274 (45900). Fluorescence spectrum (CH_2Cl_2): λ_{max} 596 nm. ^{1}H-NMR ($C_2D_2Cl_4$): 1.31 (*s*, 3 Me); 1.32 (*s*, 3 Me); 2.51 (*s*, Me); 2.53 (*s*, Me); 4.19 (*s*, SCH_2); 4.63 (*d*, ^3J = 5.1, NCH_2); 7.31 (*d*, ^3J = 8.4 2 H); 7.34–7.43 (*m*, 8 H); 7.46 (*d*, ^3J = 8.4, 2 H); 7.59 (*d*, ^3J = 8.4, 2 H); 7.62 (*d*, ^3J = 8.4, 2 H); 8.30 (*s*, 1 H); 8.56 (*s*, 1 H); 9.98 (*t*, ^3J = 5.1, NH). ^{13}C-NMR ($C_2D_2Cl_4$): 32.29; 32.32; 33.07; 33.08; 36.28; 38.64; 48.98; 102.26; 121.06; 122.12; 123.06; 124.96; 127.70; 127.92; 128.22; 128.71; 129.28; 129.82; 130.81; 130.87; 131.01; 131.34; 131.47; 132.86; 134.68; 136.81; 136.87; 137.06; 137.53; 145.82; 152.68; 152.73; 152.99; 163.86; 164.35; 165.09; 167.53; 195.04; 195.21. Anal. calc. for $C_{52}H_{47}N_3O_6S_3 \cdot H_2O$ (924.16): C 67.58, H 5.34, N 4.55; found: C 67.82, H 5.50, N 4.39. MALDI-TOF-MS: 904.1173 (M^+, $C_{52}H_{47}N_3O_6S_3^+$; calc. 905.2622).

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