Synthesis and Characterization of Functionalized Analogs of 1,3,6,8-Tetrakis(methylsulfanyl)pyrene and Their Electron-Conducting Radical-Cation Salts

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Abstract: Radical-cation salts of sulfur-substituted aromatic compounds, formed upon chemical and electrochemical oxidation of the neutral parent compounds, represent an important class of stable electron-conducting materials with many potential uses in molecular-electronics. Many electronic devices require, however, macromolecular materials bound to an electrode surface. While a large number of sulfur-substituted aromatic compounds capable of forming electron-conducting radical-cations salts have been thus far reported, none of them bears functional groups that could be used to bind these compounds to a polymer backbone or an electrode surface. In this paper, we report the synthesis of functionalized analogs of 1,3,6,8-tetrakis(methylsulfanyl)pyrene, where one of the methylsulfanyl groups has been replaced by an amide group. Substitution of the methylsulfanyl group by the amide group does not inhibit the formation of highly electron-conducting radical-cation salts. *N*-(3,6,8-Tris(methylsulfanyl)pyren-1-yl)acetamide (**3a**) forms, upon oxidation with iodine, a radical-cation salt (**4a**) similar to those formed by the parent 1,3,6,8-tetrakis(methylsulfanyl)-pyrene **2**. The electron-conductivity of radical-cation salt **4a** was found to be 1 S cm^{-1} at room temperature. The amide group was also used as a handle to introduce additional functionality on the molecule. Coupling of 3,6,8-tris-(methylsulfanyl)pyren-1-ylamine (**10**) with the γ-carboxyl group of *N*-(*tert*-butoxycarbonyl)-L-glutamic acid α-*tert*-butyl ester was achieved via the formation of a mixed anhydride with isobutylchloroformate. This functionalized 3,6,8-(trismethylsulfanyl)pyrene derivative will be used in polymerization reactions onto electrode surfaces, providing a new surface-bound electroactive polymer with potential applications in molecular devices.

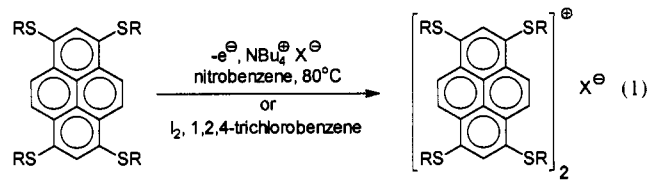
Introduction

Inokuchi *et al.* reported in 1956 that a large number of polycyclic aromatic hydrocarbons form molecular complexes with bromine and iodine and that these complexes behave as semiconductors with conductivities ranging from 10^{-3} to 10^{-1} S cm^{-1} (pressed pellet) at room temperature.[1] The groups of Fritz *et al.*[2] and Wegner *et al.*[3] reported later that radical-cation salts of polycyclic aromatic hydrocarbons can also be prepared by anodic oxidation of the hydrocarbons. These radical-cations salts show temperature-dependent conductivities typical of organic metals, with values ranging from 10^{-3} to 10^{-1} S cm^{-1} at room temperature.

These salts represent a very interesting class of organic metals with a common structure. In the crystals, aromatic molecules are arranged in stacks, leaving channels in which the counter-anions are located. Intramolecular distances of 3.2–3.3 Å between the aromatic planes are generally observed. Finally, while only one out of every two aromatic molecules is oxidized to the radical-cation state (ratio aromatic molecule/counter-anion ≈ 2), they are all crystallographically identical; *i.e.*, the radical-cation is not localized.

The radical-cation salts of simple aromatic hydrocarbons are, however, generally unstable. Most halogen complexes readily lose bromine or iodine, and other radical-cation salts are easily reduced when kept for some time at room temperature. It is now known, however, that the presence of sulfur substituents stabilizes cationic compounds. Consequently, many research groups reported in recent years the synthesis and characterization of stable electron-conducting radical-cation salts of aromatic compounds containing sulfur heteroatoms or substituents.[4,5]

Amongst the most remarkable examples of this type of compounds are the radical-cation salts (**1**) of 1,3,6,8-tetrakis-(alkylsulfanyl)pyrenes **2** reported recently by Heywang *et al.*[5] These salts (**1**) were prepared by electrochemical and chemical oxidation of the neutral 1,3,6,8-tetrakis(alkylsulfanyl)pyrenes **2** (eq 1). The resulting radical-cation salts **1** show good thermal



(1)

2 (R = Me, Et, n-Bu, C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$) **1**

(X = ClO_4^-, $FeCl_4^-$, BF_4^-, I_3^-)

stability and high electrical conductivity, with the best conductivity (677 S cm^{-1}) observed in a single crystal of the perchlorate salt of 1,3,6,8-tetrakis(methylsulfanyl)pyrene.

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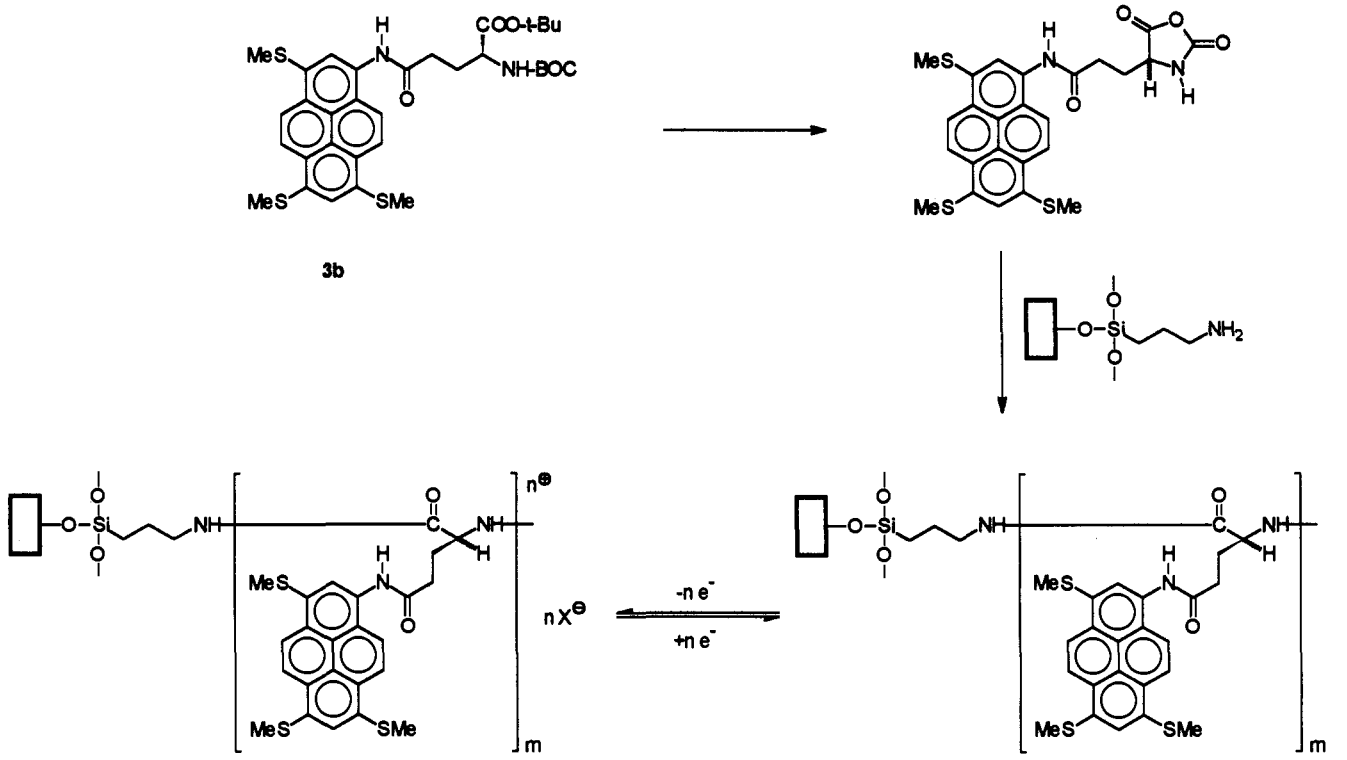
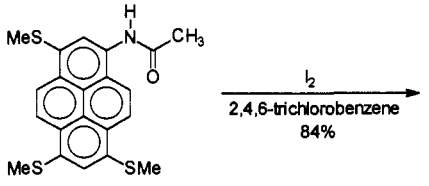
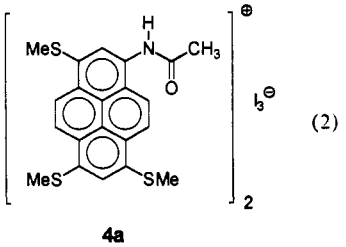
Scheme 1



Radical cation salts, such as compound **1**, represent a class of molecular materials with properties well suited for their utilization in a number of electronic devices.[6] Many devices require, however, that the material be macromolecular and/or be bound to an electrode surface. While a large number of sulfur-substituted aromatic compounds capable of forming electron-conducting radical-cation salts have been thus far reported, none of them bear functional groups that could be used to bind these compounds to a polymer backbone or to an electrode surface. In this paper, we report the synthesis and characterization of new sulfur-substituted pyrene derivatives analogous to compound **2**. Compound **3a** was synthesized and the corresponding radical-cation salt **4a** prepared by oxidation with iodine (eq 2). The conductivity



3a



4a

(2)

of radical-cation salt **4a** was measured and found to be of the same order of magnitude as that of the parent compounds **1**.

Further elaboration of the sulfur-substituted pyrene derivative was achieved by deprotection of the acetamide group and coupling of the resulting amino group with the γ-carboxyl group of *N*-(*tert*-butoxycarbonyl)-L-glutamic acid α-*tert*-butyl ester. This new compound (**3b**) presents functionality that will allow its incorporation into a macromolecular backbone and eventual binding to an electrode surface. The approach pursued is represented in Scheme 1.

Results and Discussion

A number of limitations must be considered in the design and the synthesis of new functionalized sulfur-substituted pyrene derivatives, suitable for incorporation into a macromolecular backbone and binding to an electrode surface. The functionality introduced on the pyrene ring at an early stage of the synthesis must be chosen so that it does not interfere with the subsequent introduction of sulfur substituents. The functional group must also been chosen so that further elaboration, polymerization, and binding to an electrode surface can be achieved in a way that is chemically compatible with the easily oxidizable sulfur-substituted pyrene moiety. Finally, it is of upmost importance that the presence of the functional group on the sulfur-substituted pyrene ring does not inhibit the formation of stable-electron conducting radical-cation salts upon oxidation.

Bearing this in mind, we developed a synthesis of *N*-(3,6,8-tris(methylsulfanyl)pyren-1-yl)acetamide (**3a**) and its radical-cation salt **4a** in order to test whether or not amides were adequate functional groups. Compound **3a** is prepared in five steps from pyrene with a 60% overall yield (Scheme 2). In the first step, pyrene (**5**) is nitrated in a 77% yield using the procedure described by Radner,[7] and the resulting 1-nitropyrene (**6**) is reduced to 1-aminopyrene (**7**) in a 98% yield using a method reported by Petit *et al.*[8] The resulting 1-aminopyrene (**7**) is then acetylated in 89% yield with acetic anhydride in refluxing acetone prior to bromination. Bromination was attempted at earlier stages of the synthesis but did not give the desired 3,6,8-tribromo products in

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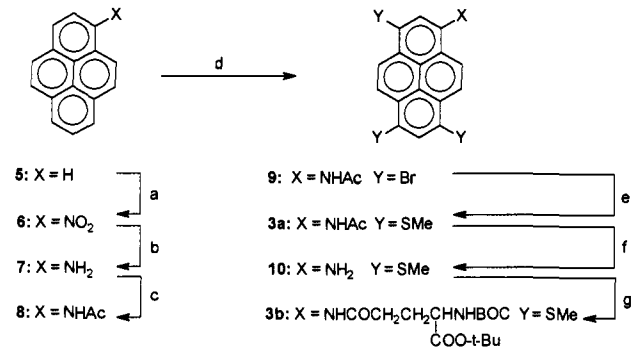
Scheme 2[a]



[a] Key: (a) HNO_3, H_2SO_4, 77%; (b) hydrazine, Raney Ni, ethanol/benzene, 98%; (c) Ac_2O, acetone, reflux, 89%; (d) Br_2, nitrobenzene, 90 °C, 98%; (e) $NaSCH_3$, DMF, 100 °C, 90%; (f) hydrazine, dioxane, reflux, 78%; (g) *i*-BuOCOCl, *N*-(*tert*-butoxycarbonyl)-L-glutamic acid *α-tert*-butyl ester, Et_3N, THF, 53%.

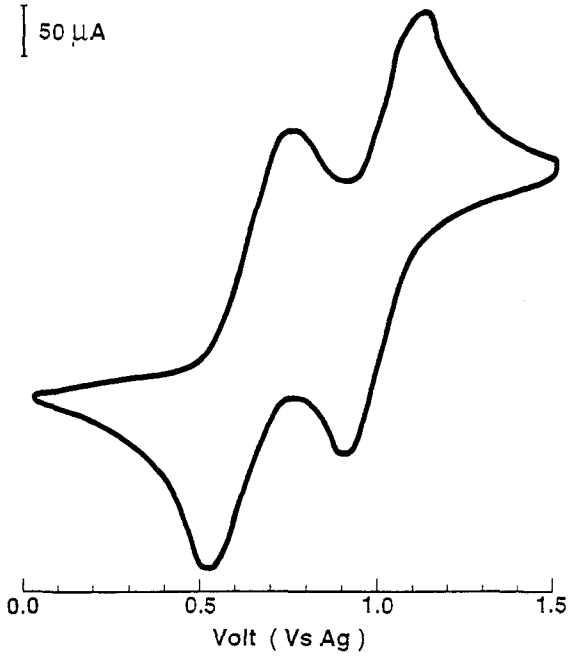


Figure 1. Cyclic voltammogram of a solution containing 3×10^{-6} M of compound **3a** and 0.05 M of $Bu_4N^+BF_4^-$ in nitrobenzene. The voltammogram was recorded at a scan rate of 200 mV s^{-1}, using a platinum wire as working electrode and a silver wire as reference electrode.

satisfactory yields. Bromination of *N*-pyrenyl-1-ylacetamide (**8**) in nitrobenzene, however, gave the desired *N*-(3,6,8-tribromopyren-1-yl)acetamide (**9**) in nearly quantitative yield.

The nearly total lack of solubility of this tribromo compound prevented us from determining at this stage whether or not bromination occurs exclusively at positions 3, 6, and 8 of the pyrene ring. This was, however, confirmed to be the case by a NOE experiment at a later stage of the synthesis (*vide infra*). Finally, introduction of the sulfur substituents was achieved by aromatic nucleophilic substitution of the bromine atoms with sodium thiomethoxide in hot DMF. Compound **3a** was obtained in a 90% yield, and no deacetylated product was observed when 3.3 molar equiv of $NaSCH_3$ per molar equiv of tribromo compound **9** was used. Compound **3a** was electrochemically characterized by cyclic voltammetry (Figure 1). The cyclic voltammogram of **3a** in nitrobenzene shows two chemically-reversible one-electron oxidation waves. This behavior demonstrates that the radical-cation of **3a** is a stable species in solution and that radical-cation salt **4a** could be prepared by electrosynthesis.

Once compound **3a** was in hand, the crucial oxidation step with iodine was attempted. Addition of a solution of iodine to a solution of **3a** in 2,4,6-trichlorobenzene resulted in the immediate formation of shiny black crystals. Although radical-cation salt **4a** is insoluble in almost any solvent, it can be recrystallized from dilute solutions in hot nitrobenzene or DMSO. The compound is stable for prolonged periods of time at room temperature and in air, but loses iodine when heated above 200 °C. Elemental analysis gaves results in accord with a molecular formula of $C_{21}H_{19}NOS_3I_{3/2}$ or $(C_{21}H_{19}NOS_3)_2{}^+I_3^-$. Radical-cation salt **4a** is therefore truly analogous to the parent radical-cation salt **1** (R = Me, $X = I_3^-$) in that oxidation with iodine leads to the formation of a salt in which one of every two pyrene units is oxidized to the radical-cation state, with triiodide acting as counter-anion. Radical-cation **4a** also exhibits a very broad absorption in the infrared region centered between 3000 and 2000 cm^{-1}. This broad absorption band is characteristic of a segregated stacked structure in a mixed valence state.[9] Finally, electron conductivity was measured on pressed pellets of the salt **4a** at room temperature using the four-probe technique.[10] The conductivity of radical-cation salt **4a** was found to be 1 S cm^{-1}, nearly as high as that of pressed pellets of the symmetric parent compound **1** (R = Me, $X = I_3^-$) which exhibited a conductivity of 3.9 S cm^{-1} when measured under identical conditions (literature value: 10 S cm^{-1}),[5]

Once it was established that amide groups do not inhibit the formation of radical-cation salts with high electron conductivity, we proceeded to further elaborate the molecule. Our objective was to substitute the acetyl group of compound **3a** with a group that could be incorporated into a macromolecular framework. We chose to use a polypeptide backbone for a number of reasons. The first is the availability of natural amino acids bearing a terminal carboxylic acid functional group on the side chain. L-Glutamic acid was chosen for this work, but the availability of other amino acids offers the option to easily vary the length of the tether. Another advantage is that polypeptides tend to adopt well-defined and somewhat rigid conformations. Consequently, polypeptides have been frequently used as the framework for molecular photonics and electronics.[11] Finally, polymerization and binding to electrode surfaces can be achieved in a manner that is chemically compatible with the easily oxidizable sulfur-substituted pyrene ring, as illustrated in Scheme 1.

Compound **3a** was therefore deacetylated by treatment with hydrazine in refluxing dioxane. The desired 3,6,8-tris(methylsulfanyl)pyren-1-ylamine (**10**) was obtained with a 78% yield. Compound **10** being considerably more soluble in DMSO than previous intermediates of the sequence, NOE experiments were conducted at this stage to establish whether tribromination of compound **8** occurred at positions 3, 6, and 8 or at positions 2, 6, and 8. Saturation of the singlet generated by the proton at position-2, resulted as expected, in an enhancement of the signal for the methylsulfanyl group at position-3, as well as that of the amino group at position-1. Enhancement of the signal for the amino group would not be observed if bromination had occurred at position-2.

Different methods were tested for the formation of an amide bond between compound **10** and the γ-carboxyl group of *N*-(*tert*-butoxycarbonyl)-L-glutamic acid *α-tert*-butyl ester. Direct coupling of the acid using DDC or *via* the prior formation of the acid chloride proved unsuccessful. Coupling could be achieved in reasonable yield, however, by activation of the carboxylic group by the formation of a mixed anhydride using isobutylchloroformate in the presence of triethylamine. Addition of compound **10** to a solution of the mixed anhydride gave compound **3b** with a 53% yield. The presence of the additional functionality does not affect the electrochemical behavior of compound **3b**. Cyclic voltammograms of **3b** exhibit two chemically-reversible one-electron oxidation waves identical to those observed in the cyclic volta-

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mmograms of compound **3a**. This confirms that the radical-cation of compound **3b** is also a stable species in solution.

Conclusion

Radical-cation salts of sulfur-substituted aromatic compounds, formed upon chemical and electrochemical oxidation of the neutral parent compounds, represent an important class of stable electron-conducting materials with many potential uses in molecular-electronics.[4,5] Many electronic devices require, however, macromolecular materials bound to an electrode surface. In the present paper, we have shown that attachment of an amide group on sulfur-substituted pyrene rings provides a handle that allows further elaboration of the molecule without inhibiting the formation of highly conducting radical-cation salts. This handle was used to link the sulfur-substituted pyrene ring to the side chain of glutamic acid. We are now in a position to prepare the *N*-carboxy anhydride of amino acid **3b** in order to polymerize it onto electrode surfaces, as illustrated in Scheme 1.

Experimental Section

Melting points are reported uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., or Guelph Chemical Laboratories, Ltd. Flash column chromatographies were performed using EM Science silica gel 60 (230–400 mesh). Dioxane, THF, and hexane were distilled over sodium/benzophenone ketyl. Methylene chloride and triethylamine were distilled over calcium hydride. Bromine, sodium thiomethoxide, hydrazine, and isobutyl chloroformate were purchased from Aldrich and used without further purification. Iodine and *N*-(*tert*-butoxycarbonyl)-L-glutamic acid α-*tert*-butyl ester were purchased from BDH and Sigma, respectively, and were used without further purification. 1-Nitropyrene (**6**) was prepared according to the procedure reported by Radner[7] and 1-aminopyrene (**7**) according to the procedure described by Petit.[8]

***N*-Pyren-1-ylacetamide (8).** A solution of acetic anhydride (6.34 g; 62.1 mmol) and 1-aminopyrene (**7**) (4.5 g; 20.7 mmol) in acetone (120 mL) was refluxed for 1 h. The precipitate was recovered by filtration, washed with acetone, and dried *in vacuo*. The melting point and NMR spectrum of the product **8** (4.78 g; 89%) were identical to those reported in the literature.[12]

***N*-(3,6,8-Tribromopyren-1-yl)acetamide (9).** A solution of bromine (3.05 g; 19.1 mmol) in nitrobenzene (30 mL) was added drop by drop over 30 min and with vigorous stirring to a suspension of *N*-pyren-1-ylacetamide (**8**) (1.5 g; 5.8 mmol) in nitrobenzene (30 mL). The reaction mixture was stirred at 90 °C for 1 h. The precipitate was recovered by filtration, washed with ethanol, and dried *in vacuo*. Recrystallization from boiling DMSO gave a pale crystalline compound (2.8 g, 98%): mp = dec; ^{1}H NMR (400 MHz, DMSO, 120 °C) δ 10.10 (br s, 1H), 8.76 (s, 1H), 8.64 (s, 1H), 8.53 (d, *J* = 9.6 Hz, 1H), 8.52 (d, *J* = 9.6 Hz, 1H), 8.43 (d, *J* = 9.6 Hz, 1H), 8.39 (d, *J* = 9.6 Hz, 1H), 2.31 (s, 3H); IR (KBr) ν_{max} 3175 (NH stretch), 1670 (C=O stretch) cm^{-1}. Anal. Calcd for $C_{18}H_{10}NOBr_3$: C, 43.59; H, 2.03; N, 2.82. Found: C, 44.60; H, 2.33; N, 2.93.

***N*-(3,6,8-Tris(methylsulfanyl)pyren-1-yl)acetamide (3a).** *N*-(3,6,8-Tribromopyren-1-yl)acetamide (**9**) (2.5 g; 5.04 mmol) was added in small portions to a solution of sodium thiomethoxide (1.16 g; 16.6 mmol) in DMF (10 mL). The reaction mixture was stirred at 100 °C under argon atmosphere for 15 h and cooled to room temperature. Water (15 mL) was added, and the yellow precipitate was recovered by filtration, washed with methanol and dried *in vacuo*. The desired product was obtained as light yellow crystals after three successive crystallizations in nitrobenzene (1.8 g; 90%): mp = dec; ^{1}H NMR (300 MHz, DMSO, 120 °C) δ 10.05 (br s, 1H), 8.47 (s, 2H), 8.40 (d, *J* = 9.5 Hz, 1H), 8.37 (s, 1H), 8.28 (d, *J* = 9.5 Hz, 1H), 8.08 (s, 1H), 2.75 (s, 6H), 2.69 (s, 3H), 2.27 (s, 3H); IR (KBr) ν_{max} 3260 (NH stretch), 1650 (C=O stretch) cm^{-1}; HRMS (EI) calcd for $C_{21}H_{19}NOS_3$ 397.0629, found 397.0657; UV (DMSO) ν_{max} 261, 310, 408, 429 nm. Anal. Calcd for $C_{21}H_{19}NOS_3$: C, 63.44; H, 4.82; N, 3.52. Found: C, 63.98; H, 4.95; N, 3.68.

Oxidation of *N*-(3,6,8-Tris(methylsulfanyl)pyren-1-yl)acetamide with Iodine. A solution of iodine (160 mg; 0.63 mmol) in 2,4,6-trichlorobenzene (2 mL) was added to a solution of *N*-(3,6,8-tris(methylsulfanyl)pyren-1-yl)acetamide (**3a**) (100 mg; 0.25 mmol) in 2,4,6-trichlorobenzene (5 mL) at 120 °C and under argon atmosphere. A dark precipitate formed immediately. The salt **4a** was recovered by filtration, washed with dichloromethane, and dried *in vacuo* (130 mg; 84%): mp = 230 °C dec. Anal. Calcd for $C_{21}H_{19}NOS_3I_{3/2}$: C, 42.90; H, 3.26; N, 2.38; S, 16.36; I, 32.38. Found: C, 42.80; H, 3.07; N, 2.57; S, 15.98; I, 32.04.

3,6,8-Tris(methylsulfanyl)pyren-1-ylamine (10). A suspension of *N*-(3,6,8-tris(methylsulfanyl)pyren-1-yl)acetamide (**3a**) (1.54 g; 3.87 mmol) in a 4:1 mixture of hydrazine and dioxane (20 mL) was refluxed for 24 h. The precipitate was recovered by filtration, washed with ethanol, and dried *in vacuo*. The desired product was isolated as a yellow solid (1.07 g; 78%): mp = dec; ^{1}H NMR (DMSO, 400 MHz, 25 °C) δ 8.22 (d, *J* = 9.4 Hz, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 8.01 (d, *J* = 9.4 Hz, 1H), 7.95 (d, *J* = 9.3 Hz, 1H), 7.80 (s, 1H), 7.36 (s, 1H), 6.52 (br s, 2H), 2.70 (s, 6H), 2.65 (s, 3H); IR (KBr) ν_{max} 3440 (NH stretch), 3360 (NH stretch) cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NS_3$ 355.0531, found 355.0510; UV (DMSO) ν_{max} 261, 311, 436, 454 nm. Anal. Calcd for $C_{19}H_{17}NS_3$: C, 64.19; H, 4.82; N, 3.94. Found: C, 64.26; H, 5.06; N, 4.50.

Nα-(*tert*-Butoxycarbonyl)-*N*-(3,6,8-tris(methylsulfanyl)pyren-1-yl)-L-glutamine α-*tert*-Butyl Ester (3b). Isobutyl chloroformate (0.22 g; 1.61 mmol) was added to a solution of *N*-(*tert*-butoxycarbonyl)-L-glutamic acid α-*tert*-butyl ester (0.5 g; 1.65 mmol) and triethylamine (0.23 mL; 1.65 mmol) in dry THF (8 mL) kept at 0 °C and under argon atmosphere. After 2 h of stirring at this temperature, triethylammonium hydrochloride was filtered off and the solution transferred into a solution of 3,6,8-tri-(methylsulfanyl)pyren-1-ylamine (**10**) (0.58 g; 1.63 mmol) in dry THF (5 mL). The resulting mixture was stirred at room temperature for 15 h. The precipitate was then collected by filtration, washed with THF, and dried *in vacuo* (0.55 g; 53%): mp = dec.; ^{1}H NMR (400 MHz, DMSO, 120 °C) δ 9.87 (br s, 1H), 8.47 (s, 2H), 8.40 (d, *J* = 9.6 Hz, 1H), 8.35 (s, 1H), 8.26 (d, *J* = 9.6 Hz, 1H), 8.08 (s, 1H), 6.44 (br d, *J* = 5.3 Hz, 1H), 4.04 (dt, *J* = 5.3 and 8.2 Hz, 1H), 2.749 (s, 3H), 2.746 (s, 3H), 2.70 (s, 3H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.15–2.24 (m, 1H), 2.00–2.09 (m, 1H), 1.47 (s, 9H), 1.43 (s, 9H); IR (KBr) ν_{max} 3365 (NH stretch), 3330 (NH stretch), 1735 (C=O stretch), 1690 (C=O stretch), 1660 (C=O stretch) cm^{-1}; HRMS (EI) calcd for $C_{33}H_{40}N_2O_5S_3$ 640.2099, found 640.2062; UV(DMSO) ν_{max} 261, 311, 410, 429 nm. Anal. Calcd for $C_{33}H_{40}N_2O_5S_3$: C, 61.85; H, 6.29; N, 4.37. Found: C, 62.00; H, 6.34; N, 4.48.

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