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Highly Emissive Water-Soluble Polysulfurated Pyrene-based Chromophores as Dual Mode Sensors of Metal ions

Marco Villa,^{*[a,b]} Myriam Roy,^{*[b]} Giacomo Bergamini,^[a] Paola Ceroni,^[a] Marc Gingras^[b]

[a] Dr. M. Villa, Prof. G. Bergamini and Prof. P. Ceroni
Department of Chemistry "Giacomo Ciamician"
University of Bologna
Via Selmi, 2, 40126 Bologna
E-mail: marco.villa11@unibo.it

[b] Dr. M. Roy, Dr. M. Villa and Prof. M. Gingras
Aix Marseille Univ, CNRS, CINaM, Marseille, France
E-mail : myriam.roy@sorbonne-universite.fr

Supporting information for this article is given via a link at the end of the document.

Abstract: We designed a polysulfurated arene system based on a tetra(phenylthio)pyrene core decorated with four carboxylic acid units. Three different regioisomers, ortho, meta and para were studied in organic and aqueous solution. These systems are soluble in water at pH ≥ 8 due to deprotonation of carboxylic acids. The addition of metal ions can not only quench the fluorescence of the central pyrene core, but also control the formation of three-dimensional nanoscopic objects in a dual mode function. Several divalent metal ions were tested and compared. Addition of ethylenediaminetetraacetic acid (EDTA) disassembles the non-emissive supramolecular system and restores the initial fluorescence of the pyrene core.

Introduction

Stimuli-responsive chemical sensors with luminescent materials have gained considerable attention because their physical or chemical properties can change with respect to external stimuli, such as heat,^[1] light,^{[2],[3]} conduction,^[4] presence of ions,^[5] pH,^[6] self-assembly,^[7] and tensile strength.^[8] In a more advanced form, these systems could be used in a dual mode sensing^{[9],[10]} of analytes, following changes of two properties, like emission intensity and aggregation, due to the formation of a supramolecular polymer. By using divalent metal ions that form complexes in a 2:1 ligand to metal stoichiometry, it is possible to generate supramolecular coordination polymers in which the "monomers" are self-assembled by metal ion binding. It thus generates changes of the photochemical properties of the initial "monomeric" state to a "polymeric" state.

In this way, pyrene-based stimuli responsive luminescent materials remain popular as ion sensors,^[11] biological markers,^[12] liquid crystals,^[13] light-emitting devices^[14] and field-effect transistors.^[15] Recently, much efforts focused on sensors compatible with water for the detection of toxic metal ions^{[16],[17]} or biomolecules. Some pyrene-based systems were utilized for the aqueous detection of trivalent metal ions like Cr(III), Al(III)^[9] and Fe(III)^[18] or divalent metal ions like Cd(II) or Zn(II)^[19] or in the sensing of lysine and arginine,^[20] but rarely for Pb(II),^{[21],[22]} In the latter case, an organic co-solvent is needed for increasing solubility and homogeneity, and not only water.

In this work, we are seeking to develop metal ions sensors with dual functions in water only, after a rational design of multivalent ligands able to self-assemble with metal ions (especially heavy ones). A pyrene core is chosen because of its exalted photophysical and electrochemical sensitivity to its

environment.^[23] Substituents on pyrene are needed, while keeping high emissivity.^[24] Alkynylations^[25] or arylations^[20] of pyrene at positions 1,3,6,8 were often reported as anchoring groups. However, heterofunctionalization is less common, especially with divalent sulfur atoms. Thus, 1,3,6,8-tetra(phenylthio)pyrenes were selected, because they are highly emissive, often soluble in solvents, and underused. For instance, we reported the synthesis and the photophysical properties of a dendrimer made from a tetrasulfurated pyrene core with phenylene sulfide dendrons,^[26] and a similar core with terpyridine ligands.^[27] The latter system behaves as a molecular antenna in which the peripheral units collect light and transfer the excitation energy to the central luminescent core. The addition of metal ions to this system can not only switch the direction of the intramolecular energy transfer, but also control the formation of three-dimensional nanoscopic objects in a dual function. Replacement of coordinating terpyridine groups by simpler ones, under complete aqueous conditions, was pursued.

In this work, we report the synthesis, characterization, metal ion coordination and sensing activities of water-soluble, polysulfurated pyrenes incorporating tetracarboxylic acids ligands, for making new supramolecular systems with tailor-made photophysical properties and aggregation states. In short, a family of tetracarboxylated tetra(phenylthio)pyrenes were synthesized and decorated with four peripheral and regioisomeric carboxylic acid groups at *ortho* (**1O**), *meta* (**1M**) or *para* (**1P**) positions (Scheme 1). Carboxylic acids can chelate divalent metal ions for generating a supramolecular object in water, with a substantial change in the photophysical response of the system. It thus represents a new avenue for making a family of water-soluble metal ion sensors with dual functions, either under complete aqueous conditions or in organic solvents.

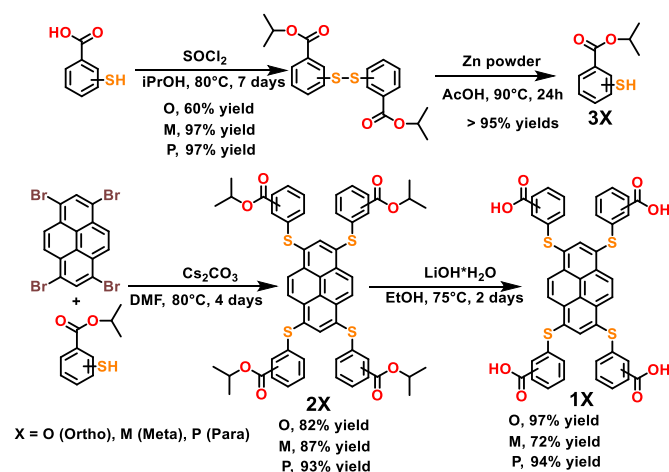
Results and Discussion

Synthesis

Although a strategy by direct nucleophilic aromatic substitutions with the commercial mercaptobenzoic acid isomers and 1,3,6,8-tetrabromopyrene is simple, we found low yields of **1O**, **1M** and **1P** and a difficult way to get pure tetraacids. The reactions produced partially substituted pyrenes. We thus needed to protect the carboxylic acids in their isopropyl ester form for diminishing some supramolecular interactions and for increasing solubility. Tetra(phenylthio)pyrene derivatives with four *ortho*

(**2O**), *meta* (**2M**) or *para* (**2P**) substituted isopropyl ester groups were synthesized by nucleophilic aromatic substitutions of 1,3,6,8-tetrabromopyrene with the corresponding isopropyl mercaptobenzoates **3O** (*ortho*), **3M** (*meta*), **3P** (*para*). The esters were hydrolyzed to the final regioisomeric tetraacids **1O** (*ortho*), **1M** (*meta*), **1P** (*para*). The description of each step is reported below. As for 1,3,6,8-tetrabromopyrene, we synthesized it on a multiple-gram scale from the bromination of pyrene in nitrobenzene.^{[28],[29],[30]} The regioisomeric isopropyl mercaptobenzoates **3O**, **3M** and **3P**, were synthesized in two steps.^{[31],[32]} The first one is the esterification of commercial *ortho*-, *meta*- and *para*-mercaptobenzoic acids by heating them with thionylchloride and isopropanol. A mixture of ester-thiols, ester-disulfides and ester-trisulfides was obtained. Without purification, the next step was the reduction of di- and trisulfides by zinc powder in warm acetic acid to produce the isomeric isopropyl mercaptobenzoates (overall reaction yields: 57% for **3O** and >92% for **3M** and **3P**).^{[31],[32]}

The isopropyl esters **2O** (*ortho*), **2M** (*meta*), **2P** (*para*) were synthesized in good yields (>82%) by nucleophilic aromatic substitutions of 1,3,6,8-tetrabromopyrene with the mercaptobenzoate isomers **3O**, **3M** and **3P** in the presence of anhydrous Cs₂CO₃ in DMF at 80°C. The resulting esters were hydrolyzed in good yields (>72%) with LiOH·H₂O in ethanol at 75°C to afford the tetraacids **1O**, **1M**, **1P** (Scheme 1).



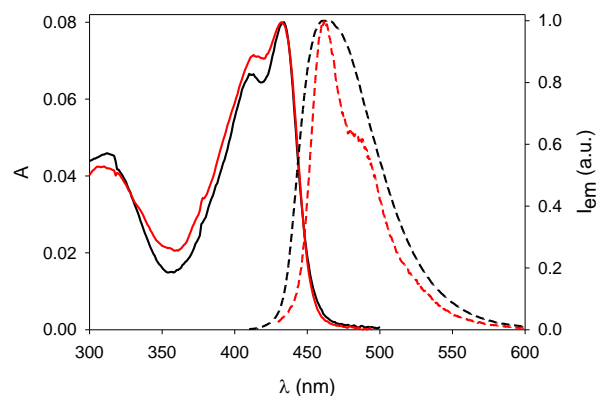
Scheme 1. A general synthetic scheme of carboxylic acids **1O** (*ortho*-isomer), **1M** (*meta*-isomer), and **1P** (*para*-isomer) under study. They arise from the carboxylic esters **2O**, **2M** and **2P**, which themselves came from reactions of isopropyl mercaptobenzoate isomers **3O**, **3M** and **3P** with 1,3,6,8-tetrabromopyrene.

Photophysical properties

The isopropyl esters **2O**, **2M** and **2P** were characterized in THF and the carboxylic acid derivatives (**1O**, **1M** and **1P**) were studied in both THF and in basic aqueous solution. Compounds **2O**, **2M** and **2P** show a band peaked at 420-430 nm (Figure S23), attributed to electronic transitions localized on the central pyrene core and a higher energy band peaked at ca. 300 nm with slight differences in terms of energy and shape of the absorption bands of the three isomers, likely due to different symmetry of the peripheral substituents. The emission bands,

lifetimes and emission quantum yields are similar for the three compounds, as shown in Table 1. This means that the difference between the three isomers does not affect much the photophysical properties of the central pyrene core. These photophysical parameters are similar to those from previous 1,3,6,8-tetra(phenylthio)pyrene-cored molecules.^[27]

Figure 1. Normalized absorption spectra (solid lines) and emission spectra



(dash lines) of **1M** in air-equilibrated THF solution (red) and air-equilibrated aqueous solution at pH=8 (black).

The photophysical properties of the regioisomeric acid **1X** (compound **1M** in Figure 1a and comparison of compounds **1O**, **1M** and **1P** in Figure S24) in THF are very similar to the properties recorded for the esters. The emission spectra are analogous for the three isomers, as well as the emission quantum yields, and lifetimes (Table 1). A comparison with the corresponding esters **2X** shows that the emission quantum yield is 5 to 10% lower, while the lifetime increases from 1.80 to 2.00 ns.

Table 1. Most relevant photophysical data of **1X** and **2X** compounds in air-equilibrated THF solution at 298 K (unless otherwise noted)

	absorption		emission				
	λ_{max}/nm	$\epsilon/10^4 M^{-1} cm^{-1}$	λ_{max}/nm	ϕ_{em}	τ/ns	$k_f/10^8 s^{-1}$	$k_{nr}/10^8 s^{-1}$
1P ^[a]	427	1.90	463	0.07	0.42	1.67	22.1
1O ^[a]	426	1.96	470	0.09	0.65	1.38	14.0
1M ^[a]	433	1.92	463	0.42	1.42	2.96	4.08
1P	429	3.94	462	0.53	2.00	2.65	2.35
1O	425	3.00	467	0.49	2.00	2.45	2.55
1M	432	3.36	463	0.51	2.00	2.55	2.45
2P	430	3.58	454	0.59	1.80	3.28	2.28
2O	420	3.49	455	0.57	1.80	3.17	2.39
2M	434	3.58	453	0.58	1.80	3.22	2.33

[a] in an aqueous solution at pH=8

When the tetraacids **1X** are dissolved in basic aqueous solution (pH=8), carboxylic acids are deprotonated so that water solubility is attained, without using organic co-solvents. No significant difference in the shape of the absorption and emission spectra is observed, compared to THF (Figure 1). On the other hand, we observe an effect in the emission quantum yields and lifetimes (Table 1).

The emission quantum yield of **2O** decreases from 0.49 to 0.09 as well as the lifetime from 2.00 ns to 0.65 ns. **2P** has a similar behavior and the emission quantum yield decreases from 0.53 to 0.07 as well as the lifetime from 2.00 ns to 0.42 ns. The isomer **2M** is less affected by the solvent change, the emission quantum yield slightly decreases from 0.51 to 0.42 and the lifetime decreases from 1.80 ns to 1.42 ns. In water there is an effect of the substituents from *ortho* and *para* to *meta*. The deprotonation in aqueous solution has an effect on the non radiative deactivation of the excited state of the molecule S1. The value of k_{nr} increases in aqueous solution compared to k_{nr} in THF and for **1O** and **1P** there is an increment of ten times, while for **1M**, only two times. We interpreted this data by a proton transfer between the solvent and the molecule in the excited state S1 that occurs only in aqueous solution where this process is extremely fast if compared to an organic solvent.^[33] A similar effect on the isomeric position of a carboxylic acid is mentioned in literature, where the weaker conjugated *meta* isomer, shows higher lifetime compared to the *para* isomer.^[34]

Metal ion complexation

Under basic aqueous solution, the carboxylic acids **1X** are deprotonated and can coordinate divalent metal ions to generate a supramolecular architecture. We investigated the complexation ability (avidity) of **1M** with different metal ions like Ca(II), Cd(II), Co(II), Cu(II), Fe(II), K(I), Li(I), Mg(II), Mn(II), Na(I), Ni(II), Pb(II), Zn(II). Complexation takes place for all the investigated metal salts, except for monovalent metal ions, as evidenced by the absorption spectral changes: the absorption band at 430 nm decreases in intensity and a new band appears at 450 nm. However, in the case of Ca²⁺ and Mg²⁺ the complexation is only partial (50%) meaning a lower association constant than for other cases. Upon excitation at the isosbestic point, a complete quenching of the tetra(phenylthio)pyrene is observed with all divalent metal ions, apart from Ca(II) and Mg(II) in which the decrease of the emission intensity is ca. 50% because of the above-mentioned lower binding constants (Figure 2).

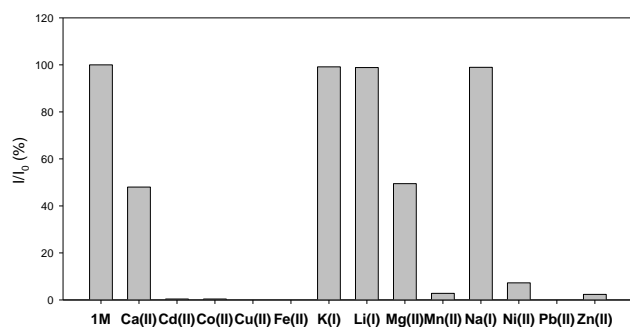


Figure 2. Relative emission quantum yields of **1M** 3.0 μM in water at pH = 8 upon addition of different metal ions (45 μM for K⁺, Na⁺ and Li⁺, and 10 μM for all other metal ions).

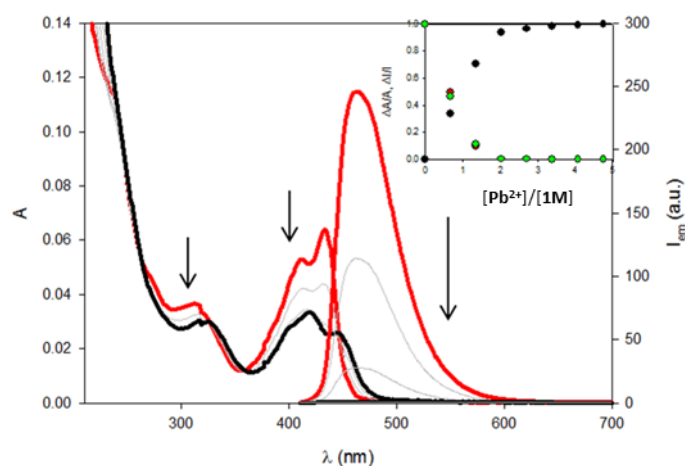


Figure 3. Absorption (left) and fluorescence (right) of a 3.0×10^{-6} M solution of **1M** in air-equilibrated water solution (pH=8) upon titration with a 3.73 mM water solution of $Pb(NO_3)_2$: red line (0 eq), black line (2 eq). Inset show the normalized absorption changes at 400 nm (red) and 470 nm (black) and emission intensity changes at 470 nm (green).

All three isomers **1P** (Figure S26), **1M** (Figure 3) and **1O** (Figure S27) show complexation with Pb^{2+} . The normalized absorption and emission intensities change show a plateau at 2 mol-equivalents of metal ions (e.g. **1M** in Figure 3) with a limit of detection of 0.2 μM. These results indicate a complex with a 1:2 molar ratio of pyrene ligand to Pb^{2+} . Considering the structure of the ligand, two carboxylic acids are too far from each other to allow an intramolecular complex, so two molecules of ligand are linked together by metal ions complexation, thus making a complex structure like $[Pb_{2n}(1)_n]$.

Confirmation of this hypothesis is given by DLS analysis of an aqueous solution of **1M** before and after addition of 2.5 mol-equivalents of $Pb(II)$ per molecule: after addition of the metal ions a significant increase of the intensity of the scattered light is observed. A polydisperse aggregate (PDI 0.47) with a mean diameter of 180 nm is formed (Figure S30).

The supramolecular polymer formed for **1M** and $Pb(II)$ can be disassembled upon addition of ethylenediaminetetraacetic acid (EDTA, 5 mol-eq.) as observed from DLS measurements (Figure S31). EDTA complexes $Pb(II)$ cations with a high binding constant ($2 \times 10^{18} M^{-1}$).^[35] The interaction of $Pb(II)$ with **1M** is thus reversible and can be used for sensing applications in water. (Figure S28)

Conclusion

We designed a new family of water-soluble, carboxylated tetra(phenylthio)pyrene ligands in which divalent metal ion coordination results in the formation of supramolecular assemblies, and quenching of the pyrene fluorescence in a dual mode function. It can occur in water only, without the need for organic co-solvents. Monovalent ions are distinctly ineffective. These sensing systems are based on a highly fluorescent tetra(phenylthio)pyrene core with four appended carboxylic acid units. Three different regioisomers of pyrene **1X** with *ortho* (**1O**),

meta (**1M**) and *para* (**1P**) carboxylic groups were thus synthesized, characterized, and studied either in THF or aqueous solution, in the presence of various metal ions. The photophysical properties of the three isopropyl esters **2O**, **2M**, **2P** and the carboxylic acids **1O**, **1M**, **1P** in THF are very similar, with a blue-green fluorescent emission and high emission quantum yields (0.5-0.6). The systems functionalized with carboxylic acids **1X** are soluble in aqueous solution at pH >8 due to deprotonation of the carboxylic acids, and the fluorescence is less intense, but still high for the *meta* isomer **1M**, probably due to a less efficient deactivation of the excited state by proton transfer. The addition of metal ions to these systems can not only quench the fluorescence of the pyrene core, reducing the emission quantum yield to almost zero, but also control the formation of three-dimensional nanoscopic objects in a dual mode function. Several divalent metal ions were tested and all of them show fluorescence quenching. The formation of supramolecular polymers is reversible, i.e. addition of ethylenediaminetetraacetic acid (EDTA) restores the initial conditions by scavenging metal ions due to a strong EDTA-metal ion complex. The coordination polymers disassemble, and fluorescence of the pyrene core is restored. New avenue for metal ions sensing in a dual function were developed in water, especially for sensing heavy metal ions, such as toxic Cd(II) and Pb(II) cations, with a limit of detection of 0.2 μM .

Experimental Section

Instrumentation and materials

All reagents, solvents and chemicals were purchased from Sigma-Aldrich, Fisher, or Alfa-Aesar and used directly unless otherwise stated (purity: reagent or analytical grade). Solvents were stored for several days over freshly activated 3 Å molecular sieves (activation for 3 h at 250 °C). All reactions were monitored by TLC or LCMS or FT-IR (ATR) spectroscopy. Isopropyl mercaptobenzoates were prepared according to the literature.^[31] The experiments were carried out in air-equilibrated solution at 298 K unless noted otherwise. UV-vis absorption spectra were recorded with a PerkinElmer 140 spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence spectra were performed with a PerkinElmer LS-50 or an Edinburgh FLS920 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Lifetimes shorter than 10 μs were measured by the above-mentioned Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a 340 nm pulsed diode and a LDH-P-C405 pulsed diode laser. Longer lifetimes were measured by the PerkinElmer LS-50. Emission quantum yields were measured following the method of Demas and Crosby^[36] (standard used: $[\text{Ru}(\text{bpy})_3]^{2+}$ in aqueous solution)^[37]. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime, 10% on the emission quantum yield in solution. TLC analyses were performed on precoated silica gel (Alugram® SiG/UV254gel) aluminium plates from Macherey-Nagel. Compounds were visualized with UV-light (254 or 365 nm). Flash chromatography was performed over silica gel 60, Merck type 230-400 mesh (40-63 μm). NMR spectra ^1H (400 MHz) and ^{13}C (100.53 MHz) were recorded on JEOL ECX-400 spectrometer signals of the residual protic solvent CHCl_3 at 7.26 ppm and $\text{DMSO-}d_6$ at 2.50 ppm were used as internal references, along with TMS. As for ^{13}C NMR spectra, the central resonance of the triplet for CDCl_3 at 77.16 ppm and the signal for $\text{DMSO-}d_6$ at 39.52 ppm were used as internal references.^[38] The resonance multiplicities in the ^1H NMR spectra are described as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet), “sept” (septet) “m” (multiplet) or “b” (broad). High resolution mass spectra were recorded at the Spectropole of Marseille (France) in triplicate with double internal

standards. Oligomers of poly(propylene glycol) were used as internal standards. Ionization was facilitated by some adducts with Ag^+ , NH_4^+ or Na^+ ions. Two spectrometers were used: a) SYNAPT G2 HDMS (Waters) instrument equipped with an ESI source and a TOF analyser in a positive mode. b) QStar Elite (Applied Biosystems SCIEX) instrument equipped with an atmospheric ionization source (API). The samples were ionized under ESI with an electrospray voltage of 5500 V; orifice voltage: 10V, and air pressure of the nebulizer at 20 psi. A TOF analyser was used in a positive mode. MALDI-TOF-MS analyses were performed on an Autoflex MALDI-TOF Bruker spectrometer (matrix DCTB), in negative mode, laser 355 nm. Infrared absorption spectra were directly recorded on solids or neat liquids on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer equipped with a universal ATR accessory (contact crystal: diamond). The determination of the hydrodynamic diameter distributions was carried out through Dynamic Light Scattering measurements employing a Malvern Nano ZS instrument equipped with a 633 nm laser diode. Samples were housed in disposable polystyrene cuvettes of 1 cm optical path length, using water as solvent. PDI (Polydispersion Index) indicates the width of DLS hydrodynamic diameter distribution. In case of a monomodal distribution (gaussian) calculated by means of cumulant analysis, $\text{PDI} = (\sigma/Z_{\text{avg}})^2$, where σ is the width of the distribution and Z_{avg} is the average diameter of the particles population respectively

Synthetic procedure and compound data

Tetraisopropyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayltetrakis(sulfaneydiyl))tetrabenzoate (2P): Tetrabromopyrene (630 mg 1.22 mmol, 1.00 mol-eq), isopropyl-3-mercaptopbenzoate (1789 mg., 6.38 mmol, 5.2 mol-eq) and dry Cs_2CO_3 (2510 mg, 7.73 mmol, 6.3 mol-eq) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry N,N-dimethylformamide (DMF, 6.0 mL) was added and the mixture was vigorously stirred at 80°C (oil bath temperature) for 4 days. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 100 mL of 1 M HCl (aq), a yellow-brown solid precipitated and was filtrated. The solid was triturated while stirring vigorously in ethanol (50 mL) at 40°C to afford a yellow solid. Recrystallization in cyclohexane gave a pure yellow solid (1113 mg., 1.13 mmol, 93 % yield). ^1H NMR (399.78 MHz, CDCl_3 , ppm): δ = 8.70 (s, 4H), 8.45 (s, 2H), 7.83 (d, 8H, J = 8.3 Hz), 7.10 (d, 8H, J = 8.3 Hz), 5.18 (sept, 4H, J = 6.3 Hz), 1.30 (d, 24H, J = 6.4 Hz). ^{13}C NMR (100.53 MHz, CDCl_3 , ppm): δ = 165.52, 143.21, 140.45, 133.53, 130.35, 129.15, 128.72, 127.41, 127.05, 126.05, 68.55, 21.99. HRMS (ESI+) calculated for $[\text{C}_{56}\text{H}_{50}\text{O}_8\text{S}_4 + \text{NH}_4^+]$: 996.2732 m/z , found $[\text{M} + \text{NH}_4^+]$ 996.2731 m/z . FT-IR (cm^{-1}) ν = 2981, 2926, 1709, 1592, 1270, 1247, 1100, 1014, 922, 874, 850, 815, 759, 689. Elemental analysis (%): Calculated : 68.69%C 5.15%H 13.10%S Found: 68.42%C 5.05%H 13.02%S.

Tetraisopropyl 2,2',2'',2'''-(pyrene-1,3,6,8-tetrayltetrakis(sulfaneydiyl))tetrabenzoate (2O): Tetrabromopyrene (1494 mg. 2.88 mmol, 1.00 eq), isopropyl-2-mercaptopbenzoate (2908 mg., 14.84 mmol, 5.15 mol-eq.) and dry Cs_2CO_3 (5632 mg., 17.32 mmol, 6.01 mol-eq.) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry N,N-dimethylformamide (DMF, 12.0 mL) was added and the mixture was vigorously stirred at 80°C (oil bath temperature) for 4 days. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 100 mL of 1 M HCl (aq), a yellow-brown solid precipitated and was filtrated. The solid was triturated while stirring vigorously in ethanol (150 mL) at 40°C to afford a yellow solid. Recrystallization in cyclohexane gave a pure yellow solid (2322 mg., 2.37 mmol, 82 % yield). ^1H NMR (399.78 MHz, CDCl_3 , ppm): δ = 8.75 (s, 4H), 8.63 (s, 2H), 8.02 (dd, 4H, J = 7.6, 1.6 Hz), 7.09 (ddd, 4H, J = 7.4, 7.4, 1.2 Hz), 7.03 (ddd, 4H, J = 7.9, 7.4, 1.6 Hz), 6.50 (dd, 4H, J = 7.9, 1.2 Hz), 5.35 (sept, 4H, J = 6.2 Hz), 1.42 (d, 24H, J = 6.3 Hz). ^{13}C NMR (100.53 MHz, CDCl_3 , ppm): δ = 166.07, 143.39, 142.31, 134.89, 132.38, 131.31, 129.77, 127.71, 127.62, 127.53, 126.17, 124.63, 69.19, 22.12. HRMS (ESI+) calculated for $[\text{C}_{56}\text{H}_{50}\text{O}_8\text{S}_4 + \text{NH}_4^+]$: 996.2731 m/z , found

[M+ NH₄⁺] 996.2731 *m/z*, FT-IR (cm⁻¹) ν = 2977, 2927, 1703, 1562, 1459, 1269, 1249, 1098, 1039, 1053, 916, 828, 738.

Tetraisopropyl 3,3',3'',3'''-(pyrene-1,3,6,8-tetrayltetrakis(sulfanediyl))tetrabenzoate (2M): Tetrabromopyrene (158 mg, 0.30 mmol, 1.00 mol-eq), isopropyl-3-mercaptopbenzoate (320 mg, 1.63 mmol, 5.43 mol-eq) and dry Cs₂CO₃ (658 mg, 2.00 mmol, 6.67 mol-eq) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry N,N-dimethylformamide (DMF, 2.0 mL) was added and the mixture was vigorously stirred at 80°C (oil bath temperature) for 4 days. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 50 mL of 1 M HCl (aq), a yellow-brown solid precipitated and was filtrated. The solid was triturated while stirring vigorously in ethanol (20 mL) at 40°C to afford a yellow solid. Recrystallization in cyclohexane gave a pure yellow solid (250 mg, 0.26 mmol, 87 % yield). ¹H NMR (399.78 MHz, CDCl₃, ppm): δ = 8.66 (s, 4H), 8.03 (s, 2H), 7.98 (br s, 4H), 7.87 – 7.81 (m, 4H), 7.25-7.20 (m, 8H), 5.19 (sept, 4H, *J* = 6.3 Hz), 1.32 (d, 24H, *J* = 6.3 Hz). ¹³C NMR (100.53 MHz, CDCl₃, ppm): δ = 165.30, 136.51, 136.43, 134.11, 132.08, 131.58, 131.07, 130.85, 129.40, 128.13, 125.86, 68.85, 21.99. HRMS (ESI⁺) calculated for [C₅₆H₅₀O₈S₄ + NH₄⁺]: 996.2732 *m/z*, found [M+ NH₄⁺] 996.2728 *m/z*. FT-IR (cm⁻¹) ν = 2977, 2927, 1714, 1702, 1418, 1281, 1261, 1101, 922, 874, 830, 747.

3,3',3'',3'''-(pyrene-1,3,6,8-tetrayltetrakis(sulfanediyl))tetrabenzoic acid (1M): A solution of **2M** (60 mg, 0.06 mmol, 1.0 eq) and LiOH·H₂O (85 mg, 2.03 mmol, 33 eq) in absolute ethanol (7 mL) was heated under an argon atmosphere at 70°C (oil bath temperature) for 37h. The reaction was monitored by FT-IR until disappearance of the ester C=O functions. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 60 mL of 1 M HCl (aq.). A yellow solid precipitated and provided a solid suspension. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow solid (35 mg, 0.04 mmol, 72% yield). ¹H NMR (399.78 MHz, DMSO-*d*₆, ppm): δ = 8.61 (s, 4H), 7.81 (s, 2H), 7.70 (d, 4H, *J* = 7.7 Hz), 7.65 (s, 4H), 7.36 (d, 4H, *J* = 7.7 Hz), 7.29 (dd, 4H, *J* = 7.7, 7.7 Hz). HRMS (MALDI-TOF, matrix DCTB) calculated for [C₄₄H₂₆O₈S₄ -H]⁻: 809.0432 Da, found [M-H]⁻ 809.0441 *m/z*, FT-IR (cm⁻¹) ν = 3500-2500, 1678, 1569, 1473, 1432, 1307, 1281, 1261, 1072, 808, 750, 680.

2,2',2''-(pyrene-1,3,6,8-tetrayltetrakis(sulfanediyl))tetrabenzoic acid (1O): A solution of **2O** (549 mg, 0.56 mmol, 1.0 eq) and LiOH·H₂O (879 mg, 20.95 mmol, 37 eq) in absolute ethanol (100 mL) was heated under an argon atmosphere at 70°C (oil bath temperature) for 72h. The reaction was monitored by FT-IR until disappearance of the ester C=O functions. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 150 mL of 1 M HCl (aq.). A yellow solid precipitated and a solid suspension appeared. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow solid (440 mg, 0.54 mmol, 97% yield). ¹H NMR (399.78 MHz, DMSO-*d*₆, ppm): δ = 8.68 (s, 4H), 8.49 (s, 2H), 7.94 (dd, 4H, *J* = 7.5, 2.3 Hz), 7.25-7.15 (m, 8H), 6.50 (dd, 4H, *J* = 7.2, 1.7 Hz), HRMS (MALDI-TOF, matrix DCTB) calculated for [C₄₄H₂₆O₈S₄ -H]⁻: 809.0432 Da, found [M-H]⁻ 809.0438 *m/z*; FT-IR (cm⁻¹) ν = 3500-2500, 2922, 1677, 1586, 1561, 1462, 1415, 1255, 1039, 1053, 833, 742, 697.

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayltetrakis(sulfanediyl))tetrabenzoic acid (1P): A solution of **2P** (401 mg, 0.41 mmol, 1.0 eq) and LiOH·H₂O (620 mg, 14.78 mmol, 36 eq) in absolute ethanol (50 mL) was heated under an argon atmosphere at 70°C (oil bath temperature) for 72h. The reaction was monitored by FT-IR until disappearance of the ester C=O functions. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with 60 mL of 1 M HCl (aq.). A yellow solid precipitated and made a suspension. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow solid (312 mg, 0.38 mmol, 94% yield). ¹H NMR (399.78 MHz, DMSO-*d*₆, ppm): δ = 8.68 (s, 4H), 8.29 (s, 2H), 7.75 (d, 4H, *J* = 8.4 Hz),

7.19 (d, 4H, *J* = 8.4 Hz). HRMS (MALDI-TOF, matrix DCTB) calculated for [C₄₄H₂₆O₈S₄ -H]⁻: 809.0432 Da, found [M-H]⁻ 809.0448 *m/z*, FT-IR (cm⁻¹) ν = 3500-2500, 2813, 1681, 1589, 1562, 1473, 1421, 1272, 1078, 1014, 853, 742, 697.

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