Pyrene-Derived Novel One- and Two-Component Organogelators

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Abstract: A new class of alkyl-chain-appended pyrene derivatives **4**–**14** were synthesized and evaluated for their gelation abilities. Depending on the nature of the linking group, these compounds gelated a number of organic solvents, either in the presence or in the absence of the acceptor molecule 2,4,7-trinitrofluorenone (TNF). Compounds with ester, ether, or alkyl linkages gelated a number of hydroxylic and hydrocarbon solvents by means of a charge-transfer interaction with TNF, while compounds with amide, urethane and urea linkers formed gels on their own in a variety of solvents by means of π–π stacking and hydrogen-bonding interactions. The X-ray crystal structure of urethane (*S*)-**12** showed hydrogen-bonding and stacking features, as suggested by the model. The gels obtained were investigated by spectroscopic and electron microscopic techniques which provided structural insights.

Keywords: aggregation · donor–acceptor systems · gels · hydrogen bonding · pi-interactions

Introduction

Gels derived from low molecular mass compounds have attracted considerable interest in recent years, and compounds with wide structural diversities have been reported to efficiently (<1% w/v) gelatinize organic liquids.[1, 2] The structural diversity of such gelators varies from simple hydrocarbons[3] to giant phthalocyanine-bearing crown ether derivatives.[4] Gels of low molecular weight compounds are formed as a consequence of the self-assembly of the gelator molecules to form entangled fibrous networks (SAFINs) through a combination of noncovalent interactions, such as hydrogen bonding, π–π stacking, donor–acceptor interactions, metal coordination, and van der Waals interactions. There are many examples of gelators which aggregate through hydrogen bonding. These are usually derived from amino acids, amino alcohols, carbohydrates and urea.[5] Cholesterol-derived gelators aggregate through van der Waals interactions resulting from the organization of the steroid units.[6] Organometallic gelators form gels through metal coordination,[7] and molecules derived from porphyrins[8] possessing large π surfaces aggregate through π–π stacking. Recently, there were reports propounding the enhancement of gel stability through host–guest interactions.[9] In spite of our lack of detailed understanding of the aggregation properties of such gelators, many futuristic applications have been envisaged. Gels derived from cholesterol have been used for chiral recognition/sensing, for studying photo- and metal-responsive functions[10] and as templates to make hollow-fiber silica.[11] The use of gels for designing polymerized and reverse aerogels and in molecular imprinting has also been documented.[12] Dye-doped organogels have been shown to be efficient media for lasing applications.[13] Organogels have been investigated as reaction media[14] and as drug delivery agents (organogels of sorbitan monostearate have been investigated for their drug delivering capability).[15] They are used in cosmetics.[16] Organogels containing supporting electrolytes have been shown to have ionic conductivities similar to those in isotropic solution, which makes them good candidates for use as gel electrolytes.[17] An organogel-based fluorescent optode membrane has been used for humidity sensing.[18] The thermoreversibility of gels can be exploited for thermosensing applications. Hindered transport through the

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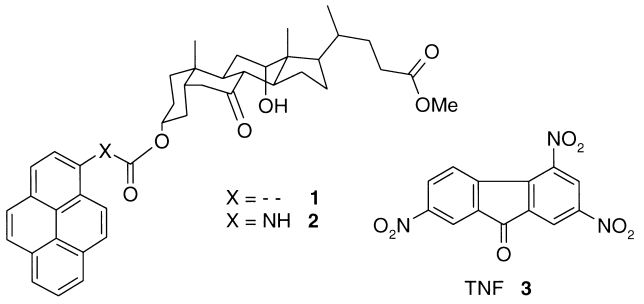
pores of the gel network could be exploited for separation techniques. Organogelators can be used for the treatment of oil spillages and safer disposal of used oils.[19]

In the course of our detailed studies on bile acid-based molecular tweezers,[20] we serendipitously discovered the *first* instance of a two-component, charge-transfer-interaction-promoted gelation of organic solvents.[21] Herein we describe detailed studies on these organogels, which form through the charge-transfer interaction of pyrene derivatives with 2,4,7-trinitrofluorenone (TNF) as the acceptor. Studies on a new class of pyrene derivatives that form organogels *on their own* through hydrogen-bonding and $\pi-\pi$ interactions are also elucidated.[22]

Results and Discussion

Our initial discovery that aromatic donor-substituted bile acid derivatives, such as **1** and **2**, gelatinized certain organic solvents *in the presence of* TNF (**3**) as the acceptor prompted



us to examine the role of the bile acid moiety in these gelators. To address this question, a number of analogues were synthesized in which the bile acid moiety was replaced by alkyl chains connected to the pyrene through a variety of linkers (Figure 1). The linkers chosen included ester (normal

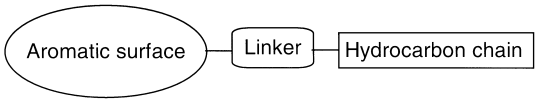


Figure 1. Schematic representation of the gelator molecules.

and reversed), amide (normal and reversed), urethane, ether, urea, and aliphatic CH_2. These compounds (Scheme 1) were synthesized following standard protocols (see Experimental Section). Many of these analogues were found to be as effective organogelators as their bile acid-appended counterparts in the presence of TNF (Table 1). Interestingly, gelators having hydrogen-bonding donor–acceptor groups (Ar-NH-CO-X) showed excellent gelling abilities with hydroxylic and hydrocarbon solvents *in the absence* of the electron-acceptor TNF. These two classes of organogelators are discussed in two separate sections.

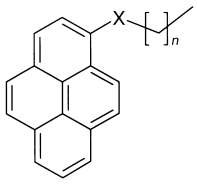
Table 1. Gelation behavior of pyrene derivatives in the presence of one equivalent of TNF.[a]

Solvent	**1**	**2**	**4a**	**7a**	**8**
cyclohexanol	G	G	G	G	G
n-octanol	S	S	G	G	G
n-butanol	G	G	G	G	G
tert-butyl alcohol	G	G	G	G	G
n-hexane	P	P	P	G	G
n-dodecane	P	P	P	G	G
n-decane	P	P	P	G	G
cyclohexane	P	P	P	G	G

[a] G = gel, P = precipitate, S = solution. Gelator concentration was 2% w/w in all cases.

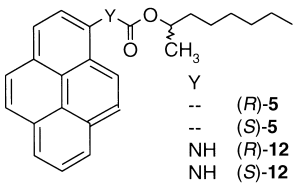
Synthesis: Reaction of pyrene with $Cu(NO_3)_2$ in $CHCl_3$ gave 1-nitropyrene, which was hydrogenated with H_2/Pd-C to yield 1-aminopyrene, which served as a precursor to **4**–**6** (Scheme 1). Acetylation of pyrene with $Ac_2O/ZnCl_2$ in AcOH yielded 1-acetylpyrene,[23] which was then oxidized with NaOCl in pyridine/water to pyrene-1- carboxylic acid, which was used for the synthesis of **7**. Pyrene was brominated with Br_2 in CCl_4 to 1-bromopyrene, which was treated with Mg in diethyl ether. The Grignard reagent was subsequently allowed to react with borane and the resulting aryl borane was oxidized with $NaOH/H_2O_2$ to give 1-hydroxypyrene, which was converted to compounds **8** and **9**.

The synthesis of the target compounds was straightforward. Compound **10a** was synthesized by reacting 1-aminopyrene with 1-octadecanoyl chloride in toluene in the presence of pyridine. Compound **11a** was obtained by the reaction of 1-aminopyrene with hexadecyl chloroformate in $CHCl_3$ in the presence of pyridine. Compound **13** was synthesized by reacting pyrene-1-isocyanate with hexadecylamine in 1,2-dichlorobenzene. The reaction of pyrene-1-carbonyl chloride with hexadecyl alcohol in the presence of Et_3N in CH_2Cl_2 yielded **4a**. Refluxing 1-hydroxypyrene and 1-tetradecyl bromide with K_2CO_3 in acetone yielded **8**. Friedel–Crafts acylation of pyrene with hexadecanoyl chloride and $AlCl_3$ in nitrobenzene gave hexadecanoylpyrene, which was subse-

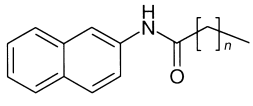


Scheme 1.

x	*n*	
COO	15	**4a**
COO	7	**4b**
CONH	15	**6**
CH_2	14	**7a**
CH_2	10	**7b**
CH_2	0	**7c**
O	13	**8**
OCO	14	**9**
NHCO	16	**10a**
NHCO	10	**10b**
NHCO	6	**10c**
NHCOO	15	**11a**
NHCOO	11	**11b**
NHCOO	9	**11c**
NHCONH	15	**13**



Y	
--	(*R*)-**5**
--	(*S*)-**5**
NH	(*R*)-**12**
NH	(*S*)-**12**



n = 16 **14**

quently converted to **7a** by a modified Wolf–Kishner reduction. The corresponding chiral and shorter chain analogues were synthesized under similar reaction conditions.

Compounds that aggregate in the presence of TNF: The gelation abilities of compounds **4**–**14** were tested in a variety of organic solvents *in the presence of* TNF. Among these compounds, only **4a**,**b**, **5**, **7a**–**c**, and **8** formed gels owing to a charge-transfer (CT) interaction between the pyrene donor and acceptor TNF. The gels derived from these compounds were stable at room temperature for several months. Compounds **7** and **8** were found to show better gelation abilities than **4** (Table 1) in the presence of TNF. While **4** was capable of gelling only hydroxylic solvents to form largely opaque orange gels, **7** and **8** formed red (transparent) and black gels, in hydrocarbon and hydroxylic solvents, respectively. This result suggests improved CT interaction between TNF and more electron-rich **7** and **8** (as compared to the esters). Shortening the hydrocarbon chain to eight carbon atoms did not have any significant effect on the gelation ability or the thermal stability of the gels formed in the presence of TNF (Table 2). The minimum gelling concentrations were typically

Table 2. Thermal stability of the gels derived from alkyl and alkoxypyrenes with TNF.

Solvent	T_{gel}[°C; c = 20 mM]		
	C_{16} alkyl(**7a**)	C_{12} alkyl(**7b**)	C_{14} ether(**8**)
cyclohexanol	62	61	64
n-octanol	64	63	65
n-butanol	71	69	75
tert-butyl alcohol	76	75	70
n-decane	71	59	79
n-dodecane	65	69	78

in the 0.5–1% (w/w) range. Surprisingly, the reverse ester **9** did not form a gel in any of the solvents mentioned for reasons not clear to us. Compounds **6** and **10**–**14** did not gel in the presence of TNF in the liquids mentioned, probably because of incompatible hydrogen-bonding and donor–acceptor interaction geometries.

Sol–gel transition temperature: The sol-to-gel transition temperature (T_{gel})[24] was measured as a function of the molar ratio of the acceptor and donor, at a constant donor concentration, and as a function of gelator concentration (at a donor to acceptor ratio of 1:1). The T_{gel} of **4b** (at 23 mM) and **7a** (at 9 mM) in *n*-octanol increased with an increase in the amount of TNF, reached a maximum at a molar ratio of 1:1, and remained almost constant thereafter (Figure 2a) suggesting a 1:1 donor/acceptor ratio as the optimum for gelation. At a 1:1 ratio of donor (**4b**) to acceptor (**3**), the T_{gel} values increased with increasing gelator concentration, as expected (Figure 2 b). Furthermore, we found that the length of the hydrocarbon chain did not affect the thermal stability of the gels in hydroxylic solvents (Table 2). The thermal stability of gels derived from alkoxy pyrene **8** was higher than that of alkyl pyrenes. This confirmed the role of a charge-transfer interaction in stabilising the gels.

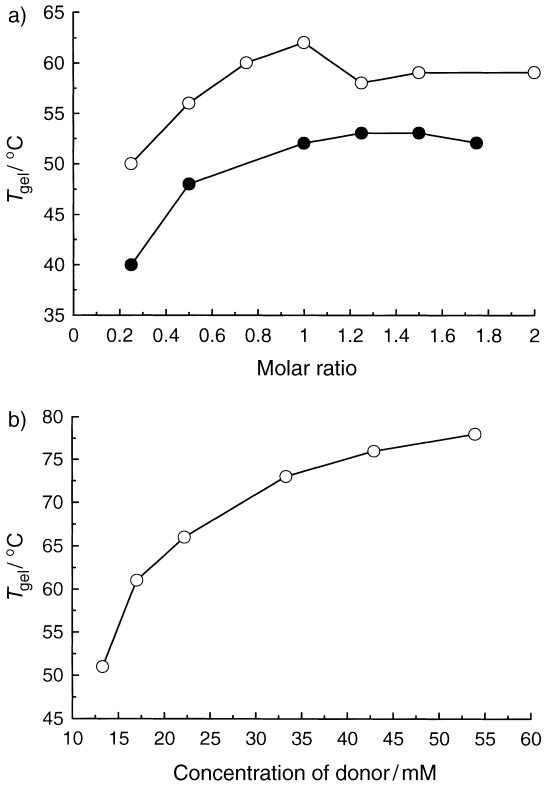


Figure 2. a) Plot of T_{gel} versus molar ratio of TNF/**4b** (23 mM of **4b**, ○) and TNF/**7a** (9 mM of **7a**, ●) in *n*-octanol. b) T_{gel} as a function of the concentration of **4b** (with equimolar TNF) in *n*-octanol.

UV/Vis studies: During the gelation of these systems, a substantial color change was observed. This was thought to be caused by an increase in the charge-transfer interaction (CT) during gelation and, therefore, the gelation of these compounds was investigated by variable-temperature absorption spectroscopy by monitoring changes in the charge-transfer band during gelation. The rate of increase of the intensity of the CT band (540 nm for **7**) was found to be larger at the sol–gel transition point when a sol was cooled gradually below its T_{gel} (Figure 3). This observation suggests that the formation of gel aggregates is driven by a charge-transfer interaction. The long alkyl chain could only be playing a secondary role in

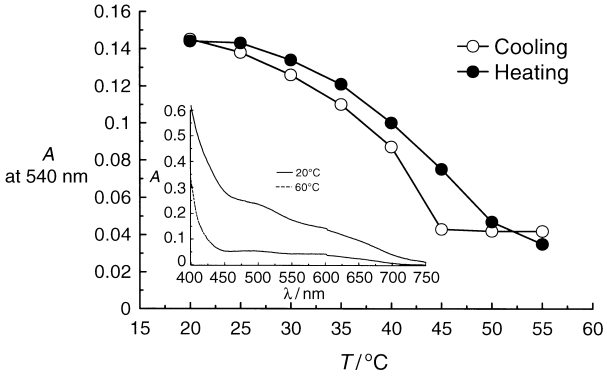


Figure 3. Absorbance A of the charge-transfer band of an *n*-dodecane gel of **7**/TNF (4.7 mM of **7**, 0.4% w/w) as a function of temperature T (1 mm cell); UV/Vis spectra of gel of **7**/TNF at 20 °C and 60 °C (inset).

modulating the solubility/crystallinity of the molecule in the given solvent.

A chiral gelator: Since the thermal stability of the two-component gels was found to be a maximum at a 1:1 molar ratio of the donor and the acceptor, the supramolecular aggregate initially formed is likely to be an alternative stack of donor and acceptor surfaces to form one-dimensional aggregates. If one of the two components is chiral, circular dichroism spectroscopy can conveniently probe the formation of chiral aggregates. Accordingly, compounds (*S*)-**5**/(*R*)-**5** were synthesized from readily available (*R*)- or (*S*)-2-octanol. Compound (*S*)-**5**/(*R*)-**5** formed a translucent orange gel in cyclohexanol in the presence of TNF (precipitates or solutions were obtained in the other solvents tested). These gels gave spectroscopic signatures similar to their achiral counterparts. CD spectral analysis of the gel derived from (*S*)-**5**/(*R*)-**5** showed positive/negative Cotton effects with high molar ellipticity at $\lambda = 375$ and 310 nm. No detectable CD was observed in the molten gel (70 °C) (Figure 4). While these results suggest that the aggregates formed in the gel are possibly helical, the available data do not allow us to propose a well-defined model at this time.

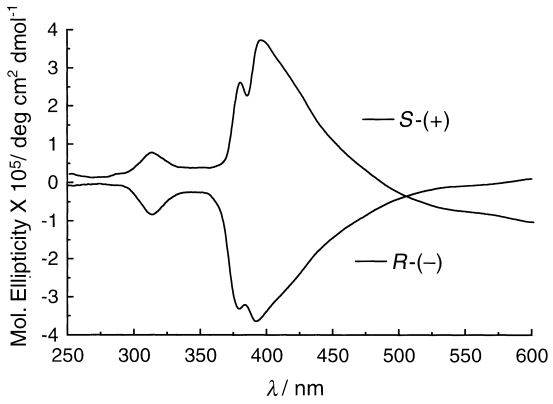


Figure 4. CD spectra of the gels derived from (*S*)-**5** (positive CD) and (*R*)-**5** (negative CD) in cyclohexanol (7.1 mM, 1 mm cell).

Compounds with hydrogen-bonded donor–acceptor linkages: Although several compounds shown in Scheme 1 did not form charge-transfer gels in the presence of TNF, we were delighted to observe that a few of them (**10**, **11**, and **13**, which possess a pyrene-NH-CO functionality) formed gels in a variety of solvents *in the absence of* TNF (Table 3). A comparison of the gelation abilities of the gelators **10a**, **11a**, and **13** indicated that **10a** and **13** were superior to **11a** and gelled a larger number of solvents. The thermal stabilities of gels of **10a** and **13** were substantially higher than that of **11a** in the same set of solvents. These two compounds formed aggregates even in dipolar aprotic solvents, such as DMSO and DMF, giving rise to gelatinous precipitates. A reduction of the length of the side chain by about four carbon atoms had only a marginal effect on the gelation abilities and thermal stabilities. However, we found that, typically, an alkyl chain length of more than eight carbon atoms was required for the compound to act as a gelator. Compounds **10c** and **11c** failed to gel any of the solvents gelled by their long-chain counterparts. Compounds **4**, **5**, and **7**–**9** with *no* hydrogen-bonding donor–acceptor functionality did not gelatinize any of the organic solvents mentioned in the absence of TNF. Furthermore, naphthyl derivative **14**, with a hydrogen-donor–acceptor moiety also did not form a gel, possibly because of insufficient π surface area. The reverse amide **6** also did not form gel in any of the solvents mentioned for reasons not clear to us. These two observations strongly support the hypothesis that both hydrogen-bonding and π–π interactions are necessary for this type of novel pyrene-based gelators to rigidify organic solvents.

Table 3. Gelation behavior of compounds in the absence of TNF.[a]

Solvent	**13**	**12**	**11**	**10**	**8**	**7**	**4**	(*R*)-**5**/(*S*)-**5**
*n*BuOH	G	C	G	G	P	P	P	S
*t*BuOH	G	C	G	G	P	P	WG	S
n-octanol	G	S	G	G	P	P	S	S
cyclohexanol	G	S	G	G	P	WG	WG	S
cyclohexane	G	G	G	G	P	S	S	S
n-hexane	G	G	G	G	P	S	S	S
n-decane	G	G	G	G	P	S	S	S
n-dodecane	G	G	G	G	P	S	S	S
CCl_4	G	S	P	G	S	S	S	S
$CHCl_3$	S	S	S	P	S	S	S	S
PhMe	G	S	S	G	–	–	S	S

[a] G = gel, WG = weak gel, P = precipitate, C = crystal, S = solution. The gelator concentration was 2% (w/w) in all cases.

Absorption spectroscopy: Variable-temperature absorption spectroscopy was used to study the gelation process. No new bands appeared in the gel phase when compared to the sol. The study involved monitoring the changes in the intensity at a chosen wavelength on cooling an isotropic solution of the gelator in the gelling solvent to a temperature below the T_{gel} and then completing a cycle by heating the gel to an isotropic solution. In the case of **10a**, **11a**, and **13**, pronounced hyperchromism was observed on heating a gel to a sol, suggesting the existence of stacked aromatic moieties in the gel that destack upon melting the gel. Absorbance-temperature plots showed hysteresis, with melting and freezing points being distinctly different (Figure 5).

Fluorescence spectroscopy: To provide further evidence for stacking and destacking of pyrene units during gelation, fluorescence measurements were carried out on the gels. Fluorescence intensities of various bands were monitored as a function of temperature. As a sol of **10a** in toluene was cooled, the intensity of both monomer ($\lambda = 407$ nm) and the excimer ($\lambda = 480$ nm) increased; the magnitude of this change was larger at the sol–gel transition point. The plots obtained were similar to those of absorption studies and showed hysteresis (Figure 6).

FT-IR studies: Infrared measurements were made on sol–gel samples of **10a**, **11a**, and **13** in cyclohexane, since we expected these compounds to associate through hydrogen-bonding interactions owing to their self-complementarity. The FT-IR

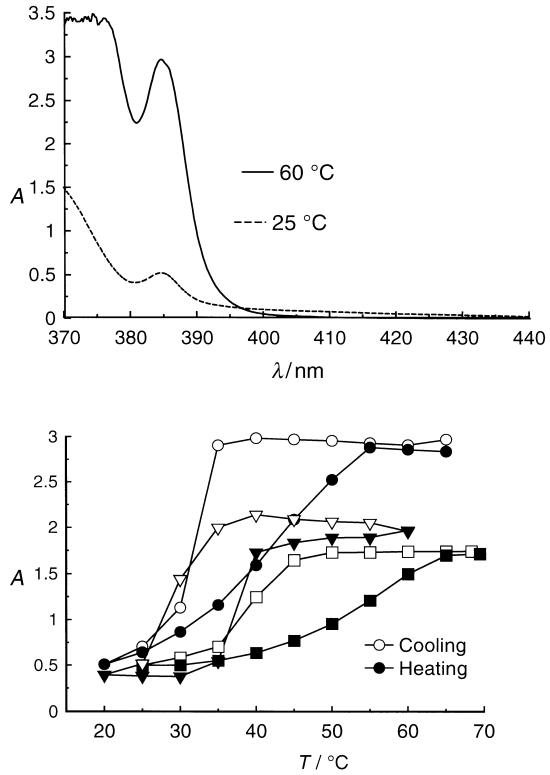


Figure 5. UV/Vis spectra of gel of **10a** in toluene at 60 °C and 25 °C (top); variable-temperature UV (1 mm cell): gel of **10a** (12.4 mM) in toluene (●); **10a** (16.5 mM) in cyclohexanol (■); **11a** (35.8 mM) in cyclohexane (▼) (bottom).

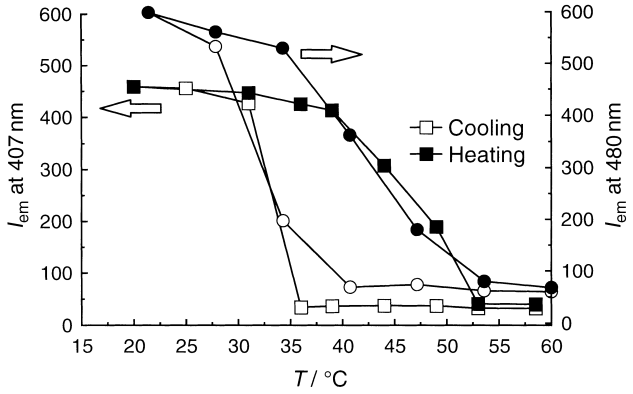


Figure 6. Variable-temperature fluorescence (λ_{ex} 355 nm, λ_{em} 480 nm): **11b** (37.3 mM) in cyclohexane (●); (λ_{ex} 355 nm, λ_{em} 407 nm): **10a** (10.3 mM) in toluene (■).

spectra were recorded for sol, gel, solid (KBr), and isotropic solutions of the compounds (Table 4). A comparison of the stretching frequencies for C=O and N–H revealed no change in their values between the sol and the gel phases. However, there was a shift of around 30 cm^{-1} and 150 cm^{-1} for C=O and N–H, respectively, when the gel phase was compared with a solution in $CHCl_3$. In addition, the stretching frequencies for these two functionalities in the gel phase hardly differed from that in the solid phases, suggesting considerable, almost solid-like aggregation in the gel as well as the sol phase, thus proving that the gel aggregates are intermolecularly hydrogen-bonded, in addition to having a π-stacking interaction.

Table 4. FT-IR data on gel/sol derived from one-component gelators.[a]

	Solid		Gel		Sol		Solution ($CHCl_3$)	
	C=O	N–H	C=O	N-H	C=O	N–H	C=O	N–H
10a	1655	3253	1652 (5.2)	3268	1651 (5.2)	3266	1683 (16.5)	3427
11a	1695	3293	1692 (36)	3262	–	–	1731 (36)	3430
13	1629	3314	1630 (5.9)	3310	1630 (5.9)	3316	1668 (6)	3420

[a] The numbers in parentheses represent the concentrations in mM.

NMR studies: NMR spectra were recorded for a [D_6]benzene gel of **10a** at various temperatures. There was no observable shift in the proton signals (specially the NH) on going from the sol to the gel phase. This is consistent with the FT-IR data, which showed as much hydrogen-bonding association in the sol state as in the gel. The only observable change in the NMR was the broadening of the peaks in the gel phase as compared to the sol.

Molecular modeling and a chiral gelator: Variable-temperature FT-IR studies suggested that the primary aggregates of these gelators are intermolecularly hydrogen-bonded, and are present even in the sol. At the gelation temperature, further aggregation/rigidification of the aggregate is augmented through π-stacking interactions. Molecular modeling (INSIGHT II) was performed to model the structure of the primary gel aggregates. Molecular mechanics (MMX) minimizations on an assembly of the gelator molecules suggested that these molecules stack through π – π interactions forming a continuous array with intermolecular hydrogen bonding between N–H of one molecule with the C=O group of the adjacent molecule. This type of an assembly induces a twist in the array leading to a helical organization. Furthermore, modeling with (*R*)-(–)-2-octyl urethane derivative of pyrene (*R*)-**12** showed a tightly packed, *P*-helical aggregate (Figure 7). It was clearly important at this time to synthesize (*R*)-**12** and study its optical properties.

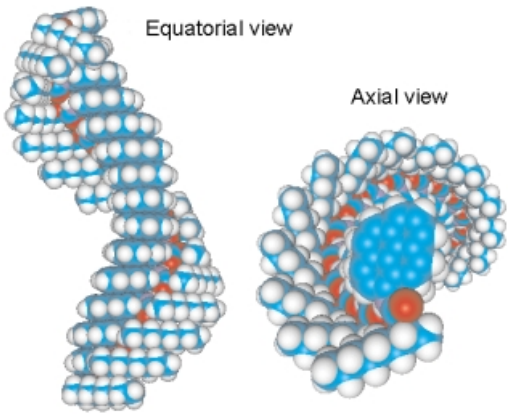


Figure 7. Insight I-minimized structure of an assembly of 15 molecules of 2-octyl carbamate (*R*)-**12** with *P* helicity.

Chiral gelators (*R*)-**12** and (*S*)-**12** were synthesized and the gelation test results are shown in Table 3. We were delighted to see that **12** could gelate a number of hydrocarbon solvents, unlike the straight-chain analogue **11c** (which produced crystals). Gels obtained from the chiral gelators gave spectro-

scopic signatures similar to their achiral counterparts. Most interestingly, the optical rotation of gelator (*R*)-**12** in cyclohexane (1.47%) at ≈65 °C (molten gel) was $-6\ \mathrm{deg\,cm^2\,g^{-1}}$, and upon cooling to room temperature (25 °C) the optical rotation changed sign, and increased to $+1680\ \mathrm{deg\,cm^2\,g^{-1}}$. The observation of such a large optical rotation is consistent with the formation of a "hellicenoid" organization.[25] The circular dichroism spectra of gels of chiral compounds (*R*)-**12** and (*S*)-**12** showed bands with opposite signs at $\lambda = 389$ nm, while the sol did not show any CD band. This observation suggests the presence of chiral helical assemblies in the gel state, thus supporting our model shown in Figure 7.

X-ray crystallography: Long needles of (*S*)-**12**, were obtained by slow evaporation of an ethanolic solution. Chiral **12**(*S*) crystallizes out in the acentric monoclinic space group $P2_1$ (no. 4) with two molecules of (*S*)-**12** in the asymmetric unit. Figure 8 shows a view of (*S*)-**12** with the crystallographic

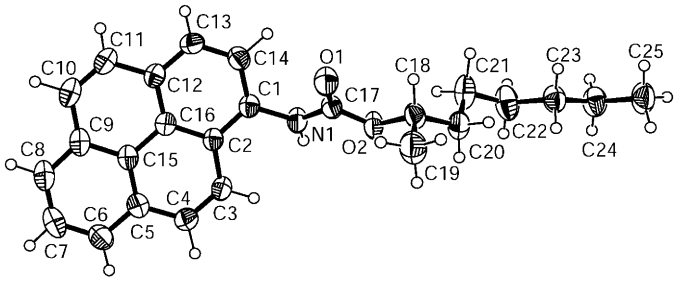


Figure 8. Structure of (*S*)-**12** (ORTEP[34] plot; the thermal displacement parameters are shown at 50% probability level).

numbering scheme. No abnormal bond lengths and angles occur in the structure of (*S*)-**12**. The amide group attached to the chiral alkyl chain is tilted 49.9(3)° from the pyrene plane (as defined by the torsion angle C17-N1-C1-C14).

The molecules of (*S*)-**12** pack along the crystallographic *a* axis (Figure 9) without any solvent molecules. The amide hydrogen atom is strongly hydrogen-bonded to the carbonyl

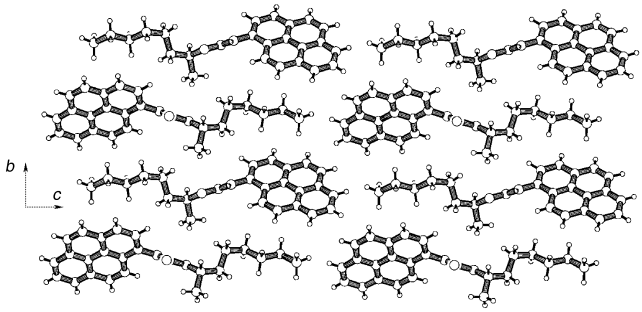


Figure 9. Packing of (*S*)-**12** along the *x* axis.

group of the adjacent molecule. The hydrogen bond parameters being 0.880 Å (N1–H1), 1.974 Å (H1···O1#), 2.853 Å (N1···O1#) and 178.44° (N1-H1···O1#, symmetry operator # = 1 + *x*, *y*, *z*). The strong hydrogen bond creates 1D arrays or columns which pack non-centrosymmetrically along the *a* axis (Figure 9). The 1D array or column formation is further enhanced by the optimum π–π interactions between the adjacent pyrene moieties (Figures 10 and 11). The adjacent pyrene moieties overlap so that stacking interactions are

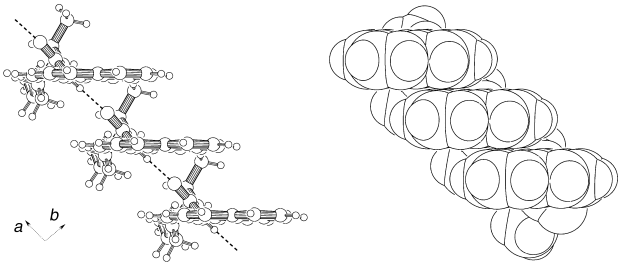


Figure 10. Packing of three molecules of (*S*)-**12** along the *z* axis showing the hydrogen bonding and stacking of the pyrene moieties, ball-and-stick (left) and CPK (right).

optimized; the intermolecular distances vary from 3.506 Å (C4···Ct1, where Ct1 is the centroid of C1, C2, C12, C13, C14 and C16) to 3.545 Å (C7···C10), which indicateds quite strong π–π interactions. The 1D arrays are packed tightly together but no intermolecular contacts shorter than the sum of the van der Waals radii between the 1D arrays occur. The absence of a helical organization in the solid state is not surprising, possibly because of crystal-packing forces. The X-ray data clearly supports our model for the formation of the primary aggregate during the gelation process.[26]

Scanning electron microscopy: The gel morphology was investigated by electron microscopy of the xerogels coated with Au. All the SEM pictures (Figure 12) show interconnected networks of fibers with a dimension in the order of 50–100 nm. Although we have proposed a model for the formation of the primary aggregates from (*R*)-**12**/(*S*)-**12**, the available data do not allow us to suggest how these units could possibly assemble to generate the macroscopic fibrillar structures seen in SEM.

Conclusion

We have demonstrated that pyrene linked with a hydrocarbon chain through a variety of linkers are efficient gelators of organic solvents. Compounds with no hydrogen-bonding donor–acceptor functionality formed colorful gels *only* in the presence of TNF in a 1:1 stoichiometry through charge-transfer interaction. They are efficient gelators of hydrocarbon solvents as well as hydroxylic solvents. CD analysis of a gel derived from a chiral gelator provided evidence for the existence of supramolecular chirality.

Compounds having hydrogen-bond donor–acceptor linkers formed gels in a variety of organic solvents through intermolecular hydrogen bonding *and* π–π interaction. FT-IR spectroscopic analysis of these suggested the presence of strong hydrogen bonds in the gel. Variable-temperature UV/Vis and fluorescence studies for the gel-to-sol interconversion showed the existence of stacked pyrene units in the gel fibers. Molecular modeling suggested face-to-face stacking of pyrene units and hydrogen bonding between the NH and the C=O

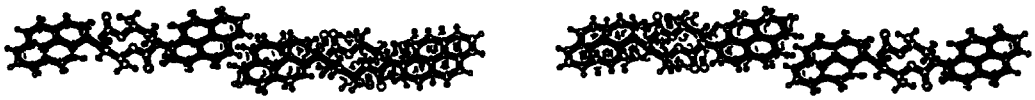


Figure 11. Stereoview of the packing of (*S*)-**12** along the *y* axis.

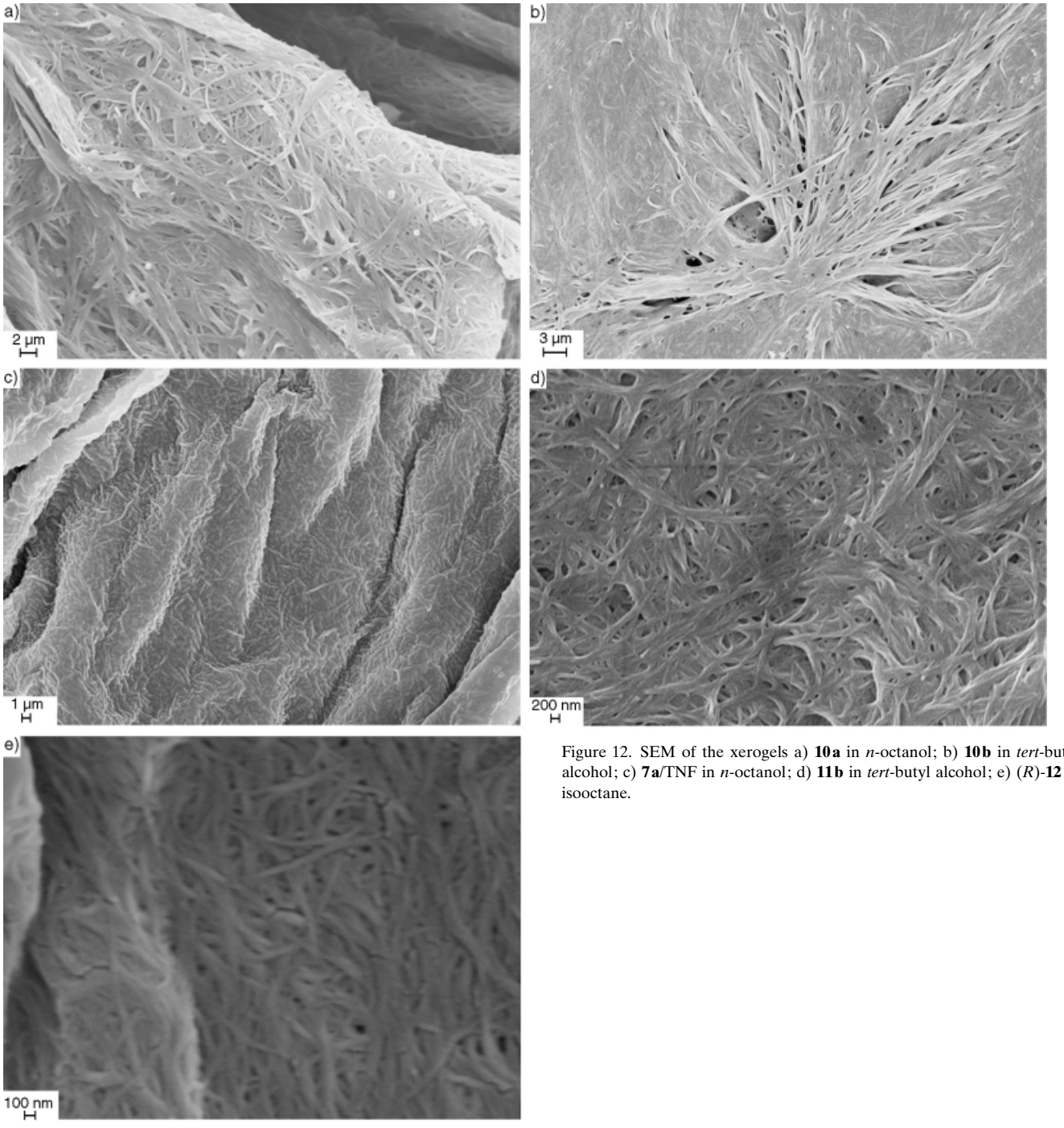


Figure 12. SEM of the xerogels a) **10a** in *n*-octanol; b) **10b** in *tert*-butyl alcohol; c) **7a**/TNF in *n*-octanol; d) **11b** in *tert*-butyl alcohol; e) (*R*)-**12** in isooctane.

groups on adjacent molecules resulting in a *helical* motif. This model was supported by CD and optical rotation measurements on gels derived from a chiral gelator. The X-ray crystal structure of this gelator showed the presence of hydrogen bonding and π stacking of pyrene units, as predicted by our model.

Our work describes the first the detailed studies on the formation of an organogel mediated by a two-component donor–acceptor interaction. We believe that further research in this area will lead to a better understanding of the detailed structure of the gel fibers, which is a must for potential futuristic applications of these novel organogels.

Experimental Section

All reactions were carried out in oven-dried glassware, unless otherwise stated. All moisture-sensitive reactions were carried out with appropriate protection (calcium chloride guard tubes/inert atmosphere). All solvents were distilled before use. Chloroform and dichloromethane were distilled over CaH_2; THF and toluene were distilled over sodium/benzophenone ketyl; and pyridine and Et_3N were distilled over KOH. All melting points are uncorrected. TLC was performed on pre-coated silica gel plates (Merck) and stained with iodine vapor or with 10% phosphomolybdic acid reagent, or observed under UV light. Column chromatography was carried out on 100–200 mesh silica gel (Acme) on gravity columns. UV/Vis spectra were recorded on a Shimadzu UV2100 spectrometer equipped with a thermoelectric variable-temperature setup. FT-IR spectra were recorded on a Jasco-70 FT-IR spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer. NMR spectra were measured on 300 MHz instruments (JEOL Lambda-300)in deuterated solvents as indicated; TMS or the residual solvent peaks were used as internal standards. Optical rotations were measured at $\lambda = 589$ nm at the specified temperatures on a JASCO DIP-370 digital polarimeter. Circular dichroism spectra were recorded on a JASCO J-700 CD spectrophotometer.

1-Acetylpyrene was synthesized by following a literature procedure. Yield: 83%; m.p. 88–89 °C (lit.[23] 90 °C).

Pyrene 1-carboxylic acid: To a mixture of 1-acetylpyrene (2.3 g, 9.38 mmol) and pyridine (2 mL) in a 100-mL round-bottomed flask equipped with an air condenser heated to 85–90 °C, was added NaOCl solution (70 mL, 3.8%, 37.6 mmol). After heating at the same temperature for 1 h, the reaction mixture was concentrated and filtered. The white precipitate obtained was dissolved in hot water and filtered to remove insolubles. The filtrate was cooled and acidified with dilute HCl to obtain a pale yellow product that, after filtration and drying, was sublimed under reduced pressure. Yield 75%, m.p. 260–261 °C (lit.[23] 261–262 °C).

1-Nitropyrene: To a mixture of pyrene (3.0 g, 15.0 mmol) and Ac_2O (4.0 mL, 42.4 mmol) in EtOAc (30 mL) was added $Cu(NO_3)_2 \cdot 3H_2O$ (5 g, 21 mmol). The mixture was stirred at 55 °C for 20 h and a thick yellow precipitate formed. The reaction mixture was cooled to room temperature and the inorganic materials were filtered off. The crude product obtained on evaporation of the solvent was purified on a silica gel column (3.2 cm × 19 cm, 10–60% $CHCl_3$/hexanes) to give the pure product (3.44 g; 93%); m.p. 150–152 °C (lit.[23] 153–155 °C).

1-Aminopyrene: To a solution of 1-nitropyrene (0.8 g, 3.23 mmol) in EtOAc (12 mL) and AcOH (1 mL), under H_2 (1 atm) was added 10% Pd/C (345 mg, 0.29 mmol). The mixture was stirred for 3 h. The solution was filtered through a bed of celite and the crude product obtained on evaporation of the solvent was crystallized from cyclohexane to yield 80% of the product. M.p. 113–114 °C (lit.[23] 115–117 °C).

1-Bromopyrene: 1-Bromopyrene was synthesized by following a literature procedure. M.p. 92–93 °C (lit[27] 94.5–95.5 °C).

Pyren-1-ol: 1-Bromopyrene (0.97 g, 3.47 mmol) and Mg pieces (0.11 g, 4.43 mmol) in dry THF (3 mL) were placed in a two-necked 50-mL round-bottomed flask fitted with a reflux condenser and a septum under an atmosphere of argon. $BH_3 \cdot SMe_2$ (0.4 mL of 10 M, 4.0 mmol) was added with a syringe. The reaction mixture was refluxed for 3 h, cooled to RT, and water (1 mL) was added dropwise to destroy excess borane. NaOH (1 M, 1.8 mL, 1.8 mmol) solution was added dropwise. After the mixture had been stirred for 5 min, 30% H_2O_2 (0.48 mL, 4.23 mmol) was added dropwise with ice cooling. The mixture was stirred for 1 h, concentrated HCl (1 mL) and water (2 mL) were added and the mixture was extracted with EtOAc (2 × 10 mL), washed with brine, and dried over anhydrous Na_2SO_4. After the volatiles had been removed in vacuo, the crude product was purified on a silica gel column (2.2 cm × 27 cm, 4–10% EtOAc/hexanes) to give the desired product (0.37 g; 49%); m.p. 173–173.5 °C (decomp) (lit.[23] 179–181 °C).

General procedure for the preparation of alkyl pyrene carboxylates: 1-Pyrene carboxylic acid (0.12 mmol) was converted to the corresponding acid chloride by treating with oxalyl chloride (0.06 mL, 0.685 mmol) and DMF (4 μL) in dry toluene (0.5 mL). After the reaction mixture had been stirred for 1.5 h, volatiles were removed in vacuo. The crude acid chloride obtained was dissolved in toluene (0.5 mL), treated with pyridine (0.5 mL) and the appropriate alcohol (0.15 mmol), and stirred for 14 h. The reaction mixture was extracted with EtOAc and the organic extract was washed with dilute HCl, saturated $NaHCO_3$ solution, water and brine. The crude product obtained on evaporation of the solvent was purified on a silica gel column (50–60% $CHCl_3$/hexanes) and subsequently crystallized from EtOH.

1-Hexadecyl pyrene-1-carboxylate (4a): Yield 89%, m.p. 65–66 °C; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 385.0 (3.85), 353.0 (4.38), 283.0 (4.43), 274.0 (4.26), 245 nm (4.63); IR (Nujol): $\tilde{\nu} = 1690$, 1615, 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.27$ (d, $J = 9.6$ Hz, 1H), 8.64 (d, $J = 7.8$ Hz, 1H), 8.29–8.04 (m, 7H), 4.51 (t, 2H), 1.90 (q, $J = 6.9$ Hz, 2H), 1.25 (m, 26H), 0.88 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.11$, 134.17, 131.03, 130.97, 130.36, 129.47, 129.29, 128.30, 127.11, 126.21, 126.17, 126.06, 124.92, 123.92, 124.80, 124.19, 124.06, 65.40, 31.91, 29.69, 29.66, 29.60, 29.56, 29.35, 28.85, 26.20, 22.66, 14.10 ppm; LRMS: m/z (%): 470 (12) $[M]^+$, 55 (100); elemental analysis calcd (%) for $C_{33}H_{42}O_2$: C 84.2, H 9.0; found: C 84.40, H 9.13.

1-Octyl pyrene-1-carboxylate (4b): Yield 68%, m.p. 52–53 °C; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 385.0 (3.9), 353.2 (4.43), 283.2 (4.49), 273.6 (4.31), 245.8 nm (4.68); IR (neat): $\tilde{\nu} = 1700$, 1620, 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.27$ (d, $J = 9.3$ Hz, 1H), 8.55 (d, $J = 8.1$ Hz, 1H), 8.29–8.17 (m, 5H), 8.11–8.04 (m, 2H), 4.52 (t, 2H), 1.83 (q, $J = 7.2$ Hz, 2H), 1.59–1.51 (m, 4H), 1.43–1.26 (m, 6H), 0.91 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.15$, 134.20, 131.05, 131.01, 130.39, 129.50, 129.32, 128.32, 127.15, 126.25, 126.20, 126.10, 124.83, 124.21, 124.10, 123.96, 65.43, 31.82, 29.32, 29.25, 28.88, 26.23, 22.67, 14.11 ppm; LRMS: m/z (%): 358 (97) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{26}O_2$: C 83.76, H 7.31; found: C 84.09, H 7.36.

2-octyl pyrene-1-carboxylate [(*R*)-5/(*S*)-5]: To a stirred solution of pyrene-1-carboxylic acid (102 mg, 0.415 mmol), dicyclohexylcarbodiimide (DCC) (118 mg, 0.572 mmol), and dimethylaminopyridine (DMAP) (22 mg, 0.18 mmol) in dry THF (2.2 mL) was added (*R*)-2-octanol (0.06 mL, 0.378 mmol). After stirring for 12 h, the reaction mixture was extracted with $CHCl_3$, washed with water and brine, and dried over anhydrous Na_2SO_4. The crude compound obtained on evaporation of the solvent was purified on a silica gel column (16 cm × 1.2 cm, 50% $CHCl_3$) to afford a yellow oil in 55% yield. $[\alpha]_D^{25} = -15.5$ ($c = 1.1$ in $CHCl_3$) for the *R* isomer; $[\alpha]_D^{25} = +15.0$ ($c = 1.2$ in $CHCl_3$) for the *S* isomer; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 384.5 (3.84), 352.5 (4.41), 283 (4.47), 271.5 (4.32), 246 nm (4.7); IR (neat): $\tilde{\nu} = 1700$, 1597, 1459, 1384, 1257, 1232, 1198, 1148, 1120, 1089, 1044, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.27$ (d, $J = 9$ Hz, 1H), 8.62 (d, $J = 8.1$ Hz, 1H), 8.28–8.16 (m, 5H), 8.10–8.03 (m, 2H), 5.39 (sextet, $J = 6$ Hz, 1H), 1.97–1.85 (m, 2H), 1.8–1.68 (m, 2H), 1.51 (d, $J = 6.3$ Hz, 3H), 1.6–1.27 (m, 6H), 0.91 ppm (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.75$, 134.08, 131.01, 130.97, 130.4, 129.42, 129.24, 128.18, 127.16, 126.23, 126.15, 126.05, 124.94, 124.83, 124.5, 124.24, 124.09, 72.04, 36.24, 31.79, 29.24, 25.6, 22.62, 20.24, 14.09 ppm; LRMS: m/z (%): 358 $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{26}O_2$: C 83.76, H 7.31; found: C 83.56, H 7.26.

1-Pyrenoyl-1-octadecyl amide (6): IR (thin film): $\tilde{\nu} = 3334$, 1634, 1522, 1523, 1468 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.56$ (d, $J = 9$ Hz, 1H), 8.22 (d, $J = 7.2$ Hz, 2H), 8.16–8.02 (m, 6H), 6.12 (brs, 1H), 3.62 (q, $J = 6.6$ Hz, 2H), 1.72 (quintet, $J = 7.5$ Hz, 2H), 1.26 (m, 28H), 0.85 ppm (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.92$, 132.35, 131.45, 131.15, 130.69, 128.54, 128.49, 128.44, 127.07, 126.25, 125.71, 125.63, 124.72, 124.41, 124.26, 40.33, 31.91, 29.77, 29.69, 29.61, 29.35, 27.08, 22.67, 14.10 ppm; LRMS: m/z (%): 497 $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{47}NO$: C 84.54, H 9.52, N 2.82; found: C 84.88, H 9.74, N 2.39.

1-Hexadecanoyl-1-pyrene: A mixture of 1-hexadecanoic acid (0.43 g, 1.67 mmol), oxalyl chloride (0.4 mL, 4.69 mmol) and DMF (4 μL) in dry toluene (2 mL) was stirred at 45 °C for 1 h. Toluene and excess oxalyl chloride were removed under reduced pressure. To the crude acid chloride, dry nitrobenzene (4 mL) and pyrene (0.33 g, 1.63 mmol) were added, stirred at 0 °C for 30 min, and then $AlCl_3$ (0.38 g, 2.88 mmol) was added in three portions at 5 min intervals. After the mixture had been stirred at room temperature for 2 h, crushed ice was added. Nitrobenzene was removed by steam distillation, the residue was extracted with EtOAc (2 × 10 mL), washed with water (10 mL), dilute HCl (10 mL), saturated $NaHCO_3$ solution (15 mL), and with brine, and dried over anhydrous Na_2SO_4. The crude product was purified on a silica gel column (2.2 cm × 15.5 cm, 30–50% $CHCl_3$/hexanes) to give the desired product (0.51 g;

71%) as a yellow solid; m.p. 60–61 °C; UV/Vis (1% $CHCl_3$/EtOH v/v): λ_{max} ($\log\varepsilon$) = 354.5 (4.33), 282 (4.56), 242 (4.68), 232.5 nm (4.70); IR (thin film): $\tilde{\nu}$ = 1670, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, J = 9.6 Hz, 1H) 8.30–8.01 (m, 8H), 3.19 (t, J = 7.5Hz, 2H), 1.85 (quintet, J = 6.9, J = 7.5 Hz, 2H), 1.47 (m, 24H), 0.88 ppm (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.49, 133.55, 133.03, 131.11, 130.59, 129.44, 129.34, 127.09, 126.35, 126.15, 125.96, 125.93, 125.04, 124.83, 124.38, 123.99, 42.73, 31.93, 29.69, 29.66, 29.62, 29.52, 29.50, 29.44, 29.36, 25.03, 22.70, 14.12 ppm; LRMS: m/z (%): 440 $[M]^+$, 229 (100); elemental analysis calcd (%) for $C_{32}H_{40}O$: C 87.23, H 9.15; found: C 87.24, H 9.30.

1-Dodecanoyl-1-pyrene: This compound was made from 1-dodecanoic acid and pyrene in 70% yield, m.p. 56–57 °C; UV/Vis (1% $CHCl_3$/EtOH): λ_{max} ($\log\varepsilon$) = 356 (4.34), 282 (4.39), 242 (4.61), 233.5 (4.61), 209.5 nm (4.46); IR (thin film): $\tilde{\nu}$ = 1668, 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.86 (d, J = 9.6 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.26–8.01 (m, 6H), 8.06 (d, J = 9.6 Hz, 1H), 3.12 (t, J = 7.2 Hz, 2H), 1.86 (q, J = 7.3 Hz, 2H), 1.47- 1.25 (m, 16H), 0.87 ppm (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.57, 133.54, 133.00, 131.10, 130.57, 129.44, 129.35, 129.21, 127.09, 126.36, 126.15, 125.96, 125.93, 125.02, 124.80, 124.37, 123.99, 59.55, 42.73, 31.90, 29.60, 29.49, 29.42, 29.33, 25.02, 22.68, 14.11 ppm; LRMS: m/z (%): 384 $[M]^+$, 229 (100%); elemental analysis calcd (%) for $C_{28}H_{32}O$: C 87.45, H 8.38; found: C 87.69, H 8.52.

1-Hexadecyl-1-pyrene (7a): In a 35-mL test tube fitted with a reflux condenser, 1-hexadecanoyl-1-pyrene (0.15 g, 0.34 mmol), hydrazine monohydrate (0.14 mL, 2.88 mmol), and KOH (0.10 g, 1.78 mmol) in digol (1.5 mL, 12.40 mmol) was heated at 125 °C in a sand bath for 2 h, and then water was removed from the reaction mixture by distilling at 205 °C. The reaction mixture was cooled to RT, extracted with $CHCl_3$ (2 × 5 mL), washed with water and brine, and dried over anhydrous Na_2SO_4. The crude product was purified on a silica gel column (1.2 cm × 15 cm, hexane) to give **7a** (0.12 g; 80%). M.p. 79–80 °C; UV/Vis (1% $CHCl_3$/EtOH v/v): λ_{max} ($\log\varepsilon$) = 342.5 (4.60), 326 (4.44), 313 (4.04), 276 (4.65), 265 (4.39), 255 (4.13), 243 (4.82), 210 nm (4.36); IR (Nujol): $\tilde{\nu}$ = 1465, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, J = 9.3Hz, 1H), 8.16–8.08 (m, 4H), 8.02–7.98 (m, 3H), 7.88 (d, J = 7.8 Hz, 1H), 3.33 (t, J = 7.7 Hz, 2H), 1.53 (quintet, J = 7.5 Hz, 2H), 1.25 (m, 26H), 0.88 ppm (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.37, 131.43, 130.92, 129.65, 128.58, 127.52, 127.23, 127.04, 126.44, 125.72, 125.05, 124.75, 124.73, 124.57, 123.53, 33.62, 31.96, 31.92, 29.83, 29.69, 29.67, 29.63, 29.59, 29.36, 22.69, 14.12 ppm; LRMS: m/z (%): 426 $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{42}$: C 90.08, H 9.92; found: C 90.49, H 10.12.

1-Dodecyl-1-pyrene (7b): A similar procedure gave **7b** in 62% yield; m.p. 72–73 °C; UV/Vis (1% $CHCl_3$/EtOH v/v): λ_{max} ($\log\varepsilon$) = 342.5 (4.65), 326.5 (4.49), 312 (408), 276 (4.69), 265 (4.42), 255 nm (4.15); IR (thin film): $\tilde{\nu}$ = 1465, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, J = 9.3 Hz, 1H), 8.17 (m, 5H), 8.02 (m, 2H), 7.87 (d, J = 7.8 Hz, 1H), 3.33 (t, J = 7.7 Hz, 2H), 1.37 (quintet, J = 7.5 Hz, 2H), 1.49 (m, 2H), 1.37–1.26 (m, 16H), 0.88 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.39, 131.47, 130.96, 129.68, 127.54, 127.25, 127.07, 126.46, 125.74, 125.08, 124.77, 124.76, 124.59, 123.55, 33.64, 31.98, 31.93, 29.85, 29.68, 29.65, 29.61, 29.36, 22.07, 14.13 ppm; LRMS: m/z (%): 384 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{34}$: C 90.75, H 9.25; found: C 90.95, H 9.33.

1-Ethylpyrene (7c): 1-Ethylpyrene was prepared following the procedure for **7b** in 98% yield; m.p. 94–95 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 9.3Hz, 1H), 8.14–8.05 (m, 4H), 7.99–7.91 (m, 3H), 7.86 (d, J = 6.9 Hz, 1H), 3.35 (q, J = 7.5 Hz, 2H), 1.45 ppm (t, J = 6.3 Hz, 3H); ^{13}C NMR (75, MHz, $CDCl_3$): δ = 138.57, 131.43, 130.92, 129.66, 128.36, 127.51, 127.12, 126.46, 126.35, 125.72, 125.05, 124.93, 124.75, 124.61, 123.33, 26.56, 16.12 ppm; LRMS m/z (%): 230 $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{14}$: C 93.87, H 6.13; found: C 94.12, H 6.22.

1-Tetradecyl-1-pyrenyl ether (8): In a 5-mL round-bottomed flask fitted with a reflux condenser, 1-pyrenol (0.021 g, 0.095 mmol) and 1-tetradecylbromide (28 μL, 0.094 mmol) in dry acetone (1.0 mL) were placed under an Ar atmosphere and K_2CO_3 (0.014 g, 0.10 mmol) was added. The reaction mixture was refluxed for 7.5 h. The solvent was removed in vacuo, extracted with EtOAc (4 mL), washed with brine, and then the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (1.0 cm × 14 cm, hexane) to give **8** (21 mg; 54%). M.p. 74–75 °C; UV/Vis (1% $CHCl_3$/EtOH v/v): λ_{max} ($\log\varepsilon$) = 382.5 (3.96), 363 (4.14), 351 (4.40), 346 (4.42), 337 (4.33), 277.5 (4.61), 267 (4.31), 241.5 nm (4.78); IR (Nujol): $\tilde{\nu}$ = 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, J = 9.0 Hz, 1H), 8.16–7.86 (m, J = 7.0 Hz. 7H), 7.53 (d, J = 8.4 Hz, 1H), 4.31 (t, J = 6.5 Hz, 2H), 2.06 (quintet, J = 6.7 Hz, 2H), 1.84 (m, 2H), 1.26 (m, 20H), 0.88 ppm (t, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.27, 131.76, 131.73, 127.26, 126.24, 126.04, 125.49, 125.09, 124.99, 124.86, 124.15, 124.06, 121.32, 120.43, 109.14, 60.01, 31.94, 29.71, 29.69, 29.66, 29.64, 29.51, 29.48, 29.37, 26.28, 22.70, 14.13 ppm; LRMS: m/z (%): 414 $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{38}O$: C 86.90, H 9.24; found: C 86.76, H 9.34.

1-Pyrenyl-1-hexadecylcarboxylate (9): 1-Hexadecylcarboxylic acid (160 mg, 0.62 mmol) was converted to the corresponding acid chloride by treating with oxalyl chloride (0.16 mL, 1.85 mmol) and DMF (4 μL) in dry toluene (1.4 mL). After the reaction mixture had been stirred at 45 °C for 1 h, volatiles were removed in vacuo. The crude acid chloride obtained was dissolved in toluene (1.5 mL), and treated with pyridine (0.6 mL) and pyrenol (146 mg, 0.63 mmol) in toluene (1 mL) and heated at 100 °C for 14 h. The reaction mixture was extracted with EtOAc and the organic extract was washed with dilute HCl, saturated $NaHCO_3$ solution, water and brine. The crude product obtained on evaporation of the solvent was purified on a silica gel column (3–5% EtOAc/hexanes) to yield **9** (185 mg; 65%). IR (neat): $\tilde{\nu}$ = 3045, 2923, 2852, 1760, 1599 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.2–8.07 (m, 8H), 7.81 (d, J = 8.4 Hz, 1H), 2.84 (t, J = 7.4 Hz, 2H), 1.92 (quintet, J = 7.5 Hz, 2H), 1.27 (m, 26H), 0.89 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.69, 144.36, 131.14, 130.97, 129.23, 128.07, 127.09, 127.02, 126.26, 125.60, 125.44, 125.17, 125.0, 124.57, 123.14, 120.24, 119.77, 34.54, 31.93, 29.71, 29.69, 29.63, 29.52, 29.37, 29.33, 29.28, 26.20, 22.70, 14.13 ppm; LRMS: m/z (%): 456 $[M]^+$.

General procedure for the preparation of alkyl amides of pyrene: An aliphatic acid (0.70 mmol) was converted to the corresponding acid chloride by stirring with oxalyl chloride (2.25 mmol) and DMF (5 μL) in dry toluene (1 mL) at RT. After 5 h, the volatiles were removed in vacuo and the resulting oil was dissolved in dry CH_2Cl_2 (6 mL) and treated with 1-aminopyrene (0.69 mmol) and Et_3N (1.0 mmol). A buff colored precipitate resulted. After the mixture had been stirred for 15 h, the precipitate was filtered and washed with EtOH. The solid obtained was then dissolved in hot 40% EtOH/$CHCl_3$ and decolorized (charcoal). The white precipitate formed on cooling the filtrate was collected by filtration and dried.

1-Octadecanoyl-1-pyrene amide (10a): Yield 73%; m.p. 153 °C; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 245.8 (4.54), 278.8 (4.36), 343.4 (4.33), 380.0 nm (3.13); IR (Nujol): $\tilde{\nu}$ = 3240, 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.34–8.00 (m, 9H), 7.80 (s, 1H), 2.59 (t, J = 7.5 Hz, 2H), 1.88 (q, J = 7.5 Hz, 2H), 1.26 (m, 28H), 0.90 ppm (t, 3H); LRMS: m/z (%): 483 (19) $[M]^+$; elemental analysis calcd (%) for $C_{34}H_{45}NO$: C 84.42, H 9.38, N 2.89; found: C 84.19, H 9.6, N 2.52.

1-Dodecanoyl-1-pyrene amide (10b): Yield 85%; m.p. 149–149 °C; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 245.8 (4.52), 278.8 (4.35), 343.4 (4.3) 389.0 nm (3.12); IR (Nujol): $\tilde{\nu}$ = 3240, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 8.20–8.02 (m, 8H), 7.78 (s, 1H), 2.60 (t, J = 7.5 Hz, 2H), 1.89 (q, 2H), 1.51–1.11 (m, 16H), 0.88 ppm (t, 3H); LRMS: m/z (%): 399 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{33}NO$: C 84.16, H 8.33, N 3.51; found: C 84.17, H 8.41, N 3.2.

1-Octanoyl-1-pyrene amide (10c): Yield 81%; IR (Nujol): $\tilde{\nu}$ = 3240, 1650, 1590, 1560, 1530, 1465 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, J = 8.1 Hz, 1H), 8.33–8.05 (m, 8H), 7.82 (s, 1H), 2.59(t, J = 7.5Hz, 2H), 1.88 (q, 2H), 1.5–1.11 (m, 8H), 0.88 ppm (t, 3H); LRMS: m/z (%): 343 $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{25}NO$: C 83.92, H 7.34, N 4.08; found: C 83.47, H 7.28, N 3.75.

General procedure for the synthesis of alkyl carbamates derived from 1-aminopyrene: To a stirred solution of the alcohol (0.62 mmol) in $CHCl_3$ (3 mL), bis(trichloromethyl) carbonate (0.20 mmol) was added and the mixture was cooled in an ice bath. Pyridine (0.62 mmol) was added slowly over a period of 5 min. After 2 h, a solution of 1-aminopyrene (0.6 mmol) and pyridine (0.7 mmol) in $CHCl_3$ (2 mL) was added over a period of 10 min. After 1 h, the reaction mixture was diluted with $CHCl_3$ (5 mL) and washed with 1N HCl, water, aqueous $NaHCO_3$, and dried over anhydrous Na_2SO_4. The crude product was chromatographed on a silica gel column (50% $CHCl_3$/hexanes).

Pyren-1-yl-carbamic acid hexadecyl ester (11a): 1-Hexadecanol (0.150 mg) was converted to the carbamate in 83% yield; m.p. 113–114 °C; UV/Vis (0.5% $CHCl_3/CH_3CN$): λ_{max} ($\log\varepsilon$) = 383 (3.26), 340 (4.44), 277(4.51), 269

(4.33), 242 nm (4.78); IR (thin film): $\tilde{\nu}=3280$, 1690, 1520 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.38$ (m, 1H), 8.2–7.9 (m, 8H), 7.21 (brs, 1H), 4.27 (t, $J=6.6$ Hz, 2H), 1.74 (m, 2H), 1.5–1.2 (m, 26H), 0.88 ppm (t, $J=6.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.84$, 131.42, 130.84, 130.64, 127.80, 127.31, 126.56, 126.14, 125.33, 125.29, 125.16, 124.87, 124.80, 120.03, 65.88, 31.94, 29.72, 29.68, 29.61, 29.58, 29.37, 29.32, 29.01, 25.93, 22.70, 14.13 ppm; LRMS: m/z (%): 485 (100) $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{43}NO_2$: C 81.60, H 8.92, N 2.88; found: C 81.45, H 8.91, N 2.53.

Pyren-1-yl-carbamic acid dodecyl ester (11b): 1-Dodecanol (0.20 g) was converted to the carbamate in 60% yield; m.p. 113.6–114.2 °C; UV/Vis (0.5% $CHCl_3/CH_3CN$): λ_{max} ($\log\varepsilon$) = 383 (3.41), 340 (4.49), 277 (4.55), 269 (4.37), 242 nm (4.82); IR (thin film) $\tilde{\nu}=1696$, 1526 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): $\delta=8.5-7.8$ (m, 9H), 7.2 (m, 1H), 4.25 (t, $J=6.3$ Hz, 2H), 1.8–1.0 (m, 20H), 0.85 ppm (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 154.83, 131.43, 130.86, 130.66, 127.83, 127.33, 126.59, 126.15, 125.34, 125.31, 125.18, 124.89, 124.83, 120.03, 65.89, 31.93, 29.68, 29.65, 29.60, 29.57, 29.37, 29.32, 29.01, 22.70, 14.13 ppm; LRMS: m/z (%): 429 (100) $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{35}NO_2$: C 81.12, H 8.16, N 3.26; found: C 81.30, H 8.28, N 3.00.

Pyren-1-yl-carbamic acid octyl ester (11c): 1-Octanol (0.170 g) was converted to the carbamate in 65% yield; m.p. 126 °C; UV/Vis (0.5%, $CHCl_3/CH_3CN$): λ_{max} ($\log\varepsilon$) = 383 (3.25), 340 (4.42), 277 (4.49), 269 (4.3), 242 nm (4.76); IR (thin film): $\tilde{\nu}=1690$ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.35$ (brm, 1H), 8.2–7.8 (m, 8H), 7.20 (brs, 1H), 4.24 (t, $J=6.6$ Hz, 2H), 1.73 (m, 2H), 1.5–1.2 (m, 10H), 0.88 ppm (t, $J=6.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.85$, 131.35, 130.78, 130.59, 128.44, 127.68, 127.25, 126.50, 126.06, 125.26, 125.21, 125.06, 124.80,124.72, 119.99, 65.84, 31.79, 29.26, 29.22, 28.99, 25.92, 22.65, 14.11 ppm; LRMS: m/z (%): 373 (100) $[M]^+$.

Pyren1-yl-carbamic acid 2-octyl ester: [(*R*)-12/(*S*)-12]: To a mixture of 1-aminopyrene (0.20 g, 0.922 mmol) and bis(trichloromethyl)carbonate (0.10 g, 0.34 mmol), was added *o*-dichlorobenzene (2 mL). The mixture was stirred at 120 °C. After 5 h, (*R*)-2-octanol (0.150 mL, 0.97 mmol) was added and the mixture was stirred at 80 °C for 15 h. Solvent was removed in vacuo and the residue adsorbed on silica gel (2 g, 60–120 mesh, $CHCl_3$ (20 mL)). The crude product was chromatographed on a silica gel column (60–120 mesh, 2 cm × 25 cm; 10% EtOAc/hexanes). The pure product was obtained in 68% yield (0.233 g); m.p. 125 °C (EtOH); $[\alpha]_D^{21}=-35.4$ ($c=1.3$ in $CHCl_3$) for the *R* isomer; $[\alpha]_D^{21}=+33.9$ ($c=1.27$ in $CHCl_3$) for the *S* isomer; UV/Vis (0.5%, $CHCl_3/CH_3CN$): λ_{max} ($\log\varepsilon$) = 383 (3.79), 340 (4.88), 277 (4.94), 242 nm (5.21); IR (thin film): $\tilde{\nu}=3278$, 1689, 1602, 1524 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.39$ (brs, 1H), 8.16–8.13 (m, 3H), 8.12–7.95 (m, 5H), 7.19 (br, 1H), 5.017 (q, $J=6$ Hz, 1H), 1.7–1.43 (m, 2H), 1.47–1.25 (m, 11H), 0.89 ppm (t, $J=6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.45$, 131.36, 130.77, 128.29, 127.6, 127.25, 126.39, 126.03, 125.21, 125.06, 124.74, 119.95, 72.60, 36.21, 31.76, 29.12, 25.41, 22.58, 20.29, 14.07 ppm; LRMS: m/z (%): 373 (25) $[M]^+$, 261 (100); elemental analysis calcd (%) for $C_{25}H_{27}NO_2$: C 80.40, H 7.29, N 3.75; found: C 80.58, H 7.34, N 3.53.

1-Hexadecyl-1-pyren-1-yl-urea (13): To a solution of 1-aminopyrene (0.14 g, 0.645 mmol) in 1,2-dichlorobenzene (2 mL) in a round-bottomed flask was added bis(trichloromethyl)carbonate (0.064 g, 0.216 mmol). The mixture was stirred at 80 °C. After 14 h cetylamine (0.11 g, 0.456 mmol) was added and the mixture was stirred at the same temperature for 3 h. The solvent was removed in vacuo and the residue was adsorbed on silica gel (2 g, 60–120, THF (3 mL)). The crude product was chromatographed on a column of silica gel (60–120 mesh, 2 cm × 25 cm, 20% EtOAc/$CHCl_3$), to yield **13** (0.2 g; 90%). UV/Vis (1% $CHCl_3/CH_3CN$): λ_{max} ($\log\varepsilon$) = 387 (3.57), 343 (4.32), 280 (4.37), 243 nm (4.64); IR (thin film): $\tilde{\nu}=3314$, 2929, 2849, 1629, 1569, 1466, 1245, 842 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 8.26–7.99 (m, 9H), 6.642 (br, 1H), 4.579 (br, 1H), 3.227 (m, 2H), 1.4–1.18 (m, 28H), 0.876 ppm (t, $J=6.3$ Hz, 3H); elemental analysis calcd (%) for $C_{33}H_{44}N_2O$: C 81.77, H 9.15, N 5.78; found: C 81.48, H 8.78, N 5.48.

1-Hexadecanoyl-2-naphthylamide (14): 1-Hexadecanoic acid (280 mg, 0.98 mmol) was converted to the corresponding acid chloride by stirring with oxalyl chloride (0.36 mL, 4.1 mmol) and DMF (4 μL) in dry toluene (0.5 mL) for 4.5 h. To the solid obtained on evaporation of the solvent in vacuo, 2-naphthylamine (188 mg, 1.31 mmol), toluene (4 mL), and Et_3N (0.2 mL, 1.44 mmol) were added and stirred at room temperature. After 22 h, water was added and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ and the combined organic extracts were washed with dilute HCl, aqueous $NaHCO_3$ solution, water and brine, dried over Na_2SO_4 and the solvent evaporated. The crude product was chromatographed on a silica gel column (16 cm × 2.2 cm, $CHCl_3$) to give **14** (333 mg; 83%). IR (Nujol): $\tilde{\nu}=3240$, 1640, 1590, 1520, 1490, 1450, 1400, 1360, 1330, 850, 820, 730, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=8{,}23$ (s, 1H), 7.78 (d, 3H), 7.48–7.33 (m, 4H), 2.41 (t, $J=7.5$ Hz, 2H), 1.77 (q, $J=7.2$ Hz, 2H), 1.33–1.26 (m, 28H), 0.88 ppm (t, $J=6.9$ Hz, 3H); LRMS: m/z (%): 409 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{43}NO$: C 82.1, H 10.58, N 3.42; found: C 81.66, H 10.59, N 3.16.

Scanning electron micrographs: To observe the morphology of the xerogels, 200 Å-thick gold films were deposited by d.c. sputtering, and were examined with a Leica 440i scanning electron microscope equipped with a LaB_6 emitter.

X-ray crystal structure analysis of (*S*)-12: Crystallographic data were collected on a Nonius Kappa CCD area-detector diffractometer using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda=0.71069$ Å). Lattice parameters were determined from 10 images recorded with 1° ϕ scans and subsequently refined on all data. The data collections were performed with ϕ and ω scans in 1° steps with an exposure time of 20 s per frame and the crystal-to-detector distance fixed to 30 mm. The data were processed with DENZO-SMN v0.93.0.[28] The WinGX[29] system was used for the crystallographic calculations, the structure was solved by direct methods with SHELXS-97[30] and refined on F^2 with SHELXL-97.[31] The graphics and geometrical analysis was produced with the ORTEP[32] and PLATON/PLUTON[33] software. The hydrogen atoms were found from the difference Fourier map and were refined isotropically. Formula $C_{25}H_{27}NO_2$, $fw=$ 373.48, $T=173.0(1)°$, monoclinic, space group $P2_1$ (no. 4), $a=4.884(2)$, $b=10.107(2)$, $c=20.415(5)$ Å, $\beta=94.3542(3)°$, $V=1004.8(5)$ Å^3, $Z=2$, $\rho_{calcd}=1.234$ Mg m^{-3}, $\mu=0.077$ mm^{-1}, $F(000)=400$, crystal size $0.40\times 0.30\times 0.20$ mm^3, T range 3.00–25.05° ($-5\le h\le 5$, $-11\le k\le 12$, $-23\le l\le 24$), reflections collected 5378, independent reflections 3203 (R(int) = 0.0475), no absorption correction, refinement with full-matrix least-squares on F^2 with 362 parameters, GOF on $F^2=1.047$, R ($I>2\sigma(I)$), $R1=0.0445$, $wR2=0.0932$, R (all data) $R1=0.0717$, $wR2=0.1030$, Largest different peak and hole 0.148 and -0.126 e Å^{-3} absolute structure parameter 0.10(16), extinction coefficient 0.043(6).

CCDC-194240 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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; or deposit@ccdc.cam.uk).

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