

Gels

# Internal Probing of the Supramolecular Organization of Pyrene-Based Organogelators

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**Abstract:** A thorough study of the unexpected spectroscopic behavior of two new luminescent pyrene-urea-based organogelators is rationalized as a function of their aggrega-

tion state and provides a key method to probe the supramolecular organization of the material.

## Introduction

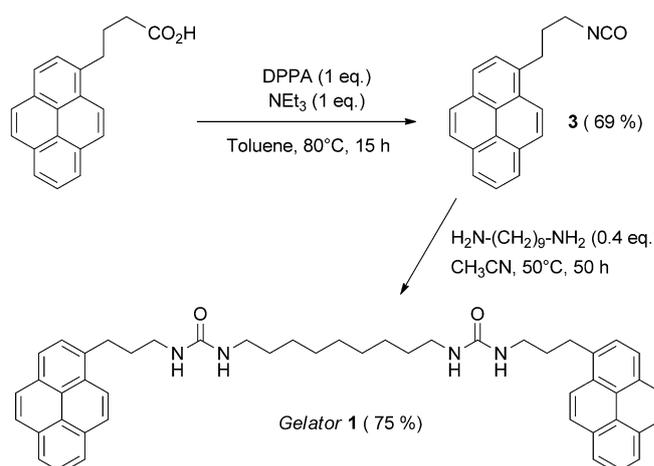
Organogelators have received much attention over the last decades<sup>[1]</sup> in very different research fields, such as sensing,<sup>[2]</sup> pharmaceuticals,<sup>[3]</sup> optics and electronics.<sup>[4]</sup> Regarding the latter, there is notably a growing interest in giving a well-defined shape<sup>[5]</sup> and/or orientation<sup>[6]</sup> to these materials to implement them in electronic or optical circuits. However, despite tremendous efforts already devoted to this issue, there is still a critical need to increase the knowledge regarding the basics which govern the supramolecular polymerization process and the related solvent effects. In this context and in order to gain control over the microstructuration of related materials, we recently contributed to the preparation of microcylinders made up of urea-based organic gelators according to a template method which involves porous alumina membranes.<sup>[7]</sup> One step further lies the definition of new tools able to internally probe the supramolecular organization, a role which can potentially be played by the pyrene moiety. Indeed, this functional unit displays original luminescent properties,<sup>[8]</sup> with typical monomer and excimer emissions as well as an electron-donor ability,<sup>[9]</sup> which are characteristics of evident importance when aiming at probing intermolecular interactions. In addition, pyrene has already been successfully introduced into a variety of organic materials for the preparation of transistors, organic light-emitting diodes or solar cells.<sup>[10]</sup>

While a significant number of bis-urea gelators has been synthesized in the past,<sup>[11]</sup> luminescent units have only been scarcely introduced into their molecular structures. With regard to pyrene, only few examples have been reported in the recent literature.<sup>[12–14]</sup> We describe herein the synthesis and un-

expected spectroscopic behavior of a new bis-urea gelator **1** featuring pyrene units and demonstrate the opportunity they offer to internally probe the structure of the corresponding gels in various solvents.

## Results and Discussion

Given the difficulties encountered in synthesizing compound **1** by adaptation of a two-step one-pot procedure,<sup>[12g]</sup> we carried out the synthesis and isolation of the 3-pyrenylpropylisocyanate intermediate **3** in 69% yield by action of diphenylphosphoryl azide (DPPA)<sup>[15]</sup> and triethylamine over 1-pyrenebutyric acid (Scheme 1). Subsequently, 1,9-diaminononane was treated with intermediate **3** (4 equivalents) to afford the desired compound **1**, which was isolated by simple filtration.



Scheme 1. Synthesis and molecular structure of compound **1**.

This bis-urea derivative displays organogelating properties in five solvents among the sixteen solvents tested, namely chloroform, 1,1,2,2-tetrachloroethane, chlorobenzene (CB), *o*-dichlorobenzene (*o*DCB), and 1,2,4-trichlorobenzene (TCB). These

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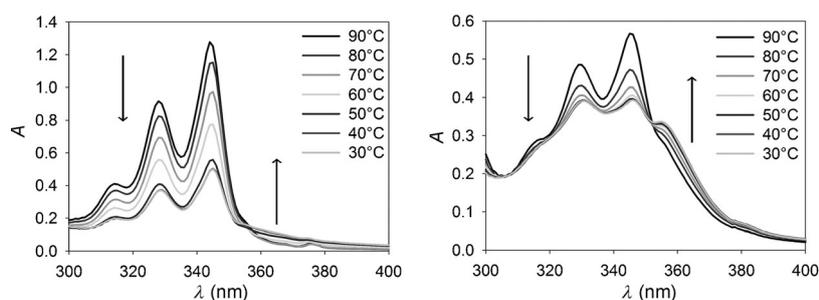
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results show that despite its relatively high melting point (229–231 °C) and poor solubility, and hence strong intermolecular interactions, compound **1** forms gels in chlorinated solvents whatever their boiling points. Scanning electron microscopy (SEM) also confirmed the tendency of compound **1** to form self-assembled nanofibers, as illustrated in Figure S1 in the Supporting Information, where networks of intertwined fibers can be observed after evaporation of the solvent.

In order to gain insight on the forces and mechanisms involved in the growth of the network, NMR, UV/Vis absorption, and fluorescence spectroscopies are usually well-suited complementary tools. In order to perform these studies, dimethylsulfoxide (DMSO) and 1,1,2,2-tetrachloroethane (TCE) were selected for the following reasons: i) compound **1** forms gels in TCE and does not in DMSO; ii) both solvents have high boiling points, which is crucial given the poor solubility of compound **1** (b.p.(TCE) = 146 °C; b.p.(DMSO) = 189 °C); and iii) they do not display similar Hansen solubility parameters (Figure S2, Supporting information), and hence, they most likely interact with the solute in different ways. In particular, DMSO has a stronger propensity to compete with intermolecular hydrogen bonding between gelating molecules.

Variable-temperature <sup>1</sup>H NMR (VT-NMR) experiments were conducted in DMSO-D<sub>6</sub> and in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 2 mg mL<sup>-1</sup> (*c* = 2.7 mM), that is, a low concentration in order to favor the dissociation of the aggregates. In both cases, these measurements show a downfield shift of the NH proton signals upon decreasing the temperature (Figures S3 and S4, Supporting Information), which is typical for the supramolecular polymerization of urea functions, other signals being also affected.<sup>[11]</sup> However, the evolution profile of the chemical shifts did not allow for quantifying the corresponding thermodynamic parameters. This reasonably stems from the very strong tendency of compound **1** to aggregate, even at elevated temperatures.

This prompted us to consider UV/Vis absorption and fluorescence spectroscopies in order to study this compound at lower concentrations. Figure 1 shows the evolution of the UV/Vis absorption spectrum of **1** (10<sup>-4</sup> M) in DMSO and oDCB upon lowering the temperature (the critical gelation concentration of **1** in oDCB is 10 mg mL<sup>-1</sup> (13.7 × 10<sup>-3</sup> M) and the gel-



**Figure 1.** Evolutions of the UV/Vis absorption spectra of **1** (*c* = 10<sup>-4</sup> mol L<sup>-1</sup>; *l* = 0.2 cm) upon lowering the temperature, DMSO (left) and oDCB (right).

to-sol transition temperature is about 75 °C (Figure S5, Supporting information).

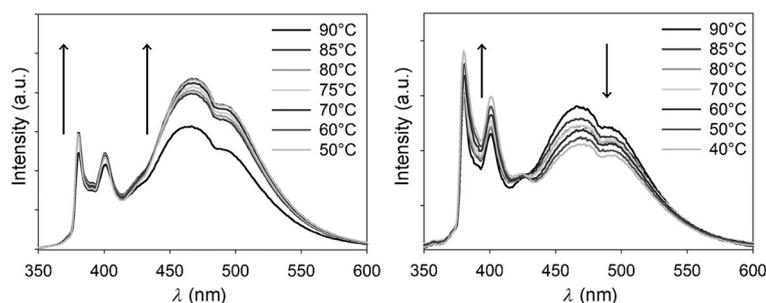
At first glance, one will note two main differences between the two solutions: the absorbance is significantly lower in oDCB and the relative intensities of the classical pyrene absorption bands at about 345, 330, and 315 nm differ. To explain such differences, the absorption spectrum of an oDCB solution of **1** (*c* = 10<sup>-4</sup> mol L<sup>-1</sup>), heated close to its boiling point (b.p.(oDCB) = 180 °C), was recorded. This spectrum proved to be practically identical to the one measured in DMSO at 90 °C (Figure 1 and Figure S6). This control experiment demonstrates that the observed differences result from a stronger aggregation in oDCB. Figure 1 shows isosbestic points, which underline the occurrence of an equilibrium between aggregated and isolated species in solution ( $\lambda_{\text{iso}} = 356$  nm in DMSO and  $\lambda_{\text{iso}} = 352$  nm in oDCB). At this stage, one should also note that the aggregation process leads to the appearance of a new well-defined absorption band centered at  $\lambda = 356$  nm in the case of oDCB. The appearance of such an absorption band has already been observed in the case of polyaromatic derivatives and was associated to the formation of J aggregates.<sup>[16]</sup>

The fluorescence spectroscopy measurements were first performed under the same experimental conditions as for UV/Vis studies and the results are in line (see Figure 2 and Figure S7) with a stronger proportion of aggregated pyrene in oDCB witnessed by a larger  $I_{\text{excimer}}/I_{\text{monomer}}$  ratio in this solvent. Importantly, one will also notice that the fluorescence intensities tend to globally increase upon decreasing the temperature, a behavior which is expected since luminescence quantum yields generally tend to decrease at high temperatures. Indeed, upon heating, the number of collisions between fluorophores and solvent molecules increases and this favors the non-radiative relaxation of the luminescent molecules.<sup>[17]</sup> Additionally, these figures display two types of non-structured emission bands centered on 466 and 492 nm, which correspond to static and dynamic excimer emissions, respectively.<sup>[8,18]</sup>

However, in light of the literature, one could have expected an excimer/monomer emission conversion upon changing the temperatures. Indeed, there are various examples of pyrene-based gelators, which show an increase of the monomer emission upon increasing the temperature, in other words, upon breaking the aggregates. We therefore carried out similar experiments at a lower concentration (*c*' = 10<sup>-5</sup> mol L<sup>-1</sup>) in order to promote the shifting of the equilibrium towards isolated

#### Abstract in Vietnamese:

Trong nghiên cứu này, chúng tôi giới thiệu về các trạng thái phổ bất thường của hai hợp chất huỳnh quang mới, có khả năng tạo gel và được cấu tạo từ các nhóm chức urê và pyrene. Kết quả chỉ ra rằng, phổ biến thiên của trạng thái kết tụ của các phân tử cung cấp một phương pháp then chốt để thăm dò cấu trúc siêu phân tử của vật liệu.

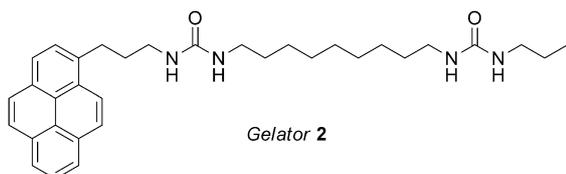


**Figure 2.** Evolutions of the emission spectra of **1** in oDCB upon lowering the temperature (left:  $c = 10^{-4}$  M; right:  $c = 10^{-5}$  M;  $\lambda_{\text{exc}} = 344$  nm).

molecules upon heating. While a similar behavior as for  $c = 10^{-4}$  mol L<sup>-1</sup> was observed in DMSO (Figures S7 and S8), the situation proved to be completely different in the case of oDCB (Figure 2 (right)). An excimer/monomer fluorescence conversion was indeed observed but, unexpectedly, the excimer emission was favored at high temperatures in this case, that is, when the molecules are supposed to disaggregate.

Two hypotheses may be proposed to account for such an unexpected observation: i) intermolecular forces occurring at low temperatures limit the formation of excimers, as reported by Kato and coworkers with a pyrene-oligopeptide conjugate<sup>[19]</sup> and ii) a molecular folding<sup>[12d]</sup> of the gelator is provoked by desolvation at high temperature.

On this ground, the synthesis of the analogous derivative **2** endowed with a single pyrene unit (Figure 3) appears as a relevant strategy to address this issue, since with fluorophore **2**, pyrene–pyrene interactions are only possible through intermolecular  $\pi$ – $\pi$  stacking. Dissymmetrical compound **2** was isolated in two steps starting from 3-pyrenylpropylisocyanate **3**. The latter was first reacted with an excess of

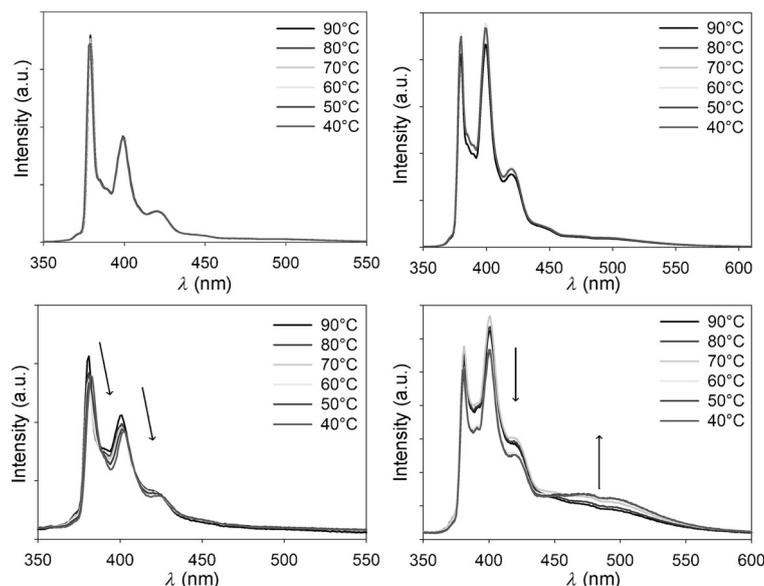


**Figure 3.** Molecular structure of compound **2**.

1,9-diaminononane (4 equivalents) in order to prepare the monourea intermediate **4** (54%) which afforded **2** by reaction with propyl isocyanate (23% yield, see the Supporting Information for details).

Compound **2**, which includes two urea functions, also displays gelling properties in chlorinated aromatic solvents (CB, oDCB, TCB). The fact that compounds **1** and **2** only form gels in chlorinated solvents shows that both gelators have similar gelation spheres in the Hansen space.<sup>[20]</sup> Once isolated and

characterized through classical techniques, spectroscopic measurements were performed on **2** at variable temperatures (Figure 4). In DMSO, no significant modification of the absorption (Figure S9) or emission spectra (Figure 4 and Figure S10) could be observed between 90 and 40 °C for the following concentrations:  $[2] = 10^{-5}$  mol L<sup>-1</sup>,  $10^{-4}$  mol L<sup>-1</sup>, and  $10^{-3}$  mol L<sup>-1</sup>. This suggests that intermolecular pyrene–pyrene interactions do not exist, either in the ground state or in the excited state. A different situation occurs with the samples prepared in oDCB, as illustrated by Figure 4 and Figure S10 and S11. Consid-

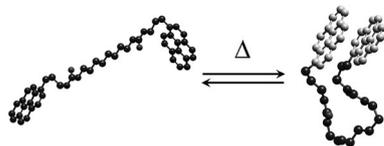


**Figure 4.** Evolution of the emission spectra of **2** in DMSO (top) and oDCB (bottom) upon decreasing the temperature (left:  $c = 10^{-5}$  mol L<sup>-1</sup>; right:  $c = 10^{-3}$  mol L<sup>-1</sup>;  $\lambda_{\text{exc}} = 344$  nm).

ering the  $10^{-5}$  M solution, the effect of the temperature on the absorption (Figure S10) and emission spectra is moderate; upon lowering the temperature, the former show a hyperchromic effect, while fluorescence spectra (Figure 4) present an enhanced quantum yield of emission, and emission bands which are slightly shifted towards lower energies. In any case, whatever the temperature, no excimer emission was detected in these diluted conditions. As a consequence, further studies were performed at higher concentrations ( $5 \times 10^{-5}$ ,  $10^{-4}$ , and  $10^{-3}$  mol L<sup>-1</sup>; Figure 4 and Figure S11) in order to increase the polymerization degree and observe the appearance of the typical excimer emission band.

Among these samples, the typical excimer emission was only detected in the most concentrated solution in oDCB and at room temperature. Upon cooling the sample from 90 °C to room temperature, this excimer emission band increases, which suggests that pyrene excimers are not generated at high temperatures, in other words, when aggregates tend to dissociate. This is in sharp contrast with what was observed in the case of the bispyrenyl compound **1**, which has a more intense excimer emission band at high temperatures. Altogether,

these assessments prompt us to hypothesize the formation of intramolecular excimers at high temperatures for fluorophore **1** and intermolecular excimers at low temperatures for the dissymmetric derivative **2**. Such a behavior is likely to result from a desolvation of the solute at high temperatures in the former, which provokes a molecular folding and favors the formation of pyrene dimer in the excited state (Figure 5).



**Figure 5.** Schematic representation of the conformational change experienced by compound **1** at high temperature.

## Conclusions

In summary, two pyrene derivatives, which belong to the bis-urea organogelator family, have been prepared and characterized through different spectroscopic techniques with a special attention on temperature versus concentration/solvent effects. We have first highlighted the peculiar behavior of the bispyrenyl compound **1** in *o*DCB. In order to gain insight into its unexpected spectroscopic properties, the analogous compound **2**, which only bears one pyrene unit, was prepared and investigated. The corresponding measurements show that this gelator does not display excimer emission at high temperatures. This confirms that intramolecular excimer formation is the most relevant mechanism to explain the more intense excimer emission observed upon heating for compound **1**. This result illustrates the potential of using a fluorophore (pyrene) as an internal probe to fine-tune the supramolecular organization within a gelator solution as a function of concentration and solvent nature, and therefore opens wide perspectives for the construction and comprehension of alternative organogels.

## Experimental Section

### Materials and Methods

All reagents were of commercial reagent grade and were used without further purification unless otherwise noted. Silica-gel chromatography was performed with SiO<sub>2</sub> obtained from Sigma-Aldrich Chemistry. NMR spectra were recorded at room temperature (unless otherwise stated) on a NMR Bruker Avance III 300 spectrometer or Bruker Avance DRX 500 spectrometer. MALDI-TOF MS spectra were recorded on a MALDI-TOF Bruker Biflex III instrument using a positive-ion mode. UV/Visible absorption spectra were recorded on a PerkinElmer Lambda19 spectrometer and fluorescence spectra were recorded on a Photon Technology International QuantaMaster 4 instrument.

### 3-Pyrenylpropylisocyanate (**3**)

To a solution of 1-pyrenebutyric acid (500 mg, 1.73 mmol) in anhydrous toluene (30 mL) were added triethylamine (0.25 mL, 1 equiv) and diphenylphosphoryl azide (0.37 mL, 1 equiv). After stirring for

2 h at room temperature, the reaction mixture was heated at 80 °C overnight. Then, the solid was purified by filtration over hyflo supercel (Petroleum ether (PE)/CH<sub>2</sub>Cl<sub>2</sub> = 75:25; TLC: PE/CH<sub>2</sub>Cl<sub>2</sub> = 25:75). The residue was dissolved in toluene and washed with a saturated NH<sub>4</sub>Cl solution (50 mL) and water (50 mL). After evaporation of toluene, compound **3** was obtained as a light yellow liquid (343 mg, 1.19 mmol, 69% yield). <sup>1</sup>H NMR (300 MHz, [D<sub>1</sub>]-Chloroform, TMS): δ = 8.26–8.11 (m, 5H, Ar-H); 8.04–7.98 (m, 3H, Ar-H); 7.86 (d, *J* = 7.8 Hz, 1H, Ar-H); 3.48–3.39 (m, 4H, Ar-CH<sub>2</sub>- and -CH<sub>2</sub>-NCO); 2.16 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). IR-ATR:  $\tilde{\nu}$  = 2911 (C–H), 2264 cm<sup>-1</sup> (NCO). MS (MALDI-TOF; dithranol) C<sub>20</sub>H<sub>15</sub>NO: 285.2 (*M*<sup>+</sup>).

### 1-Pyrenepropyl-3-[9-(3-pyrenepropylureido)nonyl]urea (**1**)

1,9-Diaminononane (94 mg, 0.6 mmol) was slowly added to a solution of 3-pyrenylpropylisocyanate **3** (343 mg, 1.2 mmol) in acetonitrile (50 mL). A gel-like precipitate was formed immediately. The reaction mixture was heated at 50 °C for 50 h. The product was collected by filtration, washed with dichloromethane, and dried with pentane. After drying under vacuum, a light yellow solid was obtained (**1**: 75% yield). M.p. = 229–231 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 120 °C, TMS): δ = 8.33 (dd, *J* = 7.7 Hz, *J*' = 1 Hz, 2H, Ar-H); 8.25–8.14 (m, 8H, Ar-H); 8.10–7.99 (m, 6H, Ar-H); 7.94 (d, *J* = 7.7 Hz, 2H, Ar-H); 5.67 (brs, 2H, NH<sub>3</sub>); 5.51 (brs, 2H, NH<sub>2</sub>); 3.35 (t, *J* = 7.6 Hz, 4H, Ar-CH<sub>2</sub>-); 3.19 (dt, *J* = *J*' = 6.6 Hz, 4H, NHCH<sub>2</sub>-); 3.01 (dt, *J* = *J*' = 6.6 Hz, 4H, NHCH<sub>2</sub>-); 1.96 (tt, *J* = *J*' = 7 Hz, 4H, Ar-CH<sub>2</sub>-CH<sub>2</sub>-); 1.4 (m, 4H, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); 1.28 ppm (m, 10H, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). IR-ATR: 3317 (N–H), 2930 (C–H), 1614 (C=O), 1570 cm<sup>-1</sup> (C=C). MS (MALDI-TOF; dithranol) (C<sub>49</sub>H<sub>52</sub>N<sub>4</sub>O<sub>2</sub> + Na)<sup>+</sup>: 751.8.

### Compound 4

A solution of 3-pyrenylpropylisocyanate **3** (725 mg, 2.54 mmol) in DMF (70 mL) was added dropwise with an addition funnel into a three-necked flask containing 1,9-diaminononane (1.608 g, 10.16 mmol, 4 equiv) in DMF (30 mL) at 80 °C. A white precipitate appeared and the reaction mixture was allowed to react at 80 °C overnight. Then, the white precipitate was filtered off and the filtrate was evaporated using a rotary evaporator. A yellow solid was obtained after cooling. The latter was washed with dichloromethane under sonication, then rinsed with EtOAc and pentane to afford the monoamine pyrene intermediate **4** as a white solid (613 mg, 54%). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 120 °C, TMS): δ = 8.34 (d, *J* = 7.8 Hz, 1H, Ar-H); 8.29–8.19 (m, 4H, Ar-H); 8.13 (m, 2H, Ar-H); 8.07 (dd, *J* = *J*' = 7.8 Hz, 1H, Ar-H); 7.96 (d, *J* = 7.8 Hz, 1H, Ar-H); 5.95 (t, *J* = 6 Hz, 1H, NH); 5.81 (t, *J* = 5.6 Hz, 1H, NH); 3.32 (t, *J* = 8 Hz, 2H, Ar-CH<sub>2</sub>-); 3.14 (dt, *J* = *J*' = 7 Hz, 2H, NH-CH<sub>2</sub>-); 2.98 (dt, *J* = *J*' = 8 Hz, 2H, NH-CH<sub>2</sub>-); 1.88 (tt, *J* = *J*' = 8 Hz, 2H, Ar-CH<sub>2</sub>-CH<sub>2</sub>-); 1.36 (m, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); 1.24 ppm (m, 12H, NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). MS (MALDI-TOF; dithranol) (C<sub>29</sub>H<sub>37</sub>N<sub>3</sub>O + H)<sup>+</sup>: 444.4.

### Compound 2

Propyl isocyanate (258 μL, 2.75 mmol, 2 equiv) was added to a solution of monoamine pyrene intermediate **4** (610 mg, 1.375 mmol) in DMF (50 mL). The clear brown solution was heated at 80 °C for 48 h. The resulting red brown solution was then cooled to room temperature, the precipitate was filtered, and the brown filtrate was evaporated under vacuum. Diethyl ether (200 mL) was added, and the corresponding brown precipitate was filtered, rinsed with diethyl ether, pentane, and finally dried under vacuum (165 mg, 23% yield). M.p. 108–110 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 120 °C,

TMS);  $\delta$  = 8.36 (d,  $J$  = 7.8 Hz, 1H, Ar-H); 8.27–8.16 (m, 4H, Ar-H); 8.10–7.94 (m, 4H, Ar-H); 5.66 (brs, 1H, NH); 5.50 (brs, 1H, NH); 5.44 (brs, 2H, NH), 3.36 (t,  $J$  = 6 Hz, 2H, Ar-CH<sub>2</sub>-); 3.19 (t,  $J$  = 6 Hz, 2H, NH-CH<sub>2</sub>-); 2.98 (m, 6H, NH-CH<sub>2</sub>-); 2.00 (m, 2H, Ar-CH<sub>2</sub>-CH<sub>2</sub>-); 1.45–1.20 (m, 16H); 0.85 ppm (t, 3H, -CH<sub>3</sub>). IR-ATR: 3314(N-H), 2926(C-H), 1616(C=O), 1572 cm<sup>-1</sup> (C=C). MS (MALDI-TOF; dithranol) (C<sub>33</sub>H<sub>44</sub>N<sub>4</sub>O<sub>2</sub> + Na)<sup>+</sup>: 561.5.

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**Keywords:** fluorescence · luminescence · organogels · pyrene · urea

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