Synthesis and photophysical properties of pyrene-functionalized nano-SiO₂ hybrids in solutions and doped-PMMA thin films

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Abstract

Luminescent pyrene-functionalized nano-SiO₂ (nano-SiO₂Pyr) hybrids were synthesized and characterized using thermogravimetry, infrared, UV-vis absorption and, X-ray photoelectron spectroscopy, as well as field emission transmission electron microscopy (FETEM). The organic substituents immobilized on the nano-SiO₂Pyr hybrids accounted for approximately 10% of the total weight. Polyethylene glycol 200 (PEG200) was found to be the most suitable solvent to suspend the nano-SiO₂Pyr hybrids compared to other commonly used organic solvents. FETEM images indicated an average SiO₂ nanoparticle diameter of approximately 12 nm and a 1- to 2-nm thick organic species functionalization layer. Several emission peaks were recorded at wavelengths of 380–580 nm and were designated as emissions arising from either the monomer or excimer of the pyrene substituents. Excimer formation was concentration and solvent polarity dependent, with higher concentrations and a stronger solvent polarity benefiting excimer formation. Further, nano-SiO₂Pyr hybrids were doped in poly(methyl methacrylate) (PMMA) thin films; fluorescence spectra indicated that the excimer could be formed almost exclusively from neighboring nano-SiO₂Pyr hybrids. Time-resolved fluorescence decays revealed that the emission lifetimes of nano-SiO₂Pyr monomers

and excimers were approximately 190 ns and 65–100 ns in the PEG200 solution, respectively, which was shortened to 0.45 ns to tens of ns in doped PMMA thin films, depending on the nano-hybrid concentration. Thus, the present study not only provides a method to prepare luminescent nano-materials but also a route to investigate excimer formation in solutions and thin films.

Keywords: Composite materials; luminescence; optical properties; thin films

1. Introduction

Pyrene (Pyr), one of the most used fluorophores, has two fluorescence emission ranges, 370–400 nm, corresponding to monomer emission, and 420–600 nm, corresponding to excimer emission [1-3]. Based on the Birks definition, the excimer is a homopolar excited dimeric complex formed due to the interaction between its first excited singlet state and unexcited molecules of the same species [4,5]. It has been revealed that formation of the Pyr excimer depends on the orientation and distance between two molecules, such that excimer emissions are generally observed in solutions with high Pyr concentrations where the diffusive encounter between the Pyr molecules easily occurs [6-8]. In Pyr derivatives, both the environment and chemical structure of the substituents bound onto the Pyr rings can largely influence their low lying excited states, luminescent emissions, and excimer formation [9,10]. Thus, the design and synthesis of novel Pyr-based compounds is an alternative route to investigate excimer formation and to control the emission wavelength and, thus, the color of products

1 with a potential application in the development of new emitters, organic light-emitting devices, and
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3 sensors [11-15].
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6 It has been previously elucidated that the formation mechanism of Pyr excimers differs
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8 considerably when Pyr derivatives are in the solid state or when Pyr substituents are anchored on
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10 solid surfaces in comparison to solutions due to the lack of organic species mobility [2]. Earlier
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12 studies have assessed excimer formation in Pyr crystals, glassy matrices, and Langmuir-Blodgett
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14 films [16-18], in which the Pyr molecules may exist in a dimeric structure, such that the photoexcited
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16 states yield a characteristic excimer emission [19]. Nieh et al. found that the preparation conditions,
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18 such as the evaporation rate, temperature, and solvent vapor pressure, of Pyr derivative polymer
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20 films have an influence on excimer emissions [20]. More recently, Melo et al. encapsulated
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22 1-pyrenesulfonate in a layered double hydroxide by cointercalation with 1-heptanesulfonate and
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24 found that the photophysical behavior of Pyr (monomer and excimer emissions) was largely
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26 dependent on the molar ratios of two components encapsulated within the layered inorganic
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28 materials [21].
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39 The present study reports on the immobilization of Pyr substituents on functionalized nano-SiO₂
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41 hybrids by a condensation reaction of 1-pyrenecarboxaldehyde (PyrCHO) with amino-functionalized
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43 SiO₂ nanoparticles prepared through a silane reaction of a commercially available nano-SiO₂ solution
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45 with 3-aminopropyltrimethoxysilane [22,23]. Recent advances in nanotechnology have led to
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47 nano-SiO₂ being widely used as a support to prepare novel materials with interesting optical and
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49 electrical properties, resulting in potential applications in the fields of optical switches, biological
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51 probes, and polarized light emitters, and others [24-26]. Surface modification of nano-SiO₂ particles
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53 with organic or inorganic species can lead to the development of various functional materials with
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1 applications in optical/electrical nano-devices, heterogeneous catalysts in industrial processes, and
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3 materials with increased mechanical properties [27,28]. The results presented herein reveal that the
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5 PyrCHO and Pyr-functionalized nano-SiO₂ (nano-SiO₂Pyr) hybrids release fluorescent emissions at
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7 approximately 550 and 480 nm, respectively, in the solid powders, attributed to the Pyr excimer
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9 emissions. When doped in poly(methyl methacrylate) (PMMA) thin films, fluorescent emissions
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11 appear mainly from 350 to 410 nm and are attributed to monomer emissions. When suspended in the
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13 solutions, several emission peaks between 370 and 550 nm are attributed to emissions from either the
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15 monomer or excimer of the nano-SiO₂Pyr hybrids. Further, compared with commonly used organic
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17 solvents, polyethylene glycol 200 (PEG200) is the most suitable solvent for nano-SiO₂Pyr hybrid
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19 suspension. Both steady state and time-resolved fluorescence spectra reveal that excimer formation is
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21 closely dependent on the nature of solvents, nano-hybrid concentrations in solutions, and the dopant
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23 concentration of PyrCHO and/or nano-SiO₂Pyr hybrids in PMMA thin films.
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36 **2. Experimental**

37 *2.1. Materials*

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39 Ludox AS40, obtained from Sigma-Aldrich, containing 40 wt % SiO₂ and with an average
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41 particle size of 12 nm, was used as the starting silica material. 3-Aminopropyltrimethoxysilane was
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43 purchased from J&K Scientific LTD. PyrCHO and PMMA were obtained from Alfa Aesar[®].
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45 PEG200 was purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as
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47 received without further purification.
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58 *2.2. Synthesis of nano-SiO₂Pyr hybrids*

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1 Ludox silica nanoparticle solution (10 g) was first suspended in a mixed methanol and DMF
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3 (100 mL) solvent and stirred with 0.6 g 3-aminopropyltrimethoxysilane at 60°C for 2 days [22]. The
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5 suspension was then isolated by centrifugation at 4,000 rpm. The white powders of
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8 3-aminopropylsilane functionalized nano-SiO₂ (nano-SiO₂NH₂, Fig. 1) were well washed with plenty
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10 of DMF and methanol, and finally dried in a vacuum. Elemental analysis: C, 4.72%, H, 3.42%, N,
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12 1.38%.
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20 Figure 1
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25 The nano-SiO₂Pyr hybrids were prepared by refluxing mixtures of nano-SiO₂NH₂ and excess
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27 PyrCHO in methanol overnight [23]. The precipitate was isolated by centrifugation at 4,000 rpm.
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29 The pale yellow powders of nano-SiO₂Pyr were well washed with plenty of methanol and dried in a
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31 vacuum. Elemental analysis: C, 6.62%, H, 3.50%, N, 0.83%.
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39 2.3. Preparation of pyrCHO and nano-SiO₂Pyr hybrid-doped PMMA thin films 40 41

42 The PyrCHO- and nano-SiO₂Pyr-doped PMMA thin films were prepared by dissolving PyrCHO
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44 or nano-SiO₂Pyr and PMMA in a mixed methanol and chloroform solvent. Transparent thin films of
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46 the mixtures were prepared by a sol-gel process under vacuum at room temperature [29,30]. To
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48 reveal the effects of PyrCHO and/or nano-SiO₂Pyr doping in PMMA films on excimer formation,
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50 thin films containing PyrCHO or nano-SiO₂Pyr hybrid mixtures with PMMA at different weight
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52 ratios were also prepared.
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2.4. Characterization

Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TGA7, under a constant-flow air atmosphere, from room temperature to 800°C at a heating rate of 10°C/min. Elemental analysis was performed on a VARIO EL3 elemental analyzer. X-ray photoelectron spectra (XPS) were recorded using a VGESCALAB MKII multifunction spectrometer, with non-monochromatized Mg-K α X-rays as the excitation source. The system was carefully calibrated by Fermi-edge of nickel, Au 4f_{2/7}, and Cu 2p_{2/3} binding energy. A pass energy of 70 eV and a step size of 1 eV were chosen when taking spectra. In the analysis chamber, pressures of 1×10^{-7} to 2×10^{-7} Pa were routinely maintained. The binding energies obtained in the XPS analysis were corrected by referencing the C1s peak to 284.60 eV.

UV-Vis absorption spectra were measured with the use of a Shimadzu UV-2550 UV-vis spectrophotometer. Fourier transform infrared spectra (FTIR) were measured by using a Nicolet NEXUS 470 spectrometer, operating at a resolution of 0.5 cm⁻¹ at 25°C. Field emission transmission electron microscopy (FETEM) images of the SiO₂ nanoparticles before and after functionalization were recorded using a JEM-2100F field emission electron microscope.

Fluorescence spectra were recorded using a Shimadzu RF-5300PC spectrophotometer with an excitation wavelength of 360 nm for the nano-SiO₂Pyr hybrids in solid powder form and of 330 nm in the solutions. Lifetimes were estimated from the decay of the main transitions with the use of the Edinburgh Instruments software package. The collected emission wavelength was set at 386, 420 and 490 nm. The fluorescence decay curves followed with two or three exponential decay kinetics, as displayed in the logarithmic plots of

$$\frac{I_t}{I_0} = A + B_1 e^{-\left(\frac{t}{\tau_1}\right)} + B_2 e^{-\left(\frac{t}{\tau_2}\right)} + B_3 e^{-\left(\frac{t}{\tau_3}\right)} \quad (1)$$

where I_0 and I_t are the fluorescence intensity at times zero and t , respectively, B_i is the pre-exponential factor, and τ is the experimental lifetime of the excited state of the PyrCHO or nano-SiO₂Pyr hybrids. The fractional contribution (C_i) of each species was calculated according to the equation of

$$C_i(\%) = \frac{B_i \tau_i}{\sum_{i=1}^n B_i \tau_i} \quad (2)$$

where n is the number of exponential terms, B_i is the contribution of each exponential term at $t = 0$, and τ_i is the associated decay times [21].

3. Results and discussion

3.1. TG, elemental analysis, XPS and FTIR characterization

Thermal stability of the present nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids was investigated by measuring their TG curves from room temperature to 700°C. Both curves revealed a mass decrease below 150°C (about 2–4% in weight, Fig. S1), ascribed to the evaporation of physically adsorbed water. A subsequent fast mass decrease was observed in the temperature range 250–600°C, attributed to decomposition of the covalently attached organic species, namely, the aminopropyl and Pyr substituents. Such a mass decrease could also arise due to the condensation reaction $2\text{Si-OH} = \text{Si-O-Si} + \text{H}_2\text{O}$ on the nanoparticle surfaces, resulting in water evaporation, although the relative amount was quite low in comparison with that of the organic species [23]. In this temperature range, the total mass decrease observed for the nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids was about 7% and 11%, respectively. The residuals observed at above 600°C corresponded to 86–88% of the total

weight and were attributed to the formation of SiO₂ powders following decomposition of organic species and loss of water [23,31].

Elemental composition of the nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids was investigated by both traditional analytic method and surface XPS technique. Based on the elemental analysis results, it can be deduced that the organic species attached onto the nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids accounted for 9.5% and 11.9 % of the total weight, respectively. This data is in agreement with the TG analysis results indicated above. A comparison of the relative molar fraction of carbon in the nano-SiO₂NH₂ hybrid with that in the nano-SiO₂Pyr hybrid suggested that not all amino substituents had reacted with PyrCHO, as further confirmed by FTIR features and described below. This may be ascribed to a steric effect caused by the larger size of Pyr substituents compared to that of alkyl chains (C₃H₆NH₂).

The XPS spectra of the nano-hybrids revealed four peaks at the binding energy of 102.8–103.8, 285.4, 400.4–401.4, and 533.6–534.2 eV, which could be assigned to Si(2p), C(1s), N(1s), and O(1s), respectively. Si and O belonged to the nano-SiO₂ core, while C and N to the modified organic layer. The high resolution spectra of C and N elements of the nano-SiO₂Pyr hybrids were shown in Fig. 2. It can be seen that, for the C element, besides the main peak at the binding energy of 284.6 eV corresponding to the C atoms from the C-C and C=C bonds, there existed another small one at about 288 eV corresponding to the C atoms from the C-N and C=N bonds [32,33]. Further, compared with the spectrum of the nano-SiO₂NH₂ hybrids (Fig. S2), the binding energy of N element slightly shifted from 400.5 to 401.0 eV, which may be also ascribed to the C=N formation.

The FTIR spectra of nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids showed several typical vibrations between the wavenumbers of 4000 and 800 cm⁻¹ (Fig. S3). Firstly, the broad band centered at 3440

cm⁻¹ was attributed to adsorbed water molecules and the amino groups of the organic species anchored onto the nanoparticle surfaces [31]. Secondly, two sharp peaks recorded at approximately 2940 and 2890 cm⁻¹ were assigned to the aliphatic -CH₂ stretching vibration bands and confirmed that the 3-aminopropyl substituent had anchored onto the silica core surface [23]. Thirdly, a sharp peak recorded at approximately 2714 cm⁻¹ in the PyrCHO spectra disappeared in the nano-SiO₂Pyr hybrid spectra due to formation of the C=N bond after the condensation reaction [32]. Fourthly, several small bands were recorded between 1530 and 1380 cm⁻¹ in the nano-SiO₂Pyr hybrid spectra, attributed to the C=N, C-C, and C=C vibrations of Pyr rings; these small bands were not present in the nano-SiO₂NH₂ spectra. Finally, the vibration bands recorded between 1095 and 805 cm⁻¹ were ascribed to the nanoparticle Si-O-Si asymmetric and Si-O symmetric stretching bands [32]. Based on the TG, elemental and XPS analysis as well as the FTIR spectra, we can conclude the formation of nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids designed in Fig. 1.

Figure 3

Fig. 3 shows the FETEM image of SiO₂ nanoparticles before and after functionalization, indicating many cyclic particles with an average diameter of approximately 12 nm, in agreement with the data provided by the manufacturer. A close inspection of the particle images indicated some irregular species or thin films on the nanoparticle surfaces after functionalization (marked in Fig. 3B), attributed to the organic Pyr substituents being covalently attached on the nano-SiO₂ surface. This feature has been previously observed in studies where a detailed characterization of different organic-modified carbon nanotubes has been performed [33,34]. In the present study, given the much

1 thinner organic layer relative to the SiO₂ nanoparticle size compared to that of carbon nanotubes, the
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3 FETEM image of the organic layer was not as clear as that observed on carbon nanotubes;
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6 nevertheless, it still represents evidence for the formation of nano-SiO₂Pyr hybrids.
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10 11 3.2. Photophysical properties and absorbance 12 13

14 Absorption features for the nano-SiO₂Pyr hybrids were investigated in various solutions. The
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16 main absorption bands appeared in the wavelength range 200–420 nm, with the relative intensity
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18 slightly related to the nature of the solvents. Compared with other commonly used organic solvents,
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20 PEG200 was the best solvent to dissolve or suspend the nano-SiO₂Pyr hybrids synthesized herein.
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22 Fig. 4A shows the absorption spectra for the nano-SiO₂Pyr hybrids in the PEG200 solution at a
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24 concentration range of 0.05–1.0 mg/mL. Similar to previous results [2,3,35], three main absorption
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26 bands were observed at approximately 234–245, 288, and 362–394 nm, with the relative absorption
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28 intensity almost linearly increasing with the hybrid concentrations, suggesting that nano-SiO₂Pyr
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30 hybrids can be easily suspended in PEG200. The latter two broad absorption bands were typical
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32 absorption bands of the Pyr substituents and were assigned to the transitions S₀ → S₂ and S₀ → S₁
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53 Fig. 4B shows the absorption spectra for the nano-SiO₂Pyr hybrids in methanol, acetonitrile,
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55 DMF, chloroform, and carbon tetrachloride at a concentration of 0.2 mg/mL. These curves also
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57 revealed two broad bands at 288 and 362–398 nm, corresponding to the transitions S₀ → S₂ and S₀
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→ S₁ of Pyr substituents, respectively. A slight but non-significant difference in the relative intensity between each peak was observed and was attributed to symmetry distortion of the Pyr structure induced by the dispersion or van der Waals forces in different solvents, as reported previously [36].

3.3. Fluorescence spectra in solutions

Fig. 5A shows the steady-state fluorescence spectra for the nano-SiO₂Pyr hybrids suspended in PEG200 solutions at a concentration range of 0.05–4.0 mg/mL. The excited wavelength was 330 nm that was determined from the excited spectrum (Fig. S4). The fluorescent emission curves revealed several sharp and broad emissions at 360–600 nm, with their relative intensity closely dependent on the nano-SiO₂Pyr concentration. At lower concentrations (below 0.2 mg/mL), the fluorescence emissions appeared mainly at 380 and 400 nm, and were assigned to the monomer emission of Pyr substituents [2,3]. When the concentration increased to 0.5 mg/mL, besides the emissions at 380 and 400 nm, a further peak at 420 nm was detected. Based on previous studies [2,3], this peak was attributed to the emission from the excimer of Pyr substituents. The results suggest that increasing nano-hybrid concentrations can result in the formation of excimers under radiation. Indeed, when the nano-SiO₂Pyr hybrid concentration was increased to 1.0 mg/mL, the relative intensity of the band at 420 nm increased considerably, along with a very broad emission band at 450–600 nm. Further increasing the nano-SiO₂Pyr concentration to 2.0 and 4.0 mg/mL resulted in very weak monomer emissions (370–400 nm) with an increase in the relative intensity of excimer emissions. This phenomenon may be attributed to the diffusive encounter between the nano-SiO₂Pyr hybrids easily occurring in solutions at higher concentrations and leading to the formation of excimers, similarly to simple Pyr compounds in solution.

Figure 5

The relative peak intensity of monomer (I_{mon} at 386 nm) and excimer (I_{exc} at 420 nm) emissions was calculated. Fig. 5B shows a plot of the ratios of $I_{\text{exc}}/I_{\text{mon}}$ against the nano-hybrid concentrations, revealing an “exponential” increase in the relative intensity, that is, the ratio of $I_{\text{exc}}/I_{\text{mon}}$ was also concentration dependent. Possible reason may be attributed to the fact that increasing concentration of the nano-SiO₂Pyr hybrids should largely enhance the possibility of the diffusion encounter of the nanoparticles. Since the monomer emissions were very low when the nano-hybrid concentration reached 4.0 mg/mL, the ratio of $I_{\text{exc}}/I_{\text{mon}}$ increased to nearly 100 (data not shown). Further, the total fluorescence emission efficiency became increasingly weaker with increasing nano-hybrid concentration, which may be attributed to a concentration quenching as often observed in solutions of luminescent macrocyclic compounds [37]. It may also be attributed to the formation of various aggregated species at higher concentrations as observed in perylene bisimide solutions [38,39].

Figure 6

Excimer formation was also dependent on the organic solvents. Fig. 6 shows fluorescence spectra for the nano-SiO₂Pyr hybrids in several organic solvents, excited at 330 nm and at a concentration of 0.2 mg/mL. Although no significant difference was recorded for the absorption spectra in Fig. 4B (transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$), the emission behavior was largely dependent on the nature of the solvents. As shown in Fig. 6, the fluorescence spectrum was mainly composed of

monomer emissions at 390 and 410 nm for the nano-hybrids in a CCl₄ solution, while those in CH₃OH, CH₃CN, and CHCl₃ solutions showed emissions at 420–500 nm. Finally, the fluorescence spectrum showed both monomer and excimer emissions in DMF solutions.

Previous work has shown that solvent polarity affects the relative intensity even when the emissions arise from the monomer [20]. In other words, the solvent polarity around the pyrene ring may lead to a stronger emission intensity at 378 nm relative to that at 398 nm in a more polar solvent environment. Compared with previous data, the monomer emission was slightly red shifted, possibly due to the Pyr substituents being anchored on the nanoparticle surface; this is in agreement with luminescent species in the condensed state and organic thin films [40,41]. Further, since the polarity of DMF is higher than that of CCl₄, stronger emissions from a shorter wavelength (390 nm) were recorded. On the other hand, Melo et al. suggested that the dielectric constant of the solvents may also have an effect on the emissions from excited Pyr derivatives [21]. Herein, it was observed that, for the nano-SiO₂Pyr hybrids, the solvent environment could not only influence the relative intensities of each monomer emission (ratio of I₃₇₈/I₃₉₈) but also the emissions from the excimer. More complicated emission bands were recorded compared with those of simple Pyr molecules in organic solvents, probably due to the fact that Pyr emissions were not only affected by the solvent properties (polarity, dielectric constant, interactions with Pyr substituents) but also by the distribution of the Pyr substituents on the surface of SiO₂ nanoparticles.

3.4. Fluorescence spectra in solids and doped-PMMA films

To further evaluate the effect of environment and Pyr distribution on emission behaviors and excimer formation, the fluorescence spectra for the nano-SiO₂Pyr hybrids in the solid powders and

1 doped PMMA thin films were investigated. Environmental differences for the Pyr species in these
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3 two systems involve nanoparticle separation in PMMA thin films and a close packed arrangement in
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5 the solid form. In the former case, excimer formation between two nano-hybrids may be avoided by
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7 adjusting the relative fractions of the hybrids in the PMMA thin films, while in the latter, excimer
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9 formation between two nano-hybrids is expected to be much easier, as in pyrene solids [19].
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14 Fig. 7A shows the fluorescence emission spectra of the nano-SiO₂Pyr hybrids and PyrCHO (as a
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16 control experiment) in solid powder form and PMMA thin films. Based on the weight, surface area
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18 of the thin films and density of PMMA, the thickness of the PMMA films prepared in the present
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20 work was estimated to be about 100 to 300 μm. During experiments, we found that, when the
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22 relative content of the nano-SiO₂Pyr hybrids in the PMMA thin films was below 2%, transparent
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24 films were obtained, which had almost no influence on the fluorescent emission of the nano-hybrids.
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26 However, higher nano-hybrid contents could make the films become opaque, resulting in a difficulty
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28 to measure the absorption and emission spectra. As shown in Fig. 7A, the PyrCHO solid powder
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30 showed a broad emission band centered at approximately 550 nm (line a), indicating that emissions
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32 mainly arose from the excimer, as indicated in the previous report [19], which could be attributed to
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34 a closely packed of the PyrCHO molecules in the solid powders. The nano-SiO₂Pyr hybrid powders
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36 showed emissions from both the monomers and excimers, with the emission bands appearing at
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38 approximately 396 nm and 470 nm, respectively (Fig. 7A, line b). This indicates the inability of
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40 some Pyr substituents to form excimers due to the increased distance between two Pyr units
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42 following anchoring on the nano-SiO₂ particle surface, resulting in the Pyr substituents unable to be
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44 as closely packed arrangement as that in the PyrCHO powders. A higher relative emission intensity
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46 was recorded for the excimers at 470 nm than that for the monomer at 396 nm, which may suggest
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1 that, although the Pyr substituents were anchored on the surface of the nano-SiO₂Pyr hybrids,
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3 excimers were still easily formed under radiation.
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6 Finally, when PMMA thin films were doped with nano-SiO₂Pyr hybrids at a ratio of 100:1
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8 (w/w), the emission spectrum revealed bands between 370 and 420 nm, along with a very weak band
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10 at approximately 470 nm (Fig. 7A, line c). Since the nano-hybrids were well separated in the PMMA
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12 films, it is likely that excimer was difficult to form between two separated nano-hybrids and
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14 therefore only those Pyr substituents within the same nano-particle could form excimers. However,
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16 because the Pyr substituents were covalently anchored on the nanoSiO₂ surface, they were difficult
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18 to encounter each other enough to form excimers, resulting in a very weak emission peak at 470 nm.
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20 Thus, a comparison of the emission features of nano-SiO₂Pyr hybrid powders (line b) with those of
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22 doped PMMA films (line c) suggests that, in the nano-SiO₂Pyr hybrid powders (line b), the Pyr
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24 excimer was formed mainly from two neighboring nano-hybrid particles with very small
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26 contributions from within the same particle.
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45 Figure 7

46 To provide more information regarding excimer formation within the nano-hybrids, a series of
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48 doped PMMA films with PyrCHO as well as mixtures of PyrCHO and nano-SiO₂Pyr hybrids were
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50 prepared and their fluorescence properties were evaluated. The emission spectra of these doped
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52 PMMA thin films are shown in Fig. 7B. Fluorescence spectra included both monomer and excimer
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54 emissions when the PyrCHO dopant content in the PMMA films was below 1% (Fig. 7B, a,b) and
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56 mostly excimer emissions when the content increased to 2% (Fig. 7B, c). Moreover, when
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1 nano-SiO₂Pyr hybrids were added to the 1% PyrCHO PMMA films, the relative intensities of the
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3 excimer emissions increased with increasing nano-hybrid concentration (Fig. 7B, d,e). These features
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5 can be attributed to the facilitated encounter and excimer formation between the luminescent species
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7 of Pyr molecules or nano-hybrids at higher concentrations, despite being encapsulated in the PMMA
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9 films.
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17 Figure 8
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22 Based on the emission features in Fig. 7, we summarized the possibility for the Pyr excimer
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24 formation in the solid powders, nano-hybrids and PMMA-doped thin films. As shown in Fig. 8, the
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26 Pyr excimer was facilely formed in the solid powders of the nano-SiO₂Pyr hybrids (A), but hardly
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28 done in the doped PMMA films due to the steric hindrance by the polymeric backbone (B).
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30 However, when the PyrCHO molecules were mixed with the nano-SiO₂Pyr hybrids in the PMMA
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32 films, excimer could be formed (C), which may be attributed to the fact that these small molecules
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34 may be easily adsorbed on the surface of the nano-SiO₂Pyr hybrids due to the molecular interactions
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36 between the organic species.
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47 3.5. Time-resolved fluorescence spectra 48 49

50 Since the nano-SiO₂Pyr hybrid solutions were the most stable in PEG200 solutions, the
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52 fluorescence decays of nano-SiO₂Pyr hybrids were investigated in PEG200 solutions as well as in
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54 doped PMMA thin films. Similar decay curves were obtained for all cases, so as an example, Fig. 9
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56 shows typical time-resolved fluorescence decay curves for the nano-SiO₂Pyr hybrids in the 0.5
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1 mg/mL PEG200 solution collected at 400, 420, and 490 nm (excitation at 330 nm). As control
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3 experiments, the nano-SiO₂Pyr hybrids and PyrCHO in doped PMMA films with various
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5 concentrations were also measured with excitation at 340 nm. These decay curves were fitted with a
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7 biexponential or, in some cases, triexponential equation. Table 1 summarizes the emission lifetime at
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9 each collected wavelength, together with the fractional contribution (C_i) of each species as given by
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11 equation [2.21].
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20 Figure 9

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25 Data in Table 1 indicates that two or three lifetimes were observed in each case, which may be
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27 ascribed to the existence of more than one luminescent species. These species may be a monomer
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29 and an excimer, or aggregates as reported by Melo et al. [21]. The monomer emission lifetime was
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31 approximately 100–200 ns for the nano-SiO₂Pyr hybrids in the PEG200 solution, which was much
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33 longer than that in the doped PMMA films (about 1 ns). This may be attributed to the encapsulation
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35 of Pyr substituents leading to the easier transfer of excited energy to the surrounding closely packed
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37 organic molecules in the condensed thin films. When the collected wavelength was set at about 386
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39 or 420 nm, the emission lifetime mainly corresponded to the contribution of the monomer, in most
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41 cases over 80%, except for the nano-SiO₂Pyr-doped PMMA thin films. When the collected
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43 wavelength was set at 470–500 nm, the main contribution corresponded to the excimer emissions.
44
45 The fractional contribution of excimers was larger in the PEG200 solutions at higher nano-hybrid
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47 concentrations and in the doped-PMMA thin film.
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Table 1

Further, a concentration effect was observed with regards to the emission lifetime – the higher the concentration, the shorter the emission lifetime – probably due to the fact that the excited Pyr species are more likely to form excimers at higher concentrations, resulting in a greater efficiency to deactivate and dissipate the excited energy. This is in agreement with the results observed in steady-state fluorescence spectra discussed above (Fig. 6). Similar phenomena were also observed in the PyrCHO-doped PMMA thin films.

Finally, three lifetimes were calculated for the 2% PyrCHO-doped PMMA thin films when the collected wavelength was set at 490 nm, indicating that several types of luminescent PyrCHO species were present – monomers, dimers, and their mixtures or aggregates in thin films [21]. Similar results were obtained from the PMMA films doped with PyrCHO and nano-SiO₂Pyr hybrid mixtures. The above data suggests that, in PMMA thin films, the luminescent Pyr species exist in several microenvironments – the monomer and excimer of PyrCHO or nano-SiO₂Pyr hybrids, PyrCHO-nano-SiO₂Pyr aggregates, and possibly nano-SiO₂Pyr-nano-SiO₂Pyr aggregates.

4. Conclusion

The results presented herein demonstrate the preparation and photophysical properties of Pyr-functionalized nano-SiO₂Pyr hybrids in solutions, solid powders, and doped PMMA thin films. The steady-state and time-resolved fluorescence spectra revealed that the immobilized Pyr substituents could form monomers, excimers, or aggregates depending on their microenvironment (solvent polarity and concentration in solutions and PMMA films). Since Pyr substituents were

covalently anchored on the nano-SiO₂ nanoparticle surfaces, their excimers were more likely formed between neighboring nano-SiO₂Pyr hybrids. The present study provides a method for the further investigation of exciton (monomer, excimer, or aggregate) behavior in nanoscale materials.

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Figure and Table legends

Fig. 1. Schematic drawing for the preparation of nano-SiO₂NH₂ and nano-SiO₂Pyr hybrids.

Fig. 2. High resolution XPS spectra of nano-SiO₂Pyr hybrids.

Fig. 3. FETEM images of (A) SiO₂ nanoparticles before functionalization and (B) nano-SiO₂Pyr hybrids.

Fig. 4. (A) Absorption spectra for nano-SiO₂Pyr in PEG200 solutions at concentrations from 0.05 to 1.0 mg/mL. (B) Absorption spectra for nano-SiO₂Pyr hybrids in methanol, acetonitrile, DMF, chloroform, and carbon tetrachloride solutions.

Fig. 5. (A) Steady-state fluorescence spectra for nano-SiO₂Pyr hybrids suspended in PEG200 solutions at concentrations from 0.05 to 4.0 mg/mL. (B) A plot for the ratios of $I_{\text{exc}}/I_{\text{mon}}$ to the concentrations of nano-SiO₂Pyr hybrids.

Fig. 6. Steady-state fluorescence spectra for nano-SiO₂Pyr hybrids in methanol, acetonitrile, DMF, chloroform, and carbon tetrachloride solutions excited at 330 nm.

Fig. 7. (A) Steady-state fluorescence emission spectra for (a) PyrCHO and (b) nano-SiO₂Pyr hybrids in solid powders and (c) nano-SiO₂Pyr hybrid-doped PMMA thin film in a ratio of 1:100 (w/w). (B) PyrCHO and/or nano-SiO₂Pyr hybrid-doped PMMA thin films; (a) 0.5% PyrCHO-PMMA, (b) 1% PyrCHO-PMMA, (c) 2% PyrCHO-PMMA, (d) 1% PyrCHO 5 mg nano-SiO₂Pyr-PMMA, and (e) 1% PyrCHO 9 mg nano-SiO₂Pyr-PMMA.

Fig. 8. Possibility for the Pyr excimer formation in the solid powders and PMMA-doped thin films. (A) Solid powders of nano-SiO₂Pyr hybrids, (B) PMMA-doped thin films of nano-SiO₂Pyr hybrids, (C) PMMA-doped thin films of nano-SiO₂Pyr hybrids and PyrCHO mixture.

Fig. 9. Time-resolved fluorescence decay curves for nano-SiO₂Pyr hybrids in the PEG200 solution collected at (a) 386, (b) 420, and (c) 490 nm, respectively.

Table 1. Fluorescence decay lifetime (ns) collected at various emission wavelengths together with the fractional contributions (%) from each luminescent species.

Synthesis and photophysical properties of pyrene-functionalized nano-SiO₂ hybrids in solutions and doped-PMMA thin films

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Table 1

Sample	Emission lifetime collected at different emission wavelength (ns)		
	386	420	490
nanoSiO ₂ Pyr in PEG (0.05 mg/mL)	186.6 (96.2%), 12.0 (3.8%) *	182.6 (92.6%), 7.3 (7.4%)	101.0 (37.0%), 3.8 (63.0%)
nanoSiO ₂ Pyr in PEG (1.0 mg/mL)	178.6 (94.3%), 10.5 (5.7%) *	168.7 (87.5%), 5.1 (12.5%)	66.7 (30.9%), 3.6 (69.1%)
nanoSiO ₂ Pyr-PMMA film	2.7 (35.6%), 13.8 (64.3%)	3.0 (51.3%), 13.2 (48.7%)	1.7 (64.6%), 7.8 (35.4%)
0.5% PyrCHO-PMMA film	1.2 (74.8%), 12.7 (25.2%)	1.2 (84.5%), 9.9 (17.5%)	1.2 (72.6%), 12.3 (27.4%)
1% PyrCHO-PMMA film	0.52 (90.0%), 6.5 (10%)	0.69 (90.7%), 6.0 (9.3%)	0.61 (60.4%), 10.6 (39.6%)
2% PyrCHO-PMMA film	0.45 (94.9%), 6.3 (5.1%)	0.60 (87.3%), 5.7 (12.7%)	1.0 (27.3%), 6.7 (23.3%), 25.1 (48.4%)
1% PyrCHO-5 mg nanoSiO ₂ Pyr-PMMA film	0.50 (90.7%), 4.7 (9.3%)	0.61 (88.3%), 4.8 (11.7%)	0.68 (22.0%), 4.8 (26.7%), 21.8 (51.3%)
1% PyrCHO-9 mg nanoSiO ₂ Pyr-PMMA film	0.56 (90.5%), 5.4 (9.5%)	0.52 (80.2%), 4.3 (19.8%)	0.86 (19.3%), 5.3 (25.8%), 23.7 (54.9%)

* collected at 398 nm

Synthesis and photophysical properties of pyrene-functionalized nano-SiO₂ hybrids in solutions and doped-PMMA thin films

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Figure 1

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