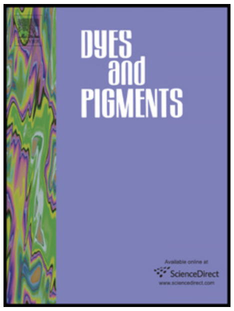

New organic-inorganic hybrid materials based on perylene diimide – polyhedral oligomeric silsesquioxane dyes with reduced quenching of the emission in the solid state

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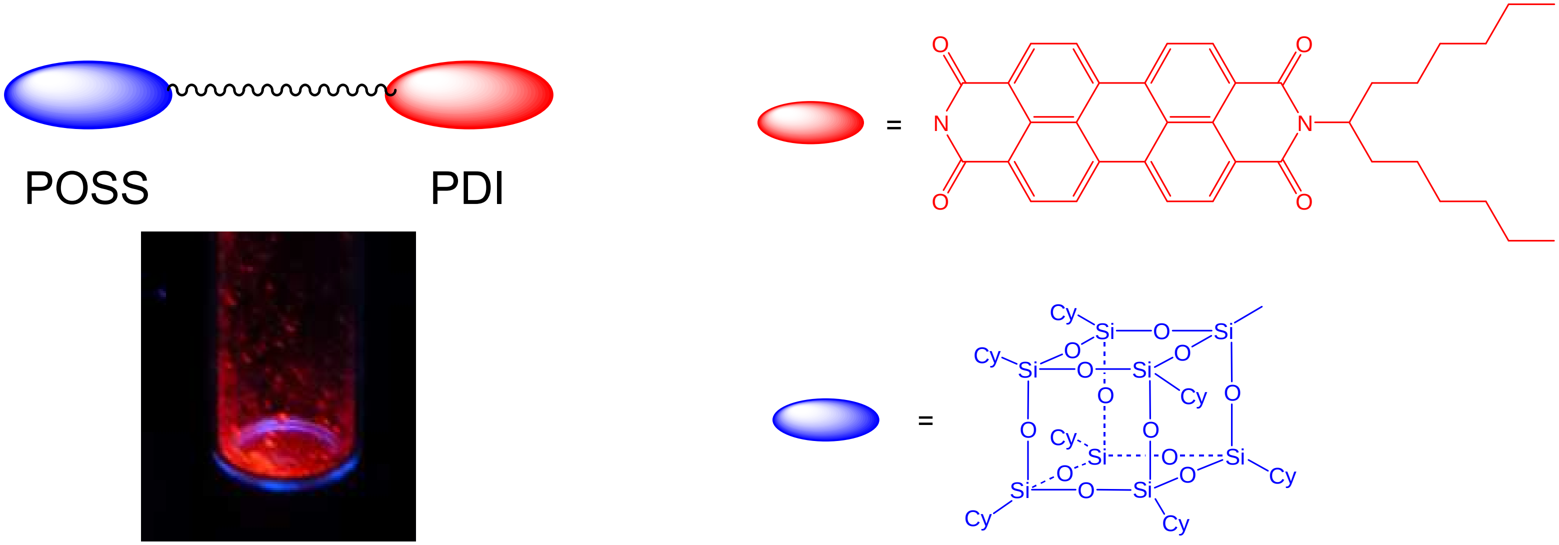
POSS
PDI
=
=

·) New soluble perylenes linked to polyhedral oligomeric silsesquioxanes cages

·) Hybrid perylene- silsesquioxane dyes show reduced aggregation caused quenching

·) Hybrid perylene- silsesquioxane dyes show enhanced red emission in the solid state

·) Bulky silsesquioxanes reduce aggregation caused quenching phenomena in perylene dyes

New organic-inorganic hybrid materials based on perylene diimide – polyhedral oligomeric silsesquioxane dyes with reduced quenching of the emission in the solid state

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Abstract.

Solid state luminescent materials are the subject of ever growing interest both from a scientific and a technological point of view because high-tech applications of light emitting materials very often require their use in the condensed phase. Aggregation caused quenching processes however represent an obstacle to the development of most luminogens in the condensed phase. This is why particularly fascinating are those materials showing high emission intensity in the solid state. Aggregation caused quenching is particularly detrimental for π–extended polycyclic aromatic hydrocarbons, for example perylene tetracarboxylic acid diimides which are characterized by a near-unity fluorescence quantum yield in solution but are far less emissive in the solid state.

Here we report on the easy preparation and on the optical investigation of perylene tetracarboxylic acid diimide derivatives linked to the inorganic cage of polyhedral oligomeric silsesquioxanes. These new hybrid perylene diimide - polyhedral oligomeric silsesquioxane dyes show in solution the typical absorption and emission features of the perylene diimide fragment, with a quantum efficiency close to unity. Moreover, in the solid state (both as spin-coated films and powders) the electronic absorption spectra indicate a reduced fluorophore aggregation and significant quantum yield efficiencies induced by the positive effect of the polyhedral oligomeric silsesquioxane cage.

Keywords: Perylene Tetracarboxylic Acid Diimide; Polyhedral Oligomeric Silsesquioxanes; Photoluminescence; Aggregation Caused Quenching.

1. Introduction.

In recent years extensive efforts have been spent on the discovery and development of efficient solid-state emissive organic materials to be applied in organic optoelectronic devices, such as organic light-emitting diodes, organic field-effect transistors, solid-state lasers and fluorescent sensors. However, most organic molecular chromophores are non-luminescent in the solid state, even if they are highly emissive in solution, due to the quenching of the emission caused by intermolecular interactions such as excimer formation and energy transfer in the condensed phase. In particular this phenomenon is quite detrimental for red-light emitting chromophores which usually consist of π–extended polycyclic aromatic hydrocarbons, prone to aggregation particularly in the condensed phase by π–π stacking [1]. Such interactions are frequently encountered in perylene tetracarboxylic acid diimides (PDI)-based materials and are usually associated to H-type excimeric dimers responsible of aggregation-caused quenching (ACQ) phenomena [2-6]. PDI, an important class of pigments, have been recently investigated as organic luminogens due to their outstanding properties such as near-unity fluorescence quantum yields in solution, high chemical and photochemical stabilities, and strong electron-accepting character [3, 7]. All these properties qualified PDIs for a wide range of optoelectronic applications such as in organic field-effect transistors (OFETs) [8-15], fluorescent solar collectors [16], electrophotographic devices [17], dye lasers [18, 19], organic photovoltaic cells (OPVs) [14, 15, 20-24], and optical power limiters [25]. Moreover PDIs are excellent chromophores for relevant photophysical processes such as energy and electron transfer [26-32]. However PDIs are characterized by significant π–π stacking and consequently intrinsic low solubility. Practical applications were made possible through the development of soluble derivatives; one successful approach has been developed by Langhals and co-workers by introducing long secondary alkyl chains ("swallow tail" substituents), that offer an excellent compromise between preparative accessibility and increased solubility [7, 33]. Still fluorescence quenching is observed in these derivatives at increasing concentration or in the solid state, nevertheless in a few instances steric shielding of the chromophores by introduction of bulky substituents, such tetraphenylmethane or branched aliphatic groups, can inhibit aggregation with a positive effect on the fluorescence quantum yields at high concentrations or in the solid state [34, 35]. Another strategy usually employed to increase the solubility of perylene derivatives is the functionalization at the aromatic core, typically at the 1,6,7,12-bay positions, by introduction of aryl or aryloxy groups. In these derivatives the electronic and optical properties of PDI are also strongly modified and many investigations have been devoted to elucidate how bay-substitutions could affect absorption and emission properties of PDIs, as well as their π–π aggregation. It has been found that the typical quenching of fluorescence emission is maintained in solution at increasing concentration and/or in the solid state due to the formation of aggregates [3], except for a series of PDI derivatives which display significant fluorescent quantum yields in the solid state, due to a packing based on J-type aggregates [36]. Finally, perylene derivatives substituted at the 2,5,8,11-bay positions, some of which show an intense fluorescence in the solid state, have been recently synthesized [37, 38].

While the effects of bulky organic substituents both at imide and bay positions on π-π stacking and supramolecular organization of PDIs have been intensely studied, much less work has been addressed towards the preparation of inorganic-organic hybrid PDI systems, which offer the possibility to combine the properties of the PDI dyes with those of an inorganic scaffold with the aim to both optimize the emission performance in the solid state and to promote processability thanks to increased solubility. To such purpose the introduction as substituents of sterically demanding inorganic scaffolds such Polyhedral Oligomeric Silsesquioxanes (POSS) is quite appealing.

POSS are an interesting family of silicon-oxygen cages with the idealized empirical formula $(RSiO_{1.5})_n$. that have attracted much attention in recent years because of their particular properties such as ease of synthesis and purification, chemical and thermal robust nature compared to most traditional organic molecules, and the facility to tailor their functionalities to particular applications [39-43]. It has been proven that incorporation of POSS in several organic materials may be a way to enhance specific properties such as thermal and thermomechanical stability, mechanical toughness, optical transparency, dielectric constant and solubility. Hence the large number of applications of POSS cages in many research fields such as aerospace [44], biomedical applications [45-47], protective coatings [39], microelectronics [48, 49] and catalysis [50-62].

More recently, silsesquioxane derivatives have been incorporated in light emitting polymers [63] and in organic light emitting diodes (OLEDs) [64-68]. This has led to preparation of devices with improved performances in terms of brightness, colour stabilities, lifetimes and quantum efficiencies compared with the parent devices prepared without introduction of the POSS cage. In particular it has been reported that the presence of bulky POSS cages could minimize aggregation of polyfluorene derivatives, with a positive effect on their photoluminescence quantum yields [69].

Despite such increasing interest towards the synthesis of POSS-functionalized organic materials, to our knowledge there are only few reports on the preparation of organic-inorganic PDI-POSS hybrid nanoparticles [70-73].

Here we report on the synthesis and optical characterization of new hybrid organic-inorganic materials based on asymmetrically substituted perylene moieties linked to POSS cages showing reduced emission aggregation quenching in the solid state.

2. Experimental Section.

2.1 Chemicals and instrumentation

POSS **1** [74] and **4** [75] were prepared according to the literature. Perylene diimides **2** [76], **5** [77] and **7** [78] (see Figure 1) were prepared starting from perylene-3,4,9,10-tetracarboxylic dianhydride [79].

All reagents and catalysts were purchased from Sigma-Aldrich and used as received, except for $CySi(OMe)_3$, purchased from Fluorochem. Toluene was distilled over Na/benzophenone, $CHCl_3$ and CH_2Cl_2 were distilled over CaH_2 before use. When anhydrous conditions were required, the reactions were performed using Schlenk line techniques under a nitrogen atmosphere.

All products were characterized by ^1H, ^{13}C and ^{29}Si NMR (Bruker Avance DRX 400 spectrometer), mass spectroscopy (VG Autospec M246), infrared spectroscopy (Jasco FT-IR 420) and elemental analysis (Perkin-Elmer CHN 2400).

Thin films were prepared by spin-coating on glass slides of a 6.6 10^{-3} M solution in $CHCl_3$ of the desired PDI-POSS compound.

Electronic absorption spectra were obtained using a Jasco V-530 spectrophotometer. Photoluminescence (PL) measurements and PL Quantum Yields (QY) for solutions were obtained by a Jobin-Yvon Fluorolog-3 spectrometer equipped with double monochromators and Hamamatsu-928 photomultiplier tube (PMT) as the detector. Photoluminescence (PL) measurements on solids were obtained with a SPEX 270 M monochromator equipped with a N_2 cooled charge-coupled device exciting either with a monochromated Xe lamp or an Ar^+ laser. The spectra were corrected for the instrument response. Absolute PL QY measurements for the solid state materials were carried out using a home-made integrating sphere according to the procedure reported elsewhere

[80].

2.2 Synthesis of $(c\text{-}C_6H_{11})_7Si_8O_{12}$-2-Propyl-9-(1-hexyl-heptyl)-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3)

Perylene **2** was prepared according to the literature procedure by reaction of 2-Allyl-9-(1-hexyl-heptyl)-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (300 mg, 0,49 mmol) with trimethoxysilane (4mL, 0.55 mmol) in anhydrous chloroform (60mL) and in the presence of Karstedt catalyst [76]. Due to its sensitivity to moisture the product was no further purified by column chromatography and directly used for condensation reaction.

A solution of **2** (360 mg, 0,49 mmol) dissolved in anhydrous toluene (50 mL) was added with POSS **1** (0.476 g, 0.50 mmol) together with *p*-toluensulfonic acid (a few mg) and stirred at 100°C for 24h under N_2 atmosphere. The reaction mixture was concentrated under reduced pressure and purified by chromatography on silica gel (CH_2Cl_2:hexane, 1:1) to give a red solid which was further crystallized from CH_2Cl_2/MeOH solution (193 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) 0.76 (m, 7H, Cy), 0.85 (t, J(H-H) = 7.0 Hz, 6H, 2xCH_3), 1.24-1.34 (m; 35H, Cy; 16H, 8xCH_2, 4H, alkylic CH_2), 1.74 (m, 35H, Cy), 1.88 (m, 2H, β-CH_2), 2.28 (m, 2H, β-CH_2), 4.19-4.22 (m, 2H, CH_2-N),5.19-5.24 (m, 1H, CH-N), 8.48-8.64 (m, 8H, aromatic CH).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ (ppm) 14.03, 22.59, 23.09, 26.63, 26.96, 27.48, 29.22, 29.68, 31.77, 32.38, 54.81, 122.85, 123.16, 126.13, 126.26, 129.14, 129.47, 131.02, 134.13, 134.26, 162.95.

^{29}Si NMR (79.5 MHz, $CDCl_3$, 298K): δ (ppm) -67.06 (1), -68.70 (7).

Elemental Analysis $C_{82}H_{118}N_2O_{16}Si_8$: found %C .60.83; %H 7.55; %N 1.59; calculated %C 61.08; %H 7.38; %N 1.74.

Mass: [M^+] 1613 (FAB^+).

Melting Point: 330°C

FT-IR (KBr): *ν*(cm^{-1}) 2923 (vs), 2848 (s), 1700 (s; C=O), 1662 (s), 1595 (s), 1579 (w), 1507 (vw), 1447 (m), 1405 (m), 1383 (w), 1339 (s), 1274 (m), 1254 (m), 1197 (m), 1108 (vs, br; Si-O), 1038(m) 1026 (m), 998 (m), 893 (m), 850 (m), 825 (w), 810 (m), 746 (m).

2.3 Synthesis of vinylsilsesquioxane-4-[2-(1-Hexyl-heptyl)-9-(phenyl)-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone] (6)

POSS **4** (416 mg, 0.4 mmol), PDI **5** (313 mg, 0.4 mmol), and bis(tri-*t*-butylphosphine)-palladium(0) [Pd[P(*t*Bu)$_3$]$_2$] were added into a 100-mL Schlenk flask under N_2 atmosphere. Anhydrous toluene (40 mL), and dicyclohexylmethylamine (Cy_2NCH_3) (0.103 mL, degassed under nitrogen for 15 min prior to use) were added, then 3 freeze-pump-thaw cycles were performed. The reaction was stirred for 6 days at 80°C under N_2 atmosphere. The mixture was then filtered on celite and the solution concentrated in vacuum. The solid was purified by column chromatography (CH_2Cl_2:Hexane, 1:1) followed by crystallization from CH_2Cl_2/methanol o give a red solid (677 mg, 37% yield).

^{1}H NMR (400 MHz, CDCl$_3$, 298K): δ (ppm) 0.81 (m, 7H, Cy), 0.85 (t, J(H-H) = 6.8 Hz, 6H, 2xCH_3), 1.28-1.34 (m; 35H, Cy; 16H, 8xCH_2), 1.77-1.82 (m, 35H, Cy), 1.90 (m, 2H, β-CH_2), 2.23-2.31 (m, 2H, β-CH_2), 5.21 (m, 1H, CH-N), 6.27 (d, J(H-H) = 19.0 Hz, 1H, CH=CH), 7.31 (d, J(H-H) = 19.0 Hz, 1H, CH=CH), 7.37 (d, J(H-H) = 8.4 Hz, 2H, aromatic phenyl), 7.69 (d, J(H-H) = 8.4 Hz, 2H, aromatic phenyl), 8.67-8.77 (m, 8H, aromatic perylene).

^{13}C NMR (100 MHz, CDCl$_3$, 298K): δ (ppm) 14.04, 22.58, 23.15, 26.67, 26.92, 27.50, 29.21, 31.76, 32.38, 54.84, 120.56, 123.07, 123.27, 123.33, 126.45, 126.72, 127.76, 128.78, 129.56, 129.87, 131.87, 134.32, 135.18, 138.40, 146.95, 163.53.

^{29}Si NMR (79.5 MHz, CDCl$_3$, 298K): -68.44, -68.59, -68.64, -79.28. (3:3:1:1).

Elemental Analysis $C_{87}H_{118}N_2O_{16}Si_8$: found %C 62.53; %H 7.06; %N 1.78; calculated %C 62.48; %H 7.11; %N 1.67.

Mass: [M^+] 1672 (FAB^+).

Melting Point: >350°C

FT-IR (KBr): *ν*(cm^{-1}) 2923 (vs), 2849 (s), 1713 (s; C=O), 1700 (s; C=O), 1674 (s), 1661 (s), 1595 (s), 1579 (m), 1509 (m), 1447 (m), 1405 (m), 1383 (w), 1342 (vs), 1292 (vw), 1274 (m), 1269 (m), 1253 (m), 1197 (s), 1108 (vs, br; Si-O), 1038(m) 1027 (m), 999 (m, sh), 966 (w), 893 (m), 850 (m), 836 (w), 827 (w), 811 (m), 786 (w), 746 (m).

3. Results and discussion

3.1 Synthesis

The synthesis of the PDI-POSS derivatives was accomplished according to two different approaches, as depicted in Scheme 1 and 2, in which the PDI dye was linked to the POSS scaffold either by a flexible alkylic chain or by a more rigid styryl bridge.

In the first approach we chose as inorganic scaffold POSS **1**, namely trisilanol $Cy_7Si_7O_9(OH)_3$ (Cy= *c*-C_6H_{11}), with three potentially reactive OH groups which is widely used to model the silanol groups of the silica surface [41, 56]. The presence of bulky cyclohexyl substituents at each silicon atom of POSS **1** should reduce π-π aggregation of the perylene moieties and impart higher solubility.

POSS **1** was reacted with the trimethoxysilane perylene derivative **2**, recently described in the literature and successfully employed for the preparation of fluorescent silica nanoparticles [76]. Corner capping reaction of **1** with **2** was performed in dry toluene and in the presence of *para*-toluensulfonic acid as a catalyst working at 100°C. Previous attempts of condensation in $CHCl_3$ or toluene at reflux but in the absence of the acid catalyst gave negative results. The reaction was monitored through ^{29}Si-NMR spectroscopy, by following the disappearance of the typical three signals of **1** (δ = -60.1, -67.7 and -69.4 ppm in a 3:1:3 ratio) and the appearance of a new set of peaks at δ = -67.06 and -68.70 ppm (in a 1:7 ratio) which have been attributed to the new PDI-POSS derivative **3**; the reaction was stopped after 24h. After purification of the crude by silica gel chromatography and crystallization from CH_2Cl_2/MeOH, **3** was obtained as a brilliant red coloured solid in 23% yield. The compound was characterized by NMR (^{1}H, ^{13}C, ^{29}Si) spectroscopy, by mass spectroscopy, by infrared spectroscopy and by elemental analysis (see experimental section 2.2). The optical characterization was performed both in solution and in the solid state (see section 3.2).

INSERT SCHEME 1

In the second approach, POSS **4**, namely $VyCy_7Si_8O_{12}$ (Cy= *c*-C_6H_{11}; Vy = CH=CH_2), which bears one vinyl group suitable for further functionalization, was reacted by Heck coupling with an halide-substituted PDI. The reaction was performed in toluene at 80°C, using bis(tri-*t*-butyl-phosphine)palladium(0) [Pd[P(^{t}Bu)$_3$]$_2$] as catalyst and dicyclohexylmethylamine as base [67, 81, 82]. First attempts with 4-bromophenyl substituted perylene failed, only the more reactive 4-iodophenyl derivative **5** gave the desired product **6** (Scheme 2). The formation of **6** was followed through ^{1}H NMR spectroscopy by monitoring the disappearance of the vinyl signals typical of **4** and the appearance of new signals relative to the *trans* double bond of **6**. After purification by silica gel chromatography and crystallization from CH_2Cl_2/MeOH, pure **6** was obtained as a brilliant red solid in 37% yield. The compound was characterized by NMR (^{1}H, ^{13}C, ^{29}Si) spectroscopy, by mass spectroscopy, by infrared spectroscopy and by elemental analysis (see experimental section 2.3). The optical characterization was performed both in solution and in the solid state (see section 3.2).

INSERT SCHEME 2

3.2 Optical Characterization

3.2.1 Absorption and emission spectra in solution

Absorption and emission spectra of **3** and **6** were recorded in chloroform solution and compared with those of the symmetrically substituted diimide **7** (Figure 1).

INSERT FIGURE 1

As expected, the introduction of a POSS fragment at one imidic position, did not affect the electronic properties of the perylene moiety and the electronic absorption spectra of **3** and **6** in $CHCl_3$ solution display the typical features of a perylene diimide (see Figure 2), with three distinct vibronic transitions (0,0), (0,1), (0,2) and one shoulder (0,4) [83]. Similarly, the emission spectra have the characteristic features of perylene diimides being mirror images of the absorption spectra [83]. The fluorescence quantum yields, measured in $CHCl_3$ solution with **7** as standard [76, 84], were 90% and 100% for **3** and **6** respectively.

INSERT FIGURE 2

3.2.2 Absorption and emission spectra in the solid state

The solid state absorption spectra of **3**, **6** and **7** were recorded on both thin films (see experimental section 2.1) and powders. The absorption spectra of thin films, reported in Figure 3, clearly show that aggregation becomes predominant for all compounds, with an increase of the (0,1) vibronic transition compared to the (0,0) transition [83]. For the standard compound **7** an additional band at about 550 nm, partially superimposed to the 530 nm (0,0) band, is also observed. This band is in agreement with the presence of strong intermolecular interactions in the solid phase of perylene based compounds [4, 5]. Interestingly, the absorption spectra of **3** and **6** do not display such a red-shifted band, suggesting weaker aggregation with respect to **7**. This hypothesis is also indirectly supported by the analysis of absorption spectra of powders of **3**, **6** and **7** before and after grinding in a mortar. In Figure 4 the absorption spectra before grinding show the presence of a broad and poorly resolved band for all compounds. However, after grinding, powders of **3** and **6** display resolved and blue-shifted absorption bands, quite similar to those displayed in the corresponding spectra in solution. The absorption spectrum of powdered **7** was unaffected by grinding suggesting that this compound possessed stronger π-π intermolecular interactions.

INSERT FIGURE 3

INSERT FIGURE 4

In addition, the PL spectra of thin films and powders of the three compounds show unstructured, red-shifted and broadened bands with respect to the solution, again suggesting the presence of intermolecular interactions (see Figure 5) [83].

In order to confirm the positive effect of the POSS fragment in reducing the aggregation of **3** and **6** with respect to **7**, measurements of PL quantum yields were performed on ungrinded powders of the three compounds (Table 1). Interestingly, while the PL QY of **7** drops from 100% to 34% by moving from solution to the solid state, the PL QY of **3** and **6** show a reduced quenching going from 90% to 70% and from 100% to 45% respectively. Such smaller decrease of the PL QY represents a further evidence of a lower degree of intermolecular interactions induced by linking the PDI moieties to POSS cages.

INSERT FIGURE 5

INSERT TABLE 1

4. Conclusion

By reaction of POSS **1** ($Cy_7Si_7O_9(OH)_3$; Cy= *c*-C_6H_{11}) or **4** ($VyCy_7Si_8O_{12}$ where Cy= *c*-C_6H_{11}; Vy = $CH=CH_2$) with appropriately functionalized asymmetric perylene diimides we have been able to synthesize two new PDI-POSS hybrid derivatives, which are characterized by a high solubility in common organic solvents which is a necessary condition for the production of thin films by the spin coating technique. These new PDI-POSS materials show in solution the typical molecular absorption and emission spectra of the isolated perylene unit, with PL QY close to 100%. Interestingly, the detrimental ACQ phenomenon, frequently encountered in PDI materials, is significantly reduced by the presence of the bulky POSS cage allowing to get PL QY up to 70% from powders.

These findings encourage further investigations on this new class of PDI-POSS hybrid materials to be applied in the production of efficient emissive devices.

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Figure Captions

Scheme 1: Synthesis of **3**

Scheme 2: Synthesis of **6**

Figure 1: Perylene diimide **7**

Figure 2: Normalized absorption (solid line) and emission (dashed line) spectra in $CHCl_3$ solution of **3** (blue), **6** (green) and **7** (red).

Figure 3: Normalized absorption spectra of thin films of **3** (blue), **6** (green) and **7** (red).

Figure 4: Normalized absorption spectra of powders of **3** (blue), **6** (green) and **7** (red) before grinding (dotted line) and after grinding (solid line). The absorption spectrum of **6** in solution (dashed line) is reported for comparison. The spectra are shifted vertically for clarity.

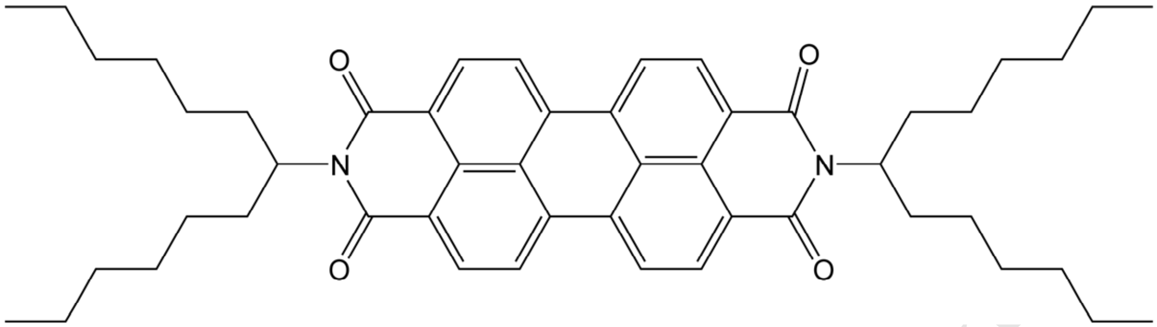
Figure 5: Normalized emission spectra of powders of **3** (blue), **6** (green) and **7** (red).

Table 1: Photoluminescence quantum yield (PL QY) of **3**, **6** and **7** measured as powder, and in $CHCl_3$ solution

Table 1: Photoluminescence quantum yield (PL QY) of **3**, **6** and **7** measured as powder, and in $CHCl_3$ solution

Compound	solution			solid	
	λ_{max} [nm]$^{(a)}$	λ_{em} [nm]	Φ_f $^{(b)}$	λ_{em} [nm]	Φ_f $^{(c)}$
3	525	533	90	656	70
6	527	535	100	668	45
7	526	533	100	669	34

[a]The longest absorption maxima; [b]λ_{exc} = 488 nm; [c] λ_{exc} = 457 nm;


O
O
N
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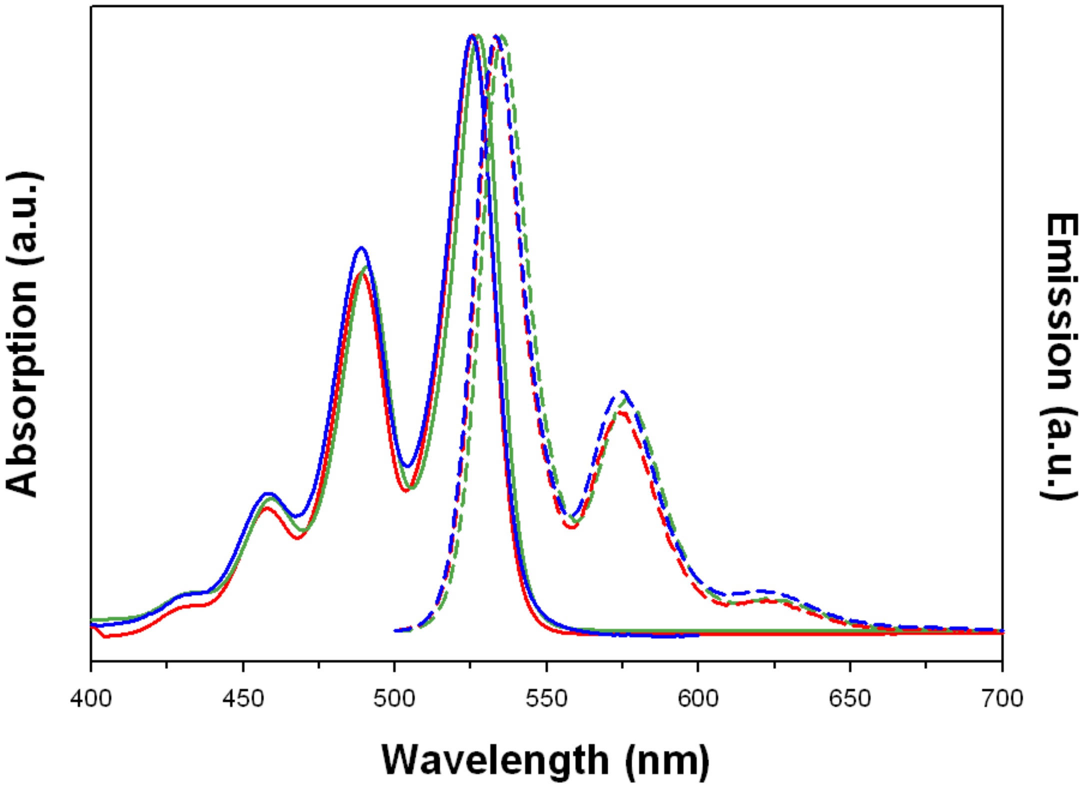
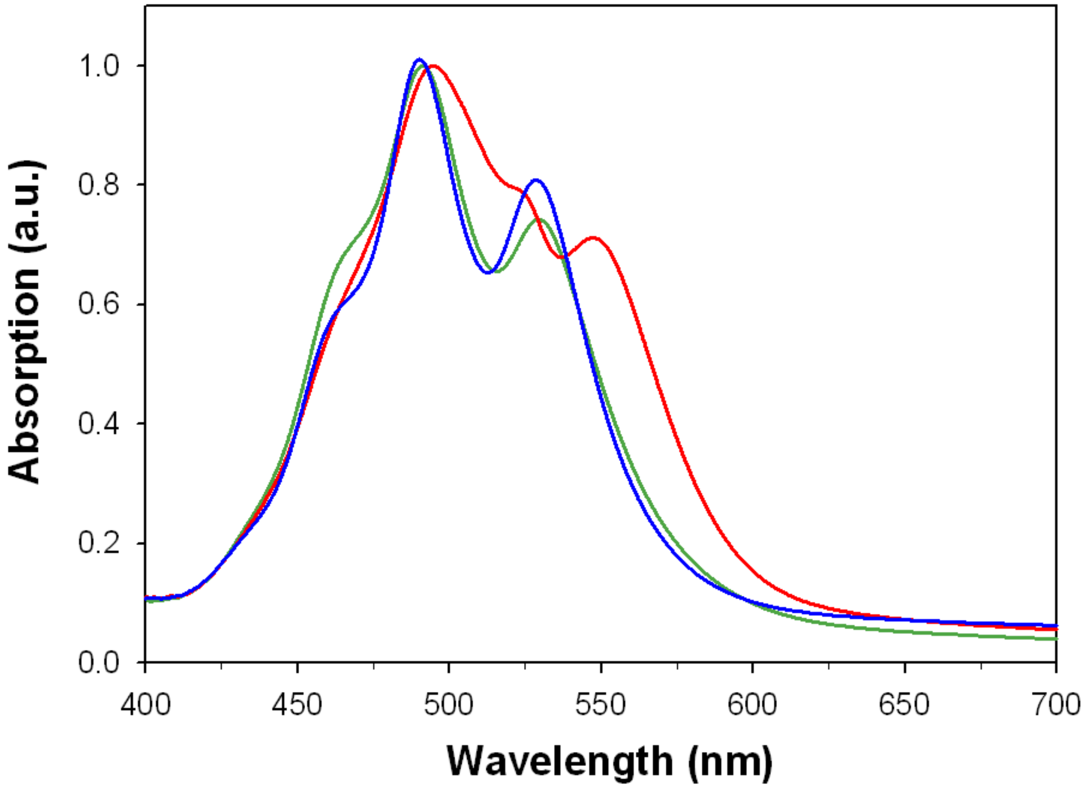
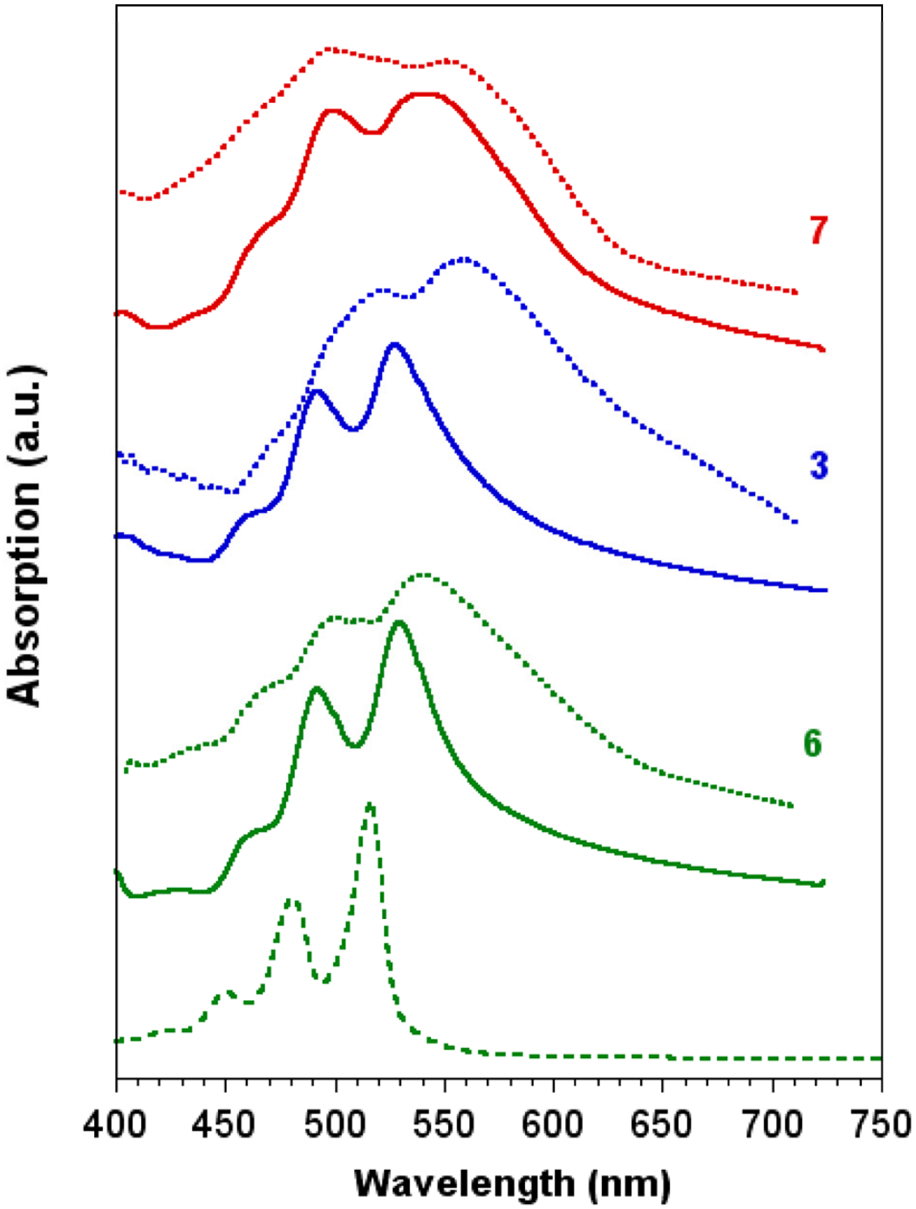
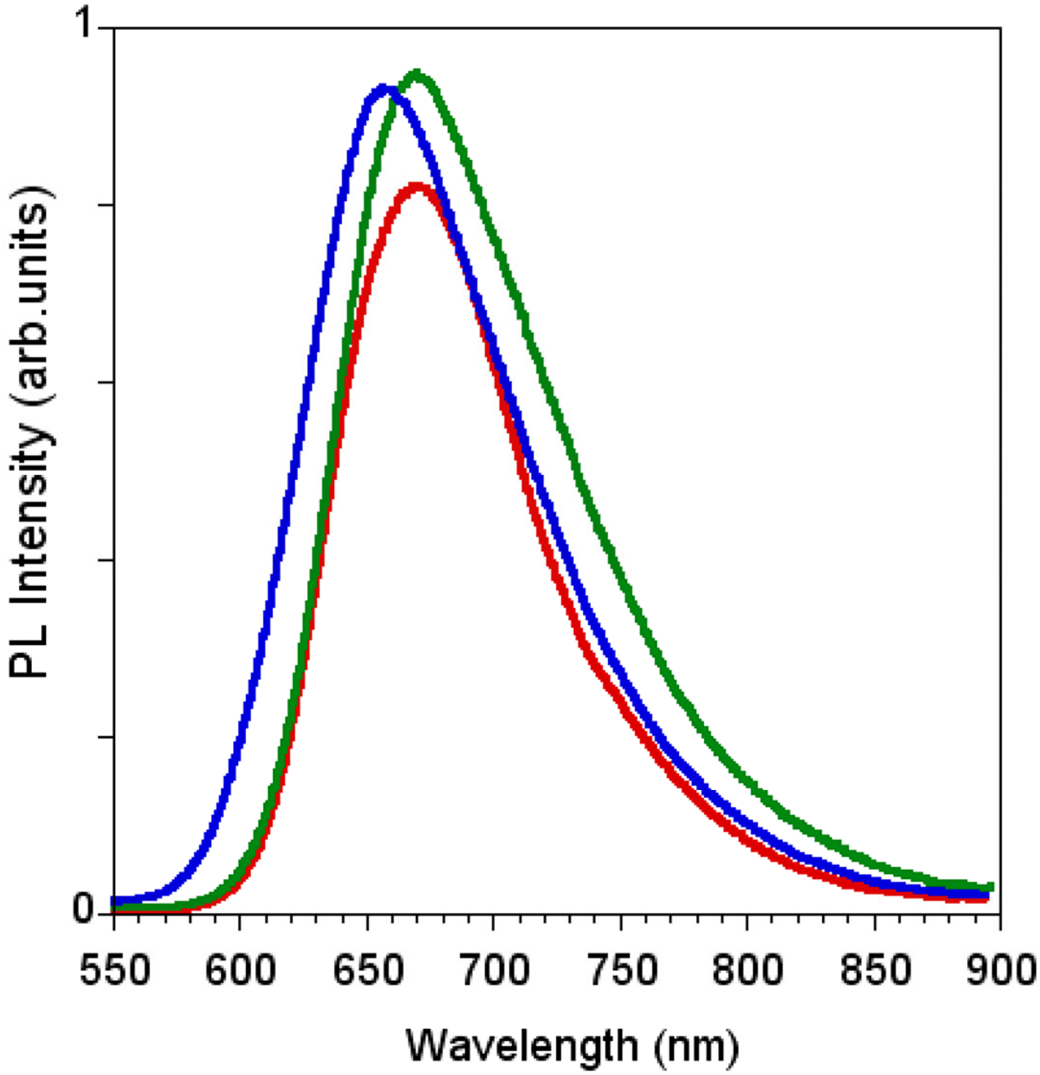
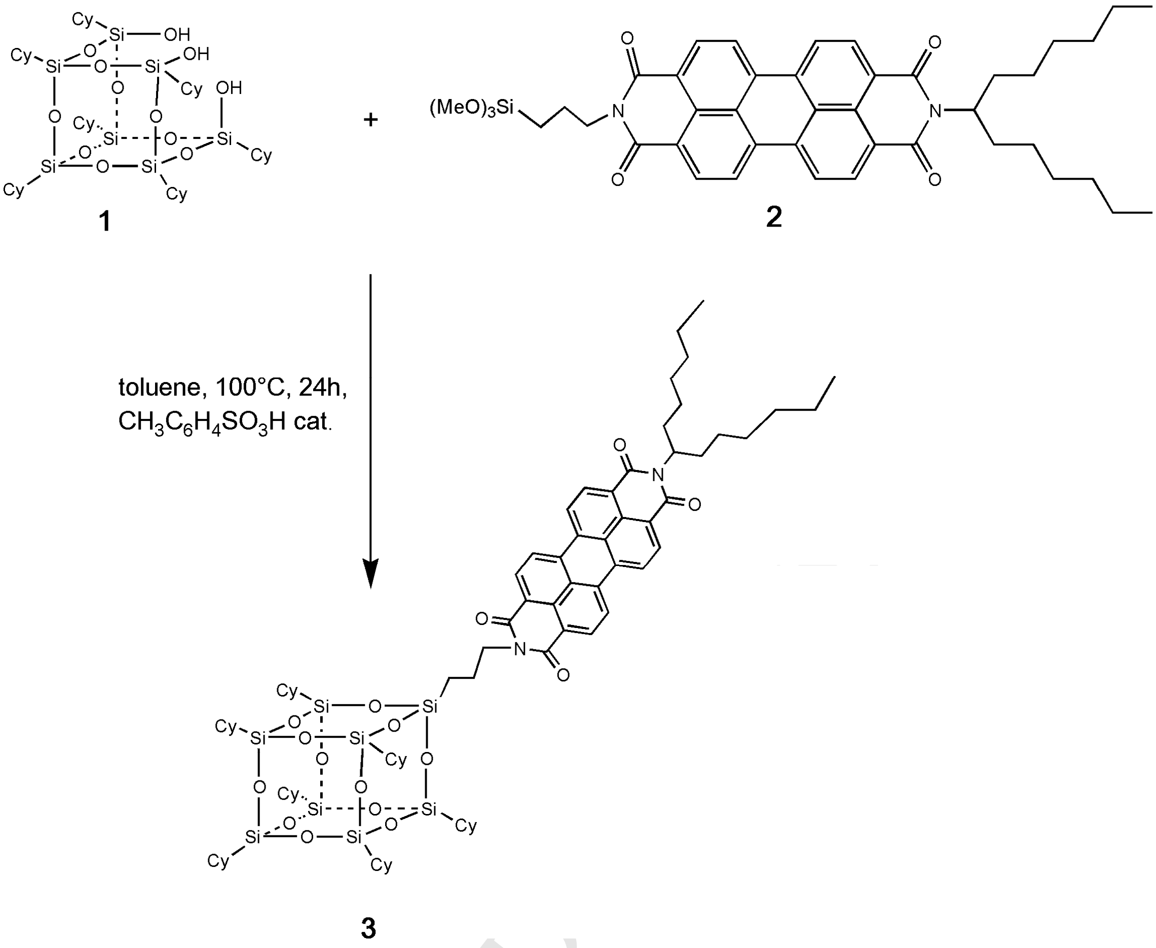
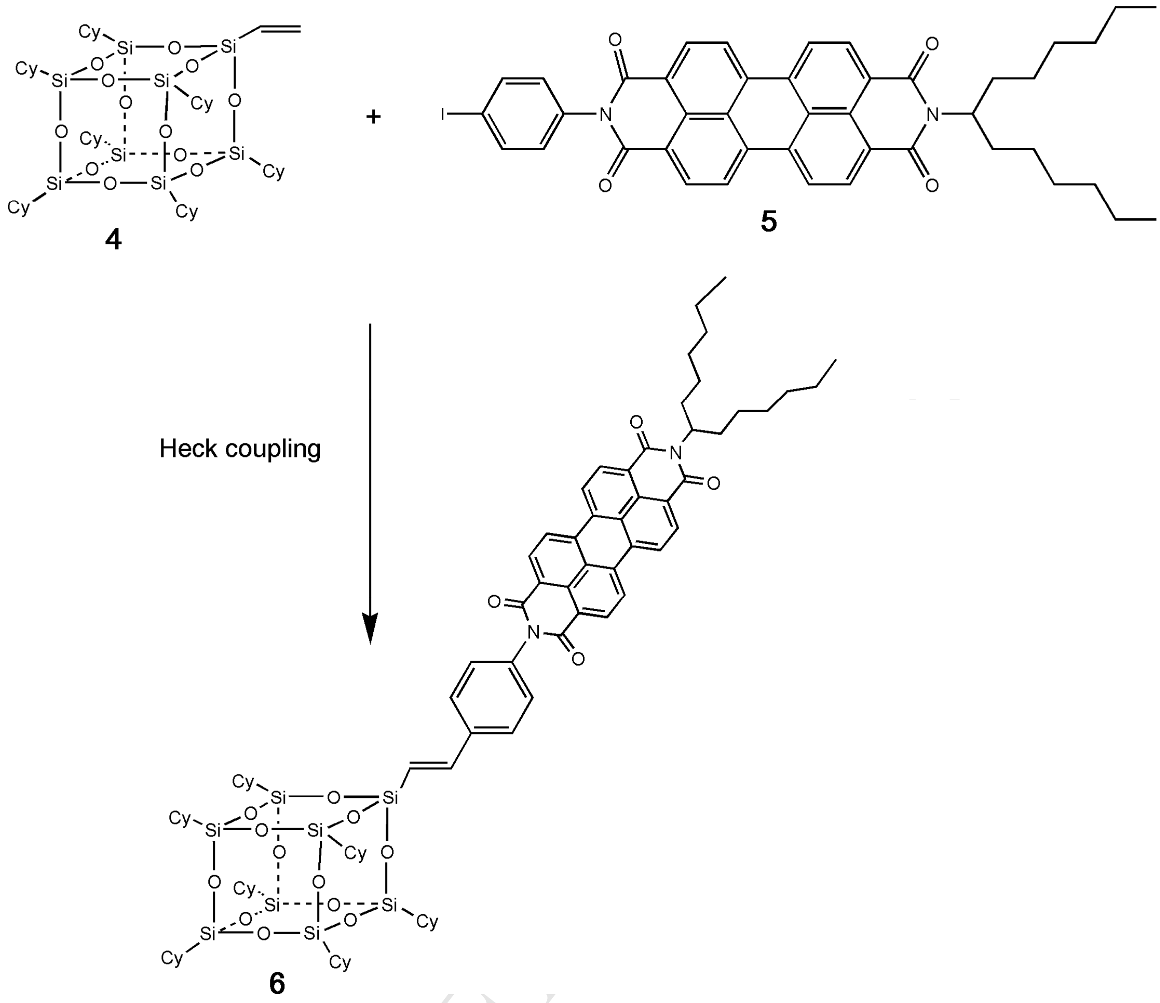

Absorption (a.u.)
Emission (a.u.)
Wavelength (nm)
400
450
500
550
600
650
700


Absorption (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650
700
Wavelength (nm)


7
3
6
Absorption (a.u.)
400
450
500
550
600
650
700
750
Wavelength (nm)


1
0
PL Intensity (arb.units)
550
600
650
700
750
800
850
900
Wavelength (nm)


1
2
3
+
(MeO)$_3$Si
toluene, 100°C, 24h,
$CH_3C_6H_4SO_3H$ cat.
Cy
Si
O
OH
N


4
+
5
Heck coupling
6
Cy
Si
O
I
N