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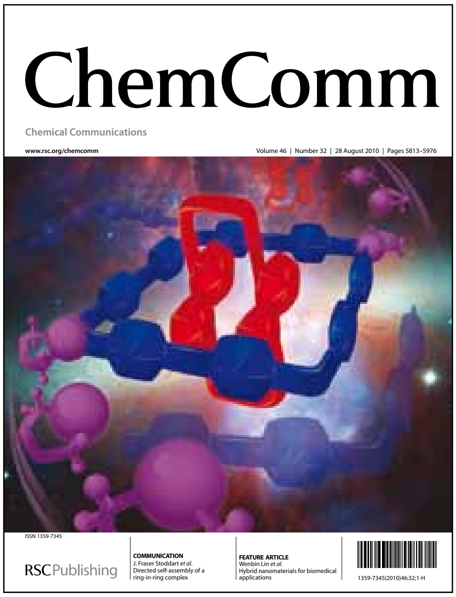

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ARTICLE TYPE

Luminescent and conductive supramolecular polymers from an *N*-annulated perylenedicarboxamide

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The tunable luminescent features along with the electric conductivity (~2 x 10^{-4} S/m) exhibited by the gel fibers formed through supramolecular polymersation of the *N*-annulated perylenedicarboxamide based π-gelator 1 is reported.

The development of flexible, lightweight organic electronics strongly depends on the optimization of materials constituted by functional molecular units with a high degree of supramolecular organization.[1] The function and complexity of supramolecular entities –tuned by the chemical structure of the interacting molecules– render active materials that have been utilized in the fabrication of efficient optoelectronic devices.[2] One-dimensional (1D) supramolecular aggregates are of special interest in the field of organic electronics since they generate aligned structures with outstanding conductive or biological properties.[3] A number of these 1D structures has been reported to be formed by a cooperative supramolecular polymerization of relatively small and simple molecules that interact by means of non-covalent forces.[4] The further entanglement of a variety of selected 1D structures generated from π-conjugated molecules have resulted in a large number of π-gels that have been used as soft- materials for organic electronics, sensing and imaging applications.[5] The presence of π-conjugated moieties in the constitutive self-assembling units of π-gelators facilitate the transfer of relevant molecular properties to the macroscopic level due to the enhanced face-to-face contacts along the molecular π–π stacking direction.[6]

Herein, we describe the synthesis, cooperative supramolecular polymerization, photophysical and semiconducting properties of an *N*-annulated perylenedicarboxamide (NPDC) (compound **1** in Figure 1). *N*-annulated perylene derivatives are π-conjugated platforms very useful to attain processable materials with highly anisotropic electronic properties.[7] The columnar aggregates formed upon the self-assembly of **1** reported herein behave as a multifunctional material exhibiting highly luminescent features and also promising values of electric conductivity that makes this compound an appealing candidate with potential applicability in the research field of soft electronics.

The synthesis of **1** was achieved by a sequence of five steps starting from perylene, following previously reported synthetic protocols in which a final two-fold Suzuki C-C cross-coupling reaction catalysed by palladium in 37% (Scheme S1). The chemical structure of compound **1** has been confirmed by NMR, FT-IR, UV-Vis spectroscopy, and HRMS analyses (see Scheme S1 and Supporting Information).[8]

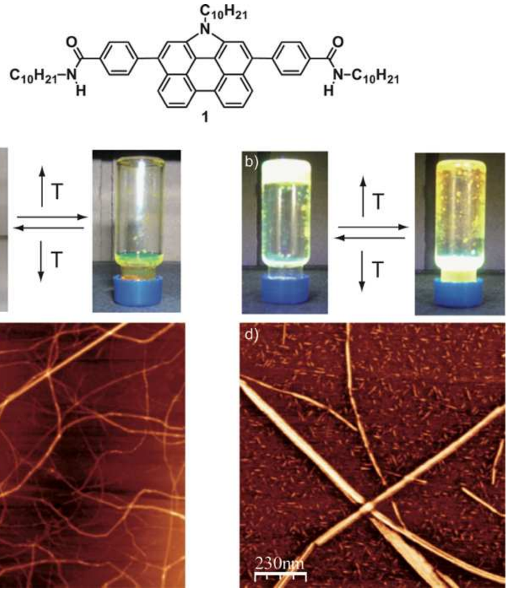

Fig. 1 Chemical structure of NPDC **1** (top). Pictures of the gel-to-sol transition of the organogel of **1** without (a) and with (b) illumination at 360 nm. (c and d) AFM images of the aggregates of **1** (MCH, 1 x 10^{-4} M, 298 K, HOPG; z scale 50 and 10 nm for (c) and (d), respectively).

The supramolecular interaction of **1** by means of H-bonding interactions between the amide functional groups and π-π stacking of the aromatic units is inferred by the downfield shift of the triplet at δ ~ 6.3, corresponding to the amide groups, and also the upfield shift of some of the aromatic resonances observed in the ^{1}H NMR spectra of **1** upon increasing the concentration (Figure S1). This supramolecular interaction favours the formation of columnar aggregates that could bundle into thick filaments immobilizing the solvent molecules to form a gel.[9] In fact, NPDC **1** forms an organogel in toluene at a concentration of 4.6wt% that experiences a gel-to-sol transition upon heating (Figure 1a). The fibrillar nature of the aggregates constitutive of the organogel of **1** in toluene has been visualized by atomic force microscopy (AFM) imaging in diluted toluene solutions deposited onto HOPG as surface (Figures 1c and 1d). These AFM images show thin wire-like structures that bundle to form small domains of fibrillar structures as indicated by the different height profiles (Figure S2).

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The morphology and properties of the aggregates formed in a supramolecular polymerization process are closely related with the mechanism that controls the self-assembly.[4] Only a cooperative mechanism affords supramolecular polymers with a large degree of polymerization and low polydispersity which enhance the final properties of the supramolecular structure.[4a] The UV-Vis spectrum of compound **1** in methylcyclohexane (MCH) shows a broad band centered at 413 nm that splits in three bands at 398, 427, and 452 nm upon the addition of a good solvent like chloroform (Figure S3). The non-sigmoidal shape of the curve obtained by plotting the variation of the absorbance at 452 nm upon increasing the amount of added $CHCl_3$ is diagnostic of a cooperative self-assembly in which **1** is molecularly dissolved in chloroform and totally aggregated in the more apolar MCH.[10] A final confirmation of the cooperative character of the supramolecular polymerization of **1** has been achieved by the non-sigmoidal cooling curves obtained by variable temperature UV-Vis experiments at two different concentrations (Figure 2). In these studies, the shape of the UV-Vis spectrum of **1** at high temperatures exhibit the same pattern to that observed for this compound in $CHCl_3$ thus confirming the disassembly of the aggregates of **1** at these conditions of temperature (Figure S3).

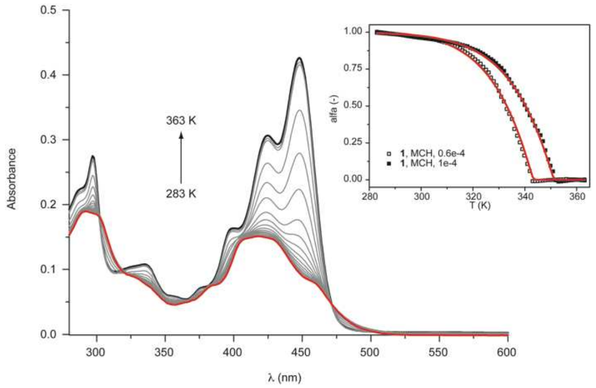

Fig. 2 Temperature dependent UV-Vis spectra of **1** in MCH (1 x 10^{-4} M, from 363 to 283 K). The black and red lines depict the UV-Vis spectra of **1** in MCH at 363 and 283 K, respectively. The inset shows the cooling curves of **1** at 0.6 x 10^{-4} and 1.0 x 10^{-4} M (0.5 K/min). The red lines in the inset correspond to the fit to the EQ model.

The mechanism followed by **1** to self-assemble has been accurately investigated by applying the recently reported equilibrium (EQ) model that allows to derive all the thermodynamic parameters associated with the two extreme reactions, i. e., the nucleation and the elongation, that define the self-assembly of **1** in solution.[11] The cooling curves of **1**, obtained by variable temperature UV-Vis experiments of MCH solutions at two different concentrations (1 x 10^{-4} and 6 x 10^{-5} M), present a non-sigmoidal shape with a critical point diagnostic of the rapid change in the regimen of the mechanism, nucleation and elongation, and, hence, in the degree of polymerization. The global fitting of the two cooling curves with the EQ model shed values of -62.78 $kJmol^{-1}$, -0.10 $kJmol^{-1}$, and -34.94 $kJmol^{-1}$ for the enthalpy of elongation ΔH_{elo}^{0}, entropy of elongation ΔS^{0}, and the nucleation penalty ΔH_{nucl}^{0}, respectively. The high degree of cooperativity in the self-assembly of NPDC **1** is confirmed by the low value calculated for the cooperativity factor σ (7.5 x 10^{-7}).

After the investigation of the self-assembling features of **1** in solution, we have evaluated the light-emitting and conductive properties of the aggregates formed from this NPDC. The attachment of the electroactive unit to the *N*-annulated perylene core results in organic materials with enhanced light-emitting properties.[7] We have visualized that both the toluene gel and the heated solution of **1** at 4.6wt% show an intense, light-greenish fluorescence upon irradiation at 360 nm (Figure 1b). The intense fluorescence observed in the gel state prompted us to investigate the emission properties of **1** at different experimental conditions to confirm the enormous influence of aggregation in the final properties of the material. The emission spectra of highly diluted solutions of **1** in chloroform or toluene, conditions at which the NPDC **1** is molecularly dissolved, show two intense maxima at 479 and 508 nm (Figure 3).[12] The aggregation experienced by **1** in MCH as solvent or in the organogel obtained in toluene drastically changes the appearance of the corresponding emission spectra. In the aggregated state, the emission spectrum covers a broad range of the visible spectral region and exhibits vibronic coupling with maxima at 480, 512, and 546 nm together with a residual emission that expands until 700 nm (Figure 3). **1** shows a high fluorescence quantum yield (ϕ_S) of 0.79 for the molecularly dissolved state in chloroform whereas upon aggregation quantum yield is decreased to 0.12 in apolar solvent which implies an aggregation-caused quenching effect. The broad emission with a red shift in the aggregated state implies the presence of a mixture of the monomers and aggregates of different energy levels which emit at different wavelength.[13]

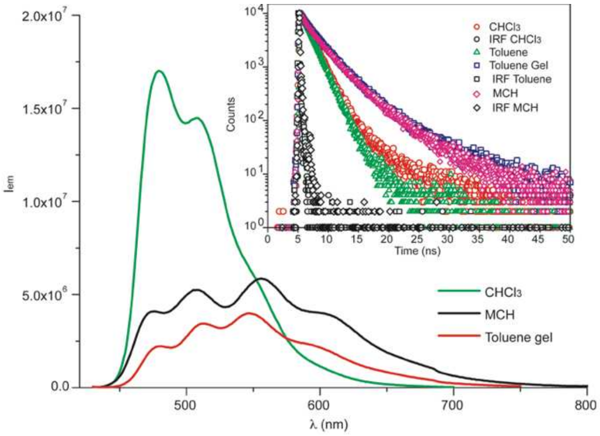

Fig. 3 Emission spectra of NPDC **1** at different conditions (green line: $CHCl_3$, 1 x 10^{-6} M; black line: MCH, 1 x 10^{-5} M; red line: toluene gel; λ_{exc}= 420 nm). The inset shows the fluorescence lifetime-decay profiles at 479 nm of **1** in $CHCl_3$ (5 x 10^{-5} M), toluene (5 x 10^{-5} M), MCH (1 x 10^{-4} M) and toluene gel (λ_{exc}= 440 nm). IRF = instrument response function.

The aggregation of **1** also exerts a strong impact on the fluorescence lifetime decay. The lifetime measurements were carried out at 479 nm (monomer emission maximum) as well as at 546 nm (aggregated emission maximum). In dilute toluene or chloroform solutions (5 x 10^{-5} M), NPDC shows a mono-exponential decay with a fluorescence lifetime of 3.28 ns which indicates **1** is molecularly dissolved (inset in Figure 3). However, the lifetime experiments in the aggregated state reveals a tri-exponential decay for the NPDC gel (toluene) with lifetimes of 2.69 (76.67%), 6.54 (19.38%), and 0.38 (3.95%) ns at 479 nm and 2.78 (62.84%), 6.32 (32.57%), and 0.33 (4.59%) ns at 546 nm. The decay profiles monitored at both wavelengths are the same with minor changes in their relative percentage. At 546 nm more number of aggregated species was present. In this manifold fluorescence lifetime decay, the major populated species are ascribed to the monomer state, corresponding to the minor

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populated one to the aggregated species.[14] Hence, there is a major contribution in emission from the monomeric state. To further characterize the light emission of the supramolecular polymers formed upon the self-assembly of the NPDC **1**, the commonly used Commission International de l' Eclairage (CIE) coordinates were determined which are 0.26 and 0.40, resulting in a chromaticity diagram that lays close to the white light region centred at CIE coordinates of (0.33, 0.33) (Figure S5a).[15]

Finally, we measured the electrical conductivity (σ) of the gel fibers formed by NPDC **1** in toluene by using Four-Probe Conductivity (FPC) and conducting probe atomic force microscopy (C-AFM).[16] The undoped fibers formed by the self-assembly of **1** show I-V response with calculated values of the electric conductivity σ of 1.92 x 10^{-4} and 2.16 x 10^{-4} S/m for the FPC and C-AFM techniques, respectively (Figure S5b,c). These σ values are in the same range of those reported for organogels prepared from well-known conductive materials like tetrathiafulvalene or oligo(thiophenes).[17]

In summary, the luminescent and conducting properties of the *N*-annulated perylenedicarboxamide **1** that self-assembles into 1D supramolecular structures through H-bonding interactions between the amide functional groups and π-π stacking of the aromatic units are reported. The presence of the peripheral side chains facilitates the bundling of the 1D supramolecular polymer fibers to form an organogel. The cooperative supramolecular polymerization of **1** in solution has been accurately analysed by applying the recently described EQ model that allows to calculate the corresponding thermodynamic parameters ($\Delta H_{elo}{}^{0}$ = -62.78 kJmol^{-1}, ΔS^{0} = -0.10 kJmol^{-1}, $\Delta H_{nucl}{}^{0}$ = -34.94 kJmol^{-1}, and a cooperativity factor σ = 7.5 x 10^{-7}). The aggregation state of compound **1** strongly influences its optical properties resulting in a broad band in the UV-Vis spectrum. These changes also affect the light-emitting property and cover a broad range of the visible spectral region in the aggregated state. The luminescent features (with CIE coordinates of 0.26 and 0.40) together with the electric conductivity (~2 x 10^{-4} S/m) of the supramolecular polymers of **1** allow considering this simple compound as a soft material with potential applicability in the research field of organic electronics and photonics.

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† Electronic Supplementary Information (ESI) available: Figures S1-S5 and experimental section. See DOI: 10.1039/b000000x/

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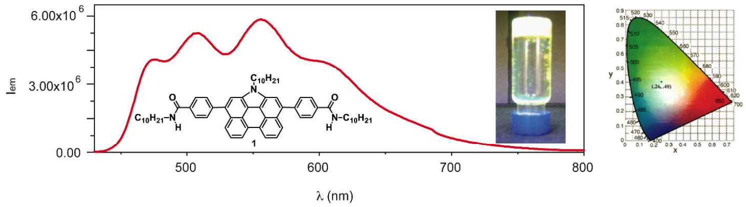
Luminescent and conductive supramolecular polymers from an *N*-annulated perylenedicarboxamide



Fátima García,[a] Julia Buendía,[a] Samrat Ghosh,[b] Ayyappanpillai Ajayaghosh,[b,]* and Luis Sánchez[a,]*

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